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Solid polymeric electrolytes of increased cation transference number

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Several results regarding the role of C6P receptor on electrolyte properties were not presented in Chapter 6 (Results) but only used as additional data to discuss results in Chapter 7 (Discussion), as the electrochemical data, studies on membrane morphology etc. were conducted by others, namely: the research team of professors Emmanuel Peled and Diana Golodnitsky (School of Chemistry, Tel Aviv University) and the research team of professors Stefania Panero and Bruno Scrosati (Dipartimento di Chimica, Universita di Roma "La Sapienza"). The author stresses that the studies described in Chapter 7 were conducted in co-operation with the research team of professor Wieczorek and synthesis of the C6P (whose effect on electrolyte was researched by above named research teams) was conducted by the author of this dissertation.

Streszczenie pracy „Elektrolity polimerowe o zwiększonej liczbie przenoszenia kationu”.

Celem niniejszej pracy było opracowanie elektrolitu o zwiększonej przewodności kationowej na bazie poli(tlenku etylenu) (PEO). W wyniku przeprowadzonej w Rozdziale 1 analizy szeregu możliwych rozwiązań modyfikacji elektrolitu polimerowego, stwierdzono, że jednym z najbardziej obiecujących jest dodatek receptora anionów. Taka modyfikacja elektrolitu została zbadana i opisana w literaturze dla szeregu elektrolitów ciekłych i stałych (przegląd tych zastosowań w Rozdziale 2). Większość badanych w literaturze receptorów, których wpływ na właściwości elektrolitu był badany, oddziałuje z anionem oddziaływaniem kwas Lewisa-zasada Lewisa. Dodatek takiego receptora może katalizować degradację rozpuszczanika lub matrycy polimerowej.

Alternatywą dla tego typu receptorów są związki oddziałujące z anionami poprzez wiązanie (lub wiązania) wodorowe. Chemia receptorów anionowych tego typu jest niezwykle bogata. Do elektrolitów były one jednak stosowane rzadko, ze względu na obawy związane z ich niestabilnością w kontakcie z elektrodą litową. Rozdział 3 zawiera krytyczną analizę danych literaturowych na temat zastosowań tego typu receptorów zarówno od strony dotychczasowych zastosowań receptorów oddziałujących z anionem poprzez wiązanie wodorowe w elektrolitach polimerowych jak i syntezy nowych receptorów zdolnych do koordynacji anionu i nadających się do zastosowania jako dodatek do elektrolitu polimerowego.

Rozdział 4 stanowi podsumowanie poprzednich trzech rozdziałów, określa dokładnie cele niniejszej pracy i stanowi wprowadzenie do prezentacji wyników.

W Rozdziale 5 przedstawione zostały techniki eksperymentalne wykorzystane w pracy.

Rozdział 6 przedstawia wpływ receptorów na aniony na właściwości elektrolitów.

Z poprzednich badań prowadzonych w zespole badawczym prof. Wieczorka wynikało, że zastosowanie pochodnych kaliks[4]arenów będących receptorami anionów jako dodatku (addytywu) do elektrolitu przewodzącego jonowo może spowodować podwyższenie liczby przenoszenia kationu litowego, jednak ten pozytywny efekt połączony był z obniżeniem przewodności jonowej elektrolitu. Drugim problemem była dość kłopotliwa, pięcioetapowa synteza receptora. Zaproponowane rozwiązanie tego problemu polegało na zastosowaniu makrocyklicznego receptora będącego pochodną kaliks[6]pirolu, łatwego w syntezie prowadzonej z relatywnie tanich substratów oraz słabiej oddziałującego z matrycą polimerową i kationami. Dodatek tego receptora powoduje zwiększenie liczby przenoszenia kationu od ok. 0,2 do ok. 0,8 przy jednoczesnych niewielkich zmianach w całkowitym

przewodnictwie jonowym. Pierwszy z celów niniejszej pracy został zatem osiągnięty. Badania elektrochemiczne potwierdzające żądane zmiany w przewodnictwie jonowym przeprowadzone były we współpracy z Uniwersytetem „La Sapienza" w Rzymie i Uniwersytetem w Tel Awiwie. Konsekwencją tego sukcesu było zwiększenie skali syntezy receptora do skali ¼-technicznej opracowany w ramach tego doktoratu (podrozdziały 6.1-6.3).

Drugim celem niniejszej pracy było wytłumaczenie mechanizmu działania receptora na aniony w elektrolicie polimerowym (podrozdziały 6.4-6.6). *A priori*, receptor na aniony powoduje zmianę stężenia jonów i aglomeratów jonowych ponieważ powoduje powstanie „nowego" anionu będącego kompleksem anion-receptor. Dodatkowo, może on pełnić funkcję plastyfikatora, dodatku sieciującego (receptor może tworzyć wiązania wodorowe z matrycą polimerową), a w wypadku aglomeracji cząsteczek receptora (co prowadzi do jego wytrącenia się), nano- lub mikrometrowego napełniacza (wpływającego na właściwości elektrolitu podobnie jak dodatek napełniacza ceramicznego), zdolnego lub niezdolnego do koordynowania jonów na swojej powierzchni. W celu zbadania zmian w fizykochemii elektrolitu polimerowego po dodaniu receptora, przeprowadzono badania porównawcze dla receptorów na aniony o różnej kompatybilności względem matrycy polimerowej. Porównanie kalorymetryczne właściwości membran z dodatkiem receptorów anionowych pokazało zależność pomiędzy kompatybilnością receptora z matrycą polimerową: receptory bardziej kompatybilne powodują np. obniżenie krystaliczności matrycy polimerowej i temperatury topnienia fazy krystalicznej poli(tlenku etylenu).

Powiązanie tych danych z mapami pierwiastkowymi i Ramana pokazało różnice w mechanizmie przewodzenia w zależności od kompatybilności.

Istotnym elementem takich porównań były badania spektroskopowe oddziaływań pomiędzy receptorami i modelowymi rozpuszczalnikami (o właściwościach koordynacyjnych I dielektrycznych jak poli(tlenek etylenu)). Badania te wykazały zależność pomiędzy oddziaływaniem receptor-rozpuszczalnik w zależności od polarności rozpuszczalnika i od długości łańcucha poli(oksyetylenowego) przy porównaniach polieterów.

Przedstawione wyniki są porównywane z wynikami innych zespołów badawczych w Rozdziale 7. W tym samym rozdziale porównana została rola badanych w tej pracy receptorów na aniony z rolą jaką spełniają inne klasy dodatków poprawiających parametry przewodnictwa jonowego w takich układach: napełniacze ceramiczne i receptory, które oddziałują z anionami jako kwas Lewisa-zasada Lewisa.

Rozdział 8 jest podsumowaniem niniejszej pracy.

Abstract - “Solid polymeric electrolytes of increased cation transference number”

The main aim of this dissertation was elaborating of the polymeric, poly(ethylene oxide)-based (PEO-based) electrolyte characterized by enhanced transport of the lithium cations. After an analysis of various modifications of the polymeric system able to transport ions (ionics), conducted in Chapter 1, it was stated that one of the most promising solutions is addition of the anion receptor to this system. Such modification was studied and described in the literature for several liquid and polymeric systems. A review of these studies is presented in Chapter 2. The majority of the receptors presented in these works interact with anion by Lewis acid-Lewis base interaction. The addition of strong and moderate Lewis acids, however, can cause a degradation of the liquid or polymeric matrix.

Receptors interacting with anions *via* hydrogen bonds are an alternative to the Lewis acids. The synthesis and binding properties of “hydrogen bond-based” anion receptors was widely studied in the literature; however, receptors of this type were not tested as additives to electrolytes dedicated for the lithium batteries. It was due to the assumption that addition of the “hydrogen bond-based” receptor will cause faster degradation of the lithium cathode. In Chapter 3, the analysis of literature data regarding application of this type anion receptors in electrolytes as well as synthesis of new receptors capable of coordinating anions and which may be applied in polymeric or liquid electrolytes are presented.

Chapter 4 summarizes the discussion of the literature data in the previous three Chapters, states the goals of the work and is an introduction to the presentation of the results.

In Chapter 5, research techniques used in this work were presented.

In Chapter 6, the role of receptor addition in the change of properties of the electrolytes is presented.

Previous studies conducted by Prof. Wieczorek’s research team reveal that addition of the anion receptors being calix[4]arene derivatives to the PEO-based polymeric electrolyte can result in enhancement of the lithium transference number. This very welcome effect, however, entailed the lowering of the ionic conductivity of the system. Another problem was related to the complicated, five-step synthesis of the receptor. The proposed solution was based on the application of anion receptor being calix[6]pyrrole derivative. This receptor was easy in synthesis from relatively cheap compounds (pyrrole and benzophenone). Moreover, interaction of this receptor with cations and the matrix should be weaker due to chemical structure of the receptor.

The addition of this derivative resulted in an increase of lithium transference number from 0.2 up to 0.8 with less significant lowering of the conductivity (for some systems, even

conductivity enhancement was observed). Thus, the main aim of this work has been achieved. The studies on the electrochemical performance of such systems were realized in co-operation with „La Sapienza" University in Rome and Tel Aviv University. A consequence of this success was up-scaling of the C6P synthesis up to ¼-technical scale (Chapters 6.1-6.3).

Another aim of this work was to explain the role of the receptor in polymeric electrolyte (Chapters 6.4-6.6). Addition of the anion receptor to the electrolyte results in the formation of a „new" anion being an anion-receptor complex. Moreover, in the polymeric system, the receptor can plasticize the matrix, cross-link the polymeric chains via hydrogen bonds and, when receptor molecules are agglomerated or the receptor precipitates, the receptor can play the role of nano- or microsized filler (similar to that of the ceramic filler in composite electrolytes) which can be able to interact with anions by surface groups.

In order to study these changes, comparative studies on role of the receptors characterized by various compatibility with the PEO matrix were conducted. Calorimetric studies revealed that there is a correlation between compatibility and changes in the properties of the membrane. For instance, PEO-compatible receptors lower the crystallinity of the membrane and the melting point of the PEO crystalline phase. These data and additional results of the Raman and EDAX mapping showed that changes in the ionic transport mechanism, which are the result of anion receptor addition, depend on the compatibility between receptor and PEO.

An important element of the research on the receptor-salt-matrix interactions were spectroscopic studies of interactions between the model solvent (glyme, oligoglymes, PEODMEs etc.) and the anion receptor. It was shown that the interaction between the matrix and the receptor are dependent on the polarity of the matrix, and, when oxyethylene oligomers were studied, on the length of the oligomeric chain.

The results presented are compared with results of other research teams in Chapter 7. In the same Chapter, the addition of „hydrogen bond" anion receptor was confronted with addition of other additives improving ionic transport properties, i.e. ceramic fillers and „Lewis acid based" anion receptors.

In Chapter 8, the results of this work are summarized.

Note from the author

In this work, citations are given according to Electrochimica Acta and Journal of Power Sources rules. Citations are located at the end of the work. Other remarks are located at a bottom of each page. Such a system, in opinion of the author, should make the process of reading easier as about 500 reviews and original articles, books as well as scientific and business reports are cited in this thesis.

Footnotes, Figures and Tables are numbered. One numeration, from the beginning to the end of this work was used.

Pictures of chemical structures of the receptors are not numbered.

Abbreviations

AMPS	2-acrylamido-2-methyl-1-propanesulfonic anion, $CH_2{=}CHCONHC(CH_3)_2SO_3^-$
CE	Coulombic efficiency
c_p	specific heat capacity in constant pressure
CV	cyclic voltammetry
DEC	diethyl carbonate
DMC	dimethyl carbonate
DME	1,2-dimethoxyethane, glyme
DMSO	dimethylsulfoxide
DSC	differential scanning calorimetry
EC	ethylene carbonate
EDS	Energy dispersive X-ray spectroscopy
EO	ethylene oxide
Et	ethyl (C_2H_5-)
FTIR	Fourier transformation infrared (spectroscopy or spectrometer)
GBL	γ-butyrolactone
GPE	gelled polymer electrolyte
IPN	interpenetrating polymer networks
Kynar	trade name for copolymer of vinylidene fluoride and hexafluoropropylene
M_W	molecular weight
M	molar [mol/kg of the (liquid or polymeric) matrix]
MESO	methylethylsulfoxide
MO	methylene oxide (CH_2O) unit
NASICON	$Na_3Zr_2Si_2PO_{12}$, a sodium „super-ionic” conductor
NEXAFS	Near Edge X-ray Absorption Fine Structure
OCV	open circuit voltage
PAMPSLi	poly(lithium 2-acrylamido-2-methyl-1-propanesulfonate), $(CH_2CH(CONHC(CH_3)_2SO_3Li))_n$
PAN	polyacrylonitrile
PC	propylene carbonate
PE	polyethylene
PEG	poly(ethylene glycol)
$PEGMac_2$	diester of metacrylic acid and poly(ethylene glycol)
PEGMEMac	monoester of metacrylic acid and poly(ethylene glycol) methyl ether
PFG NMR	Pulse Field Gradient NMR
PEO	poly(ethylene oxide)
PEOME	monomethyl ether of poly(ethylene glycol)
PEODME	dimethyl ether of poly(ethylene glycol)
Ph	phenyl (-C_6H_5) group
PMMA	poly(methyl methacrylate)
PO	propylene oxide
PPG	poly(propylene glycol)
Q^m	heat of melting
R, R^1, R^2	alkyl or aryl groups
RT	room temperature, ambient temperature
SEI	electrolyte-electrode interface
SPE	solid polymer electrolyte
SSLi	lithium salt of styrenesulfonic acid
T	temperature
Tf	trifluoromethanesulfonate anion, triflate anion ($CF_3SO_3^-$)
Tfa	trifluoromethanesulfonyl (CF_3SO_2-) group
TfSI	bis(trifluoromethane)sulfonimide anion
T_g	glass transition temperature
THF	tetrahydrofurane
T_m	temperature of melting, melting point
Ts	tosyl (p-toluenesulfonyl, -$SO_2C_6H_4CH_3$) group
VdF	vinylidene fluoride

Chapter 1

Introduction - Electrolytes Dedicated for Lithium Batteries

The volume of the worldwide primary and secondary battery market exceeds $ 50 billion a year and rises about 5% annually [1]. It is mainly due to growing demand for portable devices and related with it expectations concerning the sources powering these devices. Among them, lithium (metal lithium anode) and lithium ion batteries (with the anode consisting of lithium intercalated usually in the carbon) are among the most promising ones, due to their very high discharge capacity and high OCV (up to over 4 V) [2]. Owing to these, lithium and lithium-ion batteries can be successfully applied especially in portable devices needing high energy density and in electric vehicles. The market for lithium and lithium-ion systems can be estimated at over $8 billions a year and grows faster than those for other types of batteries [3]. It worth stressing that despite this commercial success, batteries containing lithium still need further development to fulfill market expectations. The main goals which should be achieved are miniaturization of the batteries, enhancement of their work safety, higher and stable in time energy density as well as life length improvement. The majority of these issues are addressed in books [4-6], chapters in books and review articles [7-25] dealing with various aspects of lithium and lithium-ion batteries.

At least the last three above mentioned factors are related to the development in the electrolyte formulation. Stable energy capacity of a battery is dependent mainly on its stable discharge properties whose deterioration is observed mainly due to processes at electrode-electrolyte interfaces, namely oxidation and reduction of the solvent together with salt and chemical solvent decomposition. These processes lead to the formation of a poorly conducting layer resulting in overall conductivity decrease and discharge capacity decay. The same mechanism can be responsible for shortening of the battery life length.

1.1 Types of electrolytes for lithium battery

In general, lithium electrolytes can be divided to:

- liquid electrolyte systems consisting of one or more lithium salts and one or more solvents which form the solution;
- Solid Polymer Electrolytes, polymeric materials with salt “dissolved” in the polymer matrix (usually, poly(ethylene oxide) - PEO or other polyether as poly(propylene oxide) - PPO, but also poly(ethylene imine) and poly(ethylene sulfide));
- Gel Polymer Electrolytes in which the solvent is macroscopically immobilized in electrically inert polymer matrix;

- molten salt systems, consisting of salt dissolved in ionic liquid [26-30] (lithium cells working in room temperature) or eutectic mixtures of salts [31-35] (high temperature lithium batteries);
- glassy electrolytes e.g. LIPON [36-40] or NASICON-like material produced by Ohara Inc., consisting of $Li_2O–Al_2O_3–SiO_2–P_2O_5–TiO_2–GeO_2$ [41, 42];
- inorganic liquid electrolytes such as lithium salt solutions in $SOCl_2$ [43-49], SO_2Cl_2 [50-56], SO_2 [57-62] and others; in this case, the electrolyte plays also the function of the cathode.

In the **liquid** and **gelly** electrolytes the transport of the charge carriers is realized in polar solvents (as ethylene carbonate, $\varepsilon=89$, propylene carbonate, $\varepsilon=65$, γ-butyrolactone, $\varepsilon=39$, and other) or their mixtures, conductivity is usually between $2*10^{-2}$ and 10^{-3} S cm^{-1} [63-66] - being high enough for application in the commercial lithium battery (for laptops or and cellular phones) working at ambient temperature [67]. The main problem exhibited by this type of batteries is related to processes at the electrode-electrolyte interface. Firstly, during the charging/discharging processes of the battery as well as battery storage, an additional layer is formed on the surface of the electrode (or, in other words, in electrode-electrolyte interface). This layer, usually called solid electrolyte interface (SEI), consists of products of decomposition of electrolyte and electrode and is an additional hindrance for ion carrier transportation as the resistance of the SEI is often much higher than the bulk conductivity of the electrolyte. Physicochemical properties of the SEI, such as ionic conductivity (responsible for battery resistance) or tightness (limiting further growth of the layer) depend strongly on the SEI constitution [68-73]. The velocity of the SEI growth is also dependent on the lithium transference number which is, in liquid systems, typically [74, 75] lower than 0.3. Addition of lithium transport enhancers, e.g. ceramic fillers, can result in an increase of the lithium ion transference number to 0.7 [76]). In the alternative approach, polyelectrolytes - polymers whose repeating units incorporate a counterion were used. Thus, in this case, the anion was fully immobilized due to its covalent bond with the matrix, and the lithium cation, solvated by the polar solvent, was mobile. Such systems, however, i) were characterized by conductivity one order of magnitude lower than analogous salt-matrix system [77-80] and ii) often exhibited fast degradation in contact with the lithium anode.

The last factor important for these systems is related to good charge transfer at anode-electrolyte interface, namely to the kinetics of the reaction $Li_{(anode)} \rightarrow Li^{+}_{(electrolyte)} + e^{-}$ [81, 82]. This process is mainly dependent on the properties of the SEI.

For **solid polymer electrolytes** (SPEs, mechanically strong, self-standing membranes), the main disadvantage limiting their further development is related to their very low conductivity at room (ambient) temperature (RT) - usually below 10^{-5} S cm^{-1} - and low lithium transference number (usually, in 0.2-0.3 range). Low conductivity results from relatively poor ion (especially anion) coordinating properties of the polymeric matrix and low dielectric constant of these systems [83-90] (and, thus, ion agglomerate formation) and limitations resulting from low velocity of the segmental motions of polymeric matrix [91-98]. The low lithium transference number is mainly the result of interactions existing between the cation and the polymeric host stronger than those observed between the anion and the polymer. Taking this into account, studies of materials with higher lithium transference number and higher conductivity are the most important research field. Unfortunately, immobilizing anions in the polymer chain (i.e. a solvent-free solid polyelectrolyte system [99, 100]) or introduction of large and heavy anions [101, 102], results in lowering conductivity by one order of magnitude or more. Thus, the combined effect of anion mobility reduction and polymeric matrix plasticization (while being able to maintain proper mechanical properties of the membrane) yielding a material with higher lithium transference number and conductivity is needed. Also in this case, the processes at electrode-electrolyte interface play an important role. In this case, however, this problem is less important due to the polymeric nature of the matrix as well as higher resistance of the polyethers (which play the role of matrix in the majority of the most popular SPEs) against hydrolysis in comparison with alkyl carbonates or other esters. The main problem of stability in this type of materials is related to oxidative degradation of the polymer. This disadvantage of polyether-based materials was recognized not only in studies on SPEs but was observed also in other applications of polyethers, e.g. when they are present in polyurethane building blocks (polyols). Thus, polyethers cannot be incorporated in batteries containing high potential cathodes as e.g. $LiCoO_2$.

1.2 Improvement of SPE conductivity by modification of polymer architecture

As it was stated in the previous chapter, poor conducting properties of solid polymer electrolytes are related to relatively low segmental mobility of the polymer chains. To enhance the velocity of the segmental motions, two following phenomena should be addressed: i) weakening of the cross-linking of the polymer chain, both in chemical and physical terms and ii) reduction of the polymer crystallinity leading to the increase of the long range disorder level present in the system. Thus, the modification of polymer membrane architecture is one of the possibilities for changing conducting properties of the membrane. In the case of macromolecules having the structure of a comb, a network, or a star, the local cross-linking brings a significantly weaker conductivity lowering than in the case of their linear analogs. Moreover, such a system can be totally amorphous due to the fact that long-range organization of the system is natively impossible (star-like polymers) or their crystallinity can be reduced or diminished by obtaining a system with proper formulation, e.g. in the case of comb-like polymers, monomers with different length of the side chains can be applied.

1.2.1 Comb-like polymers

In most of the polymers having such architecture, the main chain of the macromolecule is usually passive in terms of conductivity and is responsible for mechanical properties of the membrane. The transport of the charge carriers takes place because of the presence of the side chains of the polymer. Due to this, the domains of the polymer responsible for transport of the current carriers exhibit higher dynamics of the oligo(oxyethylene) chains motions - being short enough not to form *quasi*-crystalline structures and only one end of the chain is covalently bonded with the macromolecule core.

The main classes of such polymers comprise: poly(oligo(ethylene glycol)methyl ether methacrylates) [103-110], polysiloxanes with oligo(oxyethylene) side chains [111-120] and polyphosphazenes modified with poly(ethylene glycol) such as MEEP (poly(methoxy(ethoxy(ethoxyphosphazene)))) [121-128]. Additionally, copolymers of styrene or methyl methacrylate with a macromonomer such as oligo(ethylene glycol)methyl ether methacrylates) [129] or poly(oligo(ethylene glycol)methyl ether vinyl ethers) [130, 131] were also investigated.

Usually, this modification of the molecule results not only in an increase in conductivity but also in deterioration of mechanical properties of the membrane in comparison with those of linear PEO-based ones. Thus, to overcome this disadvantage, alternative structures of interpenetrating polymer networks (IPN) [132-134] and *semi*-IPN [135-138] as well as polymer blends [139-141] were studied in which comb-like polymer is responsible for electrical conductivity while the polymeric network for mechanical properties.

1.2.2 Polymer networks

Similarly to comb-like polymers, also this polymer architecture exhibits lower crystallinity in comparison with the linear one. However, the mobility of the poly(oxyethylene) chains is lower in comparison with the comb-like systems. It is due to the linking of both ends of the unitary chain to the rest of the macromolecule. Thus, the polymers of such architecture are characterized by worse conducting properties in comparison with analogous comb-like systems. On the other hand, they for the same reason exhibit better mechanical properties.

A number of different classes of polymers networks is higher than of those having comb-like architecture due to the possibility of combining more than one macromonomer. In such case, one monomer used often contains only one double bond (or another group active in polyreaction) and the other (cross-linking agent) contains two or more groups active in polyreaction [78, 103, 142-145]. In consequence, the cross-linking density can be optimized taking into account conductive and mechanical properties of the membrane. Moreover, the number of cross-linking agents easy in synthesis is higher in comparison with the functional monomer being comb-like polymer precursors. Typically, ethers of glycerol or pentaerytritol and poly(ethylene glycol) monomethacrylates or acrylates, siloxane-based precursors with methacrylate groups and huge number of other systems can be taken into consideration.

It is worth noting that the main advantage of this polymer architecture in comparison with the comb-like system is that the polymeric network do not dissolve in the liquid solvent (self-standing gel formation is observed). Thus, the weakening of the mechanical strength of the polymer matrix after soaking the polymer with a low molecular weight solvent is not as significant as in the case of comb-like architecture. Therefore, taking into account relatively low conductivity values observed for solvent-free network systems, the main impact in the studies of polymers of this architecture focuses on the liquid solvent plasticized electrolytes [146-150].

1.2.3 Star-like and hyperbranched polymers

Due to poor mechanical properties, mainly related to star-like architecture of such macromolecules, they are usually used not as a polymer matrices themselves [151-154] but rather as additives responsible for inhibition of crystallization (plasticizers) [155-158] or cross-linking agents [159].

1.2.4 Application of linear copolymers containing oligo(oxyethylene) units

Several copolymers containing ethylene oxide units were applied in order to obtain polymers with lithium ion conductivity higher than PEO, through both crystallinity lowering [160] and enhancing velocity of the segmental motions (lowering of T_g) [161]. The most widely studied ones include ethylene oxide-methylene oxide copolymers [162-165] or polyurethanes containing poly(oxyethylene) flexible domains [166-171].

In general, this class of electrolytes is characterized by conductivity similar or lower than that of previously described composites (but still much higher than in linear PEO-salt systems); on the other hand, the changes of the mechanical properties in such systems in comparison with linear PEO are smaller due to similar constitution (high M_W polymers).

1.3 Improvement of SPE properties using additives

1.3.1 Polymer composites

Composite polymeric electrolytes (PEO-ceramic filler-salt systems) are characterized by better thermal and mechanical properties in comparison with filler free systems [172, 173]. Moreover, Scrosati and coworkers proved that PEO-ceramic filler composite stabilizes resistance of the lithium anode-electrolyte interface [174, 175]. Also an increase in conductivity in most of the systems studied (especially when submicro- or nanosized filler is used) was observed. It is due to the formation of the polymer-filler interface areas with modified microstructure and, thus, enhanced conductivity. This phenomenon compensates in excess, at least in a given filler concentration range, the lowering of conductivity related to both dilution of the polymeric matrix by insulative grains and stiffening of the matrix owing to filler addition. Moreover, the lithium transference number of the electrolyte can be enhanced by the modification of the ceramic filler surface (introduction of acidic groups), and, in consequence, partial immobilization of the anion at the surface of the ceramic filler grains [176-180]. Thus, polymeric composites containing ceramic filler are among the most promising materials for potential applications in lithium batteries and were one of the most widely studied modifications of SPE. The most frequently studied additives are: TiO_2 [181-185], Al_2O_3 [186-190], SiO_2 [191, 192], ZrO_2 [193, 194], $LiAlO_2$ [195-199], $BaTiO_3$ [200-203] as well as NASICON [204-206]. These materials are often used in different allotropic forms exhibiting different impact on the system synthesized.

Also the addition of micro- or nanosized particles of the polymer immiscible with PEO was examined. The aim of this works was to determine if polymeric additives can play the same role as inorganic fillers, i.e. if ionic transport is present in the interface between the inert polymer and PEO after the filler addition [207-210].

Another possible modification of the PEO matrix is the formation of a polymeric blend. Also in this case several systems containing PEO which exhibited higher conductivity in comparison with the PEO-salt composite itself were obtained. Such a phenomenon is related to higher velocity of segmental motions of the polyether chain (both due to PEO T_g lowering and reducing PEO crytallinity [211-214].

1.3.2 Oligomeric and non-polymeric low molecular weight (M_W) plasticizers

Several oligomers, mainly of the EO [215-219], were tested as plasticizers for linear PEO-based systems. The addition of such compounds resulted in conductivity enhancement with parallel worsening of mechanical properties of the membrane.

The term “SPE” is often applied to PEO or other polymers (as PAN or PMMA) plasticized with polar solvents, such as propylene carbonate (PC), ethylene carbonate (EC) and other dialkyl or alkene carbonates as well as γ-butyrolactone (GBL). In opinion of the author, this type of the electrolytes should be ascribed to the group of gel polymer electrolytes (GPEs) as i) current carriers are solvated mostly by the additive ii) the low dielectric constant, characteristic for SPEs rises after the addition of compounds of low molecular weight iii) conduction mechanism is different from that in SPEs [220-225].

1.3.3 Internal plasticization by smart salt design

The application of the salt as PEO plasticizer was proposed by Armand [226]. As the addition of low molecular weight plasticizer usually results in weakening the mechanical strength of the membrane, introducing of the salt having an anion with plasticizing properties was expected to have a weaker influence on the mechanical properties. In the first step, $LiBPh_4$ and $Li(R_3SiO)_4Al$ salts were tested. Unfortunately, PEO-lithium salt membranes exhibited relatively low conductivity due to high polarization of the counterions. Because of this, the researchers turned their interest to plasticizing salts with negative charge highly delocalized within the anion molecule due to the presence of several electron-withdrawing groups in its chemical structure. Several methide (e.g. $Li((CF_3SO_2)_3C)$ [227-229], $Li((CF_3SO_2)_2(RCO)C)$ [230, 231], and others [232]) and imide anions (as LiTfSI [233-242] or LiBETI - $Li(C_2F_5SO_2)_2N$, [243-249] and others), were synthesized. It is worth stressing that such salts are very weak Lewis bases and, thus, can be also applied as components of liquid electrolyte.

1.4 Anion receptors and their role in electrolyte properties

1.4.1 Anion receptors

The term “anion receptor” is typically used to define either (electrically neutral) molecules or charged species (e.g. protonated amines) which can interact with anions by means of bonds different than covalent (chemical). These interactions include ion-ion and ion-dipole (Coulombic) interactions, hydrogen bond formation between the receptor and the anion, or Lewis acid (receptor)-Lewis base (anion) interactions [250]. It is easy to observe that complexes of neutral receptors and anions always have a negative charge, while the majority of the complexes containing receptors with a positive charge are either electrically neutral or positively charged. As in this application the complex of the receptor and anion acts as a counterion for the lithium cation, thus, the lithium battery requires a negative charge of the anion-receptor complex. In consequence, the anion receptor for such application should be a molecule without electric charge.

1.4.2 The role of the anion receptor in the electrolyte

In all systems presented, the addition of the anion receptor resulted in higher lithium cation transference number. This effect is relatively easy to explain: the anion-receptor complex consists of a higher number of atoms and is bigger, and, thus, the anion-receptor complex exhibits higher movement hindrances in comparison with the uncomplexed anion. Additionally, the anion-receptor complex is characterized by a significantly higher molecular mass. Thus, its mobility in the electric field is lowered by a factor being a quotient of anion molecular mass of the complex (this assumption is valid for systems with electrically neutral receptor where charges of the complex and the free anion are identical). In consequence, the mobility of the complexed anion is lower than that of the uncomplexed one and the fraction of the current transported by the anion is lower.

In the case of liquid electrolytes which are well-dissociated salt solutions in the mixture of alkyl carbonates (strong electrolytes), the anion receptor should, first of all, improve the stability of the electrolyte-anode and electrolyte-cathode interface. In this case, the effect of anion complexation in the electrolyte and the consequences of this fact such as increased salt dissociation or lithium transference number enhancement are not so important as for other systems as the conducting properties of the pristine liquid electrolyte itself are good enough for majority of applications. The surfaces of both electrodes form passive layers consisting mainly of lithium salts (e.g. LiF or Li_2CO_3). In result, the inner resistance of the battery increases. The addition of the anion receptor should result in (at least partial) dissolution of the salts incorporated in the passive layer, and, due to this, a decrease in layer resistivity. Thus, this should lead to the stabilization of battery resistance. Another effect which can be attributed to these receptors is that the composition of passive layer changes, e.g. in the case of receptors containing boron atom in their structures the formed SEI is enriched with $LiBO_2$.

This factor also enhances the conductivity of the passive layer. Taking all these facts into account, the amount of the anion receptor added to this system should be significantly lower than the one which is stoichiometric with respect to the amount of the dissolved salt. Another argument for that can be linked to the fact that a too high amount of the anion receptor can result in chemical reaction between the receptor and the anion and, in consequence, lead to anion decomposition (e.g. according to reaction Rec + PF_6^- → $[RecF]^-$ + PF_5; schemes of reaction with anions such as BF_4^- or AsF_6^- are similar). Moreover, excessive receptor addition usually lowers the conductivity of such a system because of an increase in viscosity of the system and due to the fact that the mobility of the anion-receptor complex is lower than that of the uncomplexed anion [251].

A situation different from the described above is observed for poorly dissociated systems, both liquid and gelly, where the addition of the receptor can result in better salt dissociation. Such systems can be divided into subclasses on the basis of the type of the salt used. The first one includes lithium halogenides (fluoride, chloride and, eventually, bromide). These salts are marked by high energy of the crystal lattice. Moreover, anions of these salts are not compatible with aprotic matrix (due to their lipophobic nature). Taking these into account, the problems of poor salt solubility appear paralelly to problems with poor salt dissociation. Owing to both these factors (solubility and dissociation), the conductivity of such systems is very low. The addition of the anion receptor in the stoichiometric amount (with respect to the salt) results in this case in the formation of "new" anion consisting of one big molecule incorporating both the anion and the anion receptor, which is negatively charged, and being additionally characterized by lower Lewis basicity and higher lipophilicity. Thus, the lithium salt of the anion-anion receptor complex is characterized by higher solubility and higher dissociation.

Among those systems in which salt dissociation is weak one can include lithium salts of carboxylic acids (low M_W acids such as $LiCF_3COO$, LiC_2F_5COO, and polyelectrolytes with carboxylate group in the polymeric chain) as well as polyelectrolytes being lithium salts of several poly(sulfonic acids) (as e.g. PAMPSLi, $LiCH_3(OCH_2CH_2)_nOSO_3$, and P(SSLi). In the last case, mainly salts being strong Lewis basis are used as receptors). Here, the problem of salt solubility does not occur. Thus, the aim of the anion receptor addition is improving salt dissociation, and, through this, enhance the conductivity. In this case, the anion receptor amount can be stoichiometric or lower than stoichiometric.

As far as polymeric electrolytes are concerned, an addition of the anion receptor can result in a change of various properties. Of course, the anion receptor plays the same role as the "anion trap" but can also be a plasticizer, one of the monomers from which the polymer matrix is synthesized (both by means of polyaddition and polycondensation), and the cross-linking agent.

1.4.3 Properties expected of the anion receptor as an optimal electrolyte additive.

Chemical stability. In the ideal situation, the receptor should be chemically stable against oxidation in contact with the cathode and reduction in contact with the anode (Li/Li^+ has potential equal to -3.05 V vs. the standard hydrogen electrode, the lowest of all known metals and potential of Li intercalated on the graphite is only about 0.3 V higher). This very demanding "thermodynamic" approach is hard to achieve or even impossible. However, taking into account kinetic parameters related to both diffusion through the passive layer at electrolyte-electrode interface and kinetics of the chemical reduction of the receptor, a compound suitable for application can be obtained. Thus, the crucial parameter of this feature of stability can be studied by means of e.g. cyclic voltammetry applying one of the electrode materials as the working electrode. Usually, stability down to 0 V and up to 4.5 V versus Li/Li^+ is regarded sufficient for application in a $Li/LiMn_2O_4$ cell. In the case of $Li/LiCoO_2$ one, a higher stability of the electrolyte against oxidation (above 5 V vs. Li/Li^+) is expected.
Another factor related to stability is that, in the simplest approach, the anion receptor as well as the solvent should be aprotic [252]. This leads to the conclusion that all the anion receptors with relatively mobile protons, i.e. molecules containing urea -NHCONH-, urethane -OCONH-, amide -CONH-, pyrrole, and amine -NH- groups cannot be applied in the liquid systems with the lithium anode. This is, however, not the case when polymeric electrolyte is taken into consideration. In this situation, the usage of matrix containing mobile protons such as poly(ethylene imine) was successfully considered. Thus, the application of the anion receptor with similar groups containing mobile proton is possible and should not result in the faster growth of the passive layer [253, 254]. These results obtained for SPE are in opposition to the negative prognosis of several authors, analyzing the application of the anion receptor containing mobile protons in the liquid system (e.g. [255]).

Binding strength of the receptor tailored to coordinating properties of the system is especially important for application in the polymeric matrix. In the simplest model, one should take into account the donor and acceptor properties of the solvent (or polymer). If the acceptor properties of the solvent are stronger than these of the receptor, the anion will be coordinated by the solvent. When the donor properties of the solvent are stronger than these of the anion, the receptor will interact with the solvent and not the anion [256]. This approach is valid for the interaction of the anion with receptors with one group active in anion-receptor interactions in the molecule (e.g. triphenylborane BPh_3 or its perfluorinated analogue $B(C_6F_5)_3$). In a more complicated approach, especially when interactions between the anion and the multidentate receptor are analyzed, the correlations described above are also valid (see e.g. [257]), but also other factors, related to geometric fitting of the anion to the receptor molecule as well as difference in entropy of configuration between the receptor, the anion-receptor, and the solvent-receptor complex (e.g. effect of the "macrocyclic hole" in the case of cyclic anion receptors) play an important role. Thus, even when a single chemical moiety of the receptor is characterized by poor affinity to the anion (not strong enough when compared to the coordinating properties of the solvent), several weak interactions together with an advantageous enthropic effect can result in the formation of the stable anion-receptor complex.

It is also worth noting that the addition of the anion receptor being a too strong Lewis acid can result (in the case of the liquid matrix) in solvent decomposition or (in the case of the polymeric matrix) in matrix depolymerization.

Selectivity of the anion receptor in the battery systems is important; however, the term "selectivity" in battery systems has a different meaning than in e.g. analytical chemistry. In the case of electrolytes, there is no need to obtain the anion receptor which can interact strongly and selectively only with one particular anion and its interactions with other anions are weak (which is crucial when the anion receptor is applied to an anion-selective sensor or as the phase transport catalyst selective for one particular anion). In this case, strong interaction of the receptor with the anion and negligible interaction with cation and (liquid or polymeric) matrix is needed. Interactions with the cation result in lowering the conductivity of the lithium cation (and, in consequence, overall conductivity), leading, in turn, to a decrease in lithium transference number. Moreover, interactions between the anion receptor and the polymeric matrix result in an increase of viscosity (in the case of the liquid matrix) or lowering the velocity of the polymeric segmental motions (in the case of polymeric one). In both cases, mobility of the ions and, in result, conductivity, is decreased.

Compatibility between the receptor and the phase active in ion transport is also needed. In the case of lithium batteries with liquid electrolyte, poor compatibility of the system results in poor receptor solubility. In the polymeric systems, poor compatibility results in phase separation (i.e. receptor agglomeration) leading to receptor precipitation (with receptors of the defined chemical formula) or elimination of the receptor from the system with the oligomeric receptor (e. g. $B(PEOME)_3$) is possible.

Low production costs of the anion receptor are a factor which should be taken into account when discussing application of the anion receptor as a possible additive to the electrolyte. Thus, simplicity of the synthesis and the cost of the raw materials are other important factors which should be considered.

Chapter 2

Anion Receptors - Various Approaches to Complex Formation

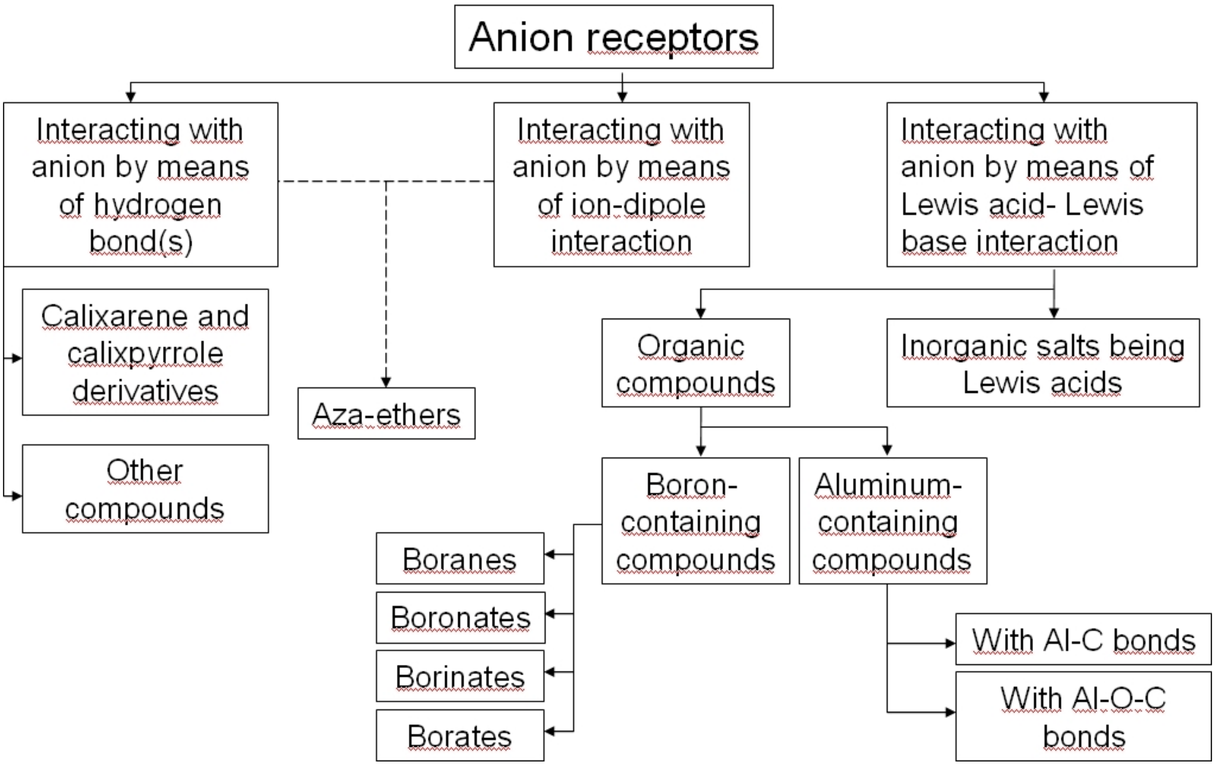


Figure 1. Chemistries of the anion receptor.

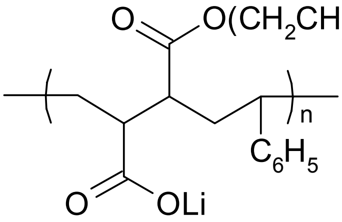
The previous chapter defines the main reasons for the application of the anion receptor in electrolytes dedicated for lithium batteries and functional expectations regarding this group of additives. This chapter defines various groups of compounds capable of interacting with the anion by means of non-covalent interactions which were successfully introduced to a number of liquid, gelly and solid lithium conducting systems. The addition of the anion receptor to the electrolyte resulted in obtaining material characterized with at least one (but often more) of the desired properties such as higher lithium transference number, increased overall ionic conductivity, lower and more stable resistivity of the SEI. Such an effect was achieved by applying various receptor chemistries (Figure 1) and, consequently to these, types of interactions between the anions and the receptors. The anion receptors are characterized by different electrochemical and chemical stability (against oxidation, reduction or hydrolysis), and belong to all i types of compounds, i.e. low M_W, oligomeric and polymeric. The main types of anion receptors grouped by means of type of interaction between the anion and the receptor and the receptor chemistry are presented in Table 1.

It is worth stressing that independently of the studies of the molecular anion receptors as additives, also polymeric composites with ceramic fillers with acidic groups on the surface of the grain were researched. The chemistry of their interactions is similar to the case of receptors interacting with the anion by means of Lewis acid-Lewis base interaction. These studies are not the object of the presented discussion due to fact that surface modified ceramic fillers are dispersed in the matrix in the phase scale (characterized in nano- or micrometers, depending on their grain size), in opposition to the anion receptors which, when dissolved in the matrix, are dispersed in the molecular scale.

Receptor class	Typical compounds	Advantages	Disadvantages
Strong Lewis acids	$AlCl_3$, $AlBr_3$, $SnCl_4$, BF_3, …	Very strong anion coordination	Poor resistivity against hydrolysis. Addition of such receptors can result in polymer or solvent degradation, especially when salts with anion being weak Lewis bases are present in the studied system.
Receptors containing aluminum	$AlEt_3$, $Al(OR)_3$		In the case of alkylaluminum compounds, high hydrolysis ability, poor resistance against hydrolysis, the receptor can explode in the presence of water. Poor solubility in the case of alkoxycompounds.
Systems containing boron atom	$B(OR)_3$, $R^1B(OR^2)_2$, $R^1_2B(OR^2)$, BR_3	Relatively good stability against hydrolysis, successful application in practical systems	Relatively weak interaction with the anion, need of introducing the groups withdrawing electrons (CF_3, C_2F_5) in order to increase Lewis acidity of the boron atom.
Aza-ethers	See chapter 3.1	Receptor-anion complex characterized by high M_W and volume and lipophilic (complex formation results in t_{Li+} increase)	Complicated and expensive synthesis of the receptors, weak resistance against hydrolysis.
Compounds interacting with anion by means of hydrogen bonds	Calixarene and calixpyrrole derivatives, linear compounds	Stable against hydrolysis, receptor-anion complex characterized by high M_W and volume and lipophilic (complex formation results in t_{Li+} increase)	Weak interaction between the receptor the and anion (the need of receptor design oriented for several independent interactions between the receptor and the anion). Possibility of chemical reaction between the lithium anode and the receptor - application in polymeric rather than in liquid systems.

Table 1. Types of anion receptors studied as additives to electrolytes

2.1 Salts being strong Lewis acids


1, R=OCH_3

2.1.1 Addition of salts being strong Lewis acids to polyelectrolytes

Several authors applied salts being hard Lewis acids to improve the conducting properties of polyelectrolytes. Prosini and Banow applied $AlCl_3$ to the polymer blend consisting of PEO, PEODME and lithium salt of poly(styrenesulfonic acid). Application of $AlCl_3$ significantly increased the conductivity of the system. Unfortunately, a fast increase of the interfacial resistance was observed. This observation is confirmed by the storage test and long-term current-time response (both at 89°C) [258]. Florjańczyk studied the effect of BF_3 addition to gelly, **1**-based polyelectrolyte. Also in this case, the addition of the anion receptor resulted in enhancing conductivity 6 times for PC-DMSO-**1** system and, for less polar systems, by more than one order of magnitude (e.g. for PEODME-**1**, PC-PEODME-**1**, or MESO-**1** systems). This phenomenon was ascribed to the anion-receptor complex formation (this was proved by NMR studies: addition of BF_3 to **1** resulted in a change in ^{13}C NMR chemical shift of carboxylic group (no solvent). ^{7}Li NMR spin lattice relaxation studies for **1**-BF_3-DMSO-PC system revealed a change in the cation-anion interaction in comparison with the receptor-free system). In consequence, the reduction of the anion hardness after addition of the Lewis acid was observed (proved by DSC studies i.e. adding the receptor resulted in lowering of T_g of the system) [259, 260]. Similarly to the system studied by Banow, poor stability of the membrane in contact with the metallic lithium was observed, however, the BF_3-containing system was characterized by slightly more stable resistance [261, 262].

Sadoway *et al.* studied the effect of BF_3 addition to the polymeric blend consisting of lithium methacrylate, polydimethoxysilane and (poly(ethylene glycol) methyl ether methacrylate. The system containing BF_3 was characterized by the lithium transference number equal 1, electrochemical stability up to 4.5 V vs. Li/Li^+, and conductivity two orders of magnitude higher than the BF_3-free system [263, 264]. Interestingly, in the case of polymer consisting of the same monomers but with addition of lauryl methacrylate, such an effect of BF_3 addition to the system was not observed [265].

As one could expect lithium transference number equal to 1 should be observed for all polyelectrolyte-based systems independently of the receptor addition. Values lower than 1 prove a harmful degradation of the system.

2.1.2 Addition of salts being strong Lewis acids to SPEs

Several salts being Lewis acids were tested in polymeric systems in order to improve their conductivity and to reduce the resistivity of the passive layer in the electrode-electrolyte interface. Wieczorek [266, 267] studied the effect of the addition of aluminum salts ($AlCl_3$ and $AlBr_3$) to the electrolyte consisting of $LiClO_4$ and PEO or ethylene oxide-methylene oxide copolymer. An addition of $AlCl_3$ and $AlBr_3$ resulted in scission of the PEO and P(MO-EO) polymeric chains, especially at elevated temperatures. After the receptor addition, conductivity rose in the case of both matrices and both compounds studied (the maximum was observed after the addition of 20% of the receptor). Also a lowering of PEO crystalline phase fraction was observed by means of DSC for all the systems studied and IR for PEO and $AlBr_3$. The T_g increase after the receptor addition was also noticed. The IR studies for PEO-$AlBr_3$-$LiClO_4$ system showed that fraction of “spectroscopically free” anions is practically equal to 1.

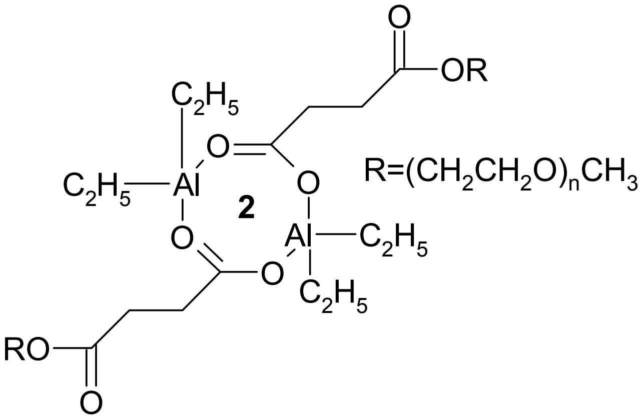
Zygadło-Monikowska [268] studied the effect of BF_3 and $AlEt_3$ addition to $Li[(C_6H_5O)_2PO_2]$ salt dissolved in copolymer of acrylonitrile and butyl acrylate. An addition of BF_3 resulted in a conductivity increase by 2 (at room temperature, RT) up to 4 (at 70ºC) orders of magnitude. A similar conductivity increase was observed after adding BF_3 to a $Li[(C_6H_5O)_2PO_2]$-PEO system. Interestingly, the addition of the $Al(C_2H_5)_3$, which also should exhibit anion coordination properties, did not change conductivity of the system. It can be due to weaker Lewis acidity of this receptor. This result was proved by NMR and FTIR experiments.

Borkowska [269] tested the addition of $AlBr_3$ to a PEOME-$LiClO_4$, liquid system which is often used as a model due to its coordinating and physicochemical properties similar of these of PEO. In this case, Lewis acid addition resulted in an increase of viscosity and T_g. For 1 M $LiClO_4$ solutions, the addition of the receptor resulted in reduction of the fraction of ion pairs (by means of IR spectroscopy) whereas for 0.1 M $LiClO_4$ solutions the effect was opposite. A conductivity maximum was observed for 1% of $AlBr_3$ (with respect to PEOME) in the case of 1 M $LiClO_4$. Contrastively, the conductivity decrease upon receptor addition was observed for 0.1 M $LiClO_4$ system.

The addition of $AlBr_3$ partially stabilizes resistivity of lithium-electrolyte interface but does not fully protect the electrode against corrosion.

2.2 Organic receptors containing aluminum atoms

Aluminum alkoxycompounds are an interesting class of anion receptors, however, their synthesis is more complicated in comparison with similar boron compounds due to the fact that it is impossible to start it from Al_2O_3. Alternative synthetic paths need to be conducted from trialkylaluminum compounds (which are dangerous in handling due to their flammability in the air and vulnerability to moisture and oxygen) or other alkoxycompounds (where there occurs the problem of alcohol remaining in the membrane). Moreover, aluminum compounds are less stable than analogous boron compounds. Despite of all these inconveniences, several authors studied such systems as alternatives for boron-based ones. $Al((OCH_2CH_2)_nOCH_3)_3$ was used as an additive to solid polymer electrolytes [270]. This receptor exhibits similar thermal (between 200 and 300ºC) and electrochemical (4.2 V vs. Li/Li^+ at 60ºC and 4.5 V at RT) stability as analogous boron receptors and polyethers. Also in analogy to boron receptors, its addition resulted in higher conductivity of the system due to plasticization (lower T_g was measured for the receptor-containing system) [271]. Matsuda studied the effect of this aluminum-based receptor addition to the PEO-$LiClO_4$ system. The receptor addition, as in the case of boron-based receptor, resulted in an increase in the discharge capacity for higher discharge rate (0.5 C at 60ºC) and its decrease for lower discharge rate (0.1 C at 60ºC).



Another class of aluminate receptors **2** with poly(oxyethylene) chains in their structure was studied by the group of Florjańczyk [272, 273]. The addition of this receptor to PEO-lithium salt SPEs resulted in an increase in both conductivity (up to 10^{-4} S cm^{-1} at 100ºC and 10^{-7} S cm^{-1} at RT) and lithium transference number (measured by means of both NMR diffusion coefficient measurements and polarization technique). Similarly to other low molecular weight receptors containing $-CH_2CH_2O-$ groups, these properties changes can be related to the fact that the receptor forms anion-receptor complexes (this was confirmed by the studies of solution i.e. a change of ^{27}Al NMR chemical shift after adding salt was observed) and, additionally, plasticizes the polymeric matrix.

Di Noto studied a system consisting of polymeric matrix obtained by the condensation of aluminum isopropoxide and PEG doped with $LiClO_4$. This amorphous matrix exhibits high ionic conductivity ($1.2 \cdot 10^{-4}$ S cm^{-1} at 60ºC and 10^{-5} S cm^{-1} at RT) due to good salt dissociation (above 90% of anions are "spectroscopically free" by means of IR spectroscopy) and relatively low T_g [274, 275].

2.3 Boroxine ring receptors.

Receptors containing the B_3O_3 boroxine ring are a relatively easy-in-synthesis class of receptors. In most cases, they are obtained by direct reaction of B_2O_3 with respective alcohol under reflux. The second product of the reaction, water, is usually removed by aseotropic distillation with toluene or other aromatic hydrocarbon. As a result, defined (e.g. **3a**, **3b**, **5**) or statistic (e.g. **4**) low molecular additives, polymers and polymer networks (e.g. **6**, **7**) can be obtained.

The interaction of this class of receptors with the anion incorporates three boron atoms being electron-deficient. Thus, this class of receptors is selective for anions having several various geometries but not particularly for the one characteristic for TfSI$^-$. In consequence, the majority of the studied systems (excluding LiTfSI-containing one) exhibit both higher lithium transference number and conductivity.

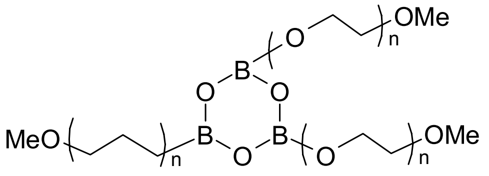
In fact, all presented matrices and additives are rather not pure and well defined compounds but statistic mixture of containing both borates and boroxine rings. Purification in all presented systems [276-283] was not conducted. As they exhibit high oxidation resistivity (above 4.7 V vs. Li/Li$^+$), they are interesting as electrolytes for high OCV cells.

Boroxine compounds can be applied to the systems studied as either separate chemical entity (low M_W additive) or can be incorporated into polymeric structure.

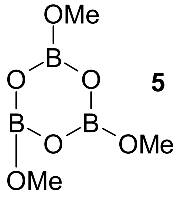
2.3.1 Boroxine ring receptors of low M_W

Several receptors containing the boroxine ring were tested as bifunctional additives to solid polymeric electrolytes (as the anion trapping agent and as the plasticizer). Their addition resulted in conductivity enhancement to the level of $2 \cdot 10^{-5}$ S cm^{-1} at RT and 10^{-3} S cm^{-1} at 80ºC and lithium transference number increase up to 0.79 (polarization technique) and 0.69 (Sorensen technique) for a **4**-LiTf-PMMA solid state system. These results, however, were worse than for a matrix-free receptor-salt system which is a "sticky solid" system. Also when the addition of boroxine ring receptors to the EO-PO copolymer was studied, conductivity enhancement and a lithium transference number increase were observed. Lower conductivity was obtained when the receptors were added to the polymer matrix **8**. It is due to fact that **4** is not fully compatible with **8**. Heterogeneous systems were also obtained when the receptor **4** was added to poly(ethyl methacrylate) PEMA or poly(acrylonitrile) PAN.

Systems based on PMMA-LiTf-**3a/3b/4** mixtures exhibited different mechanisms of conductivity depending on the poly(oxyethylene) chain length. For a receptor with a higher n such as **4**, conductivity is dependent on segmental motions of the oligo(oxyethylene) chains of the receptor while in the case of **3a**, **3b** and **5** conductivity depends on the type of the polymeric matrix used [284].



3a n=3
3b n=2
4 n=7.2



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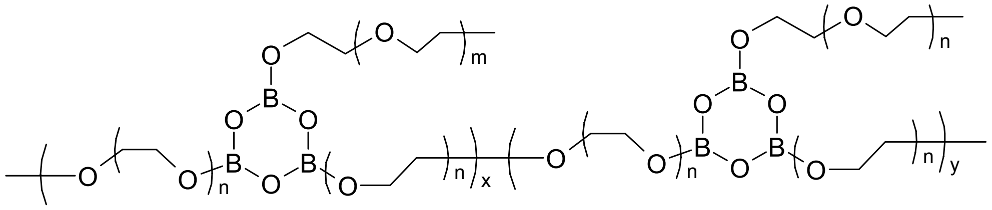
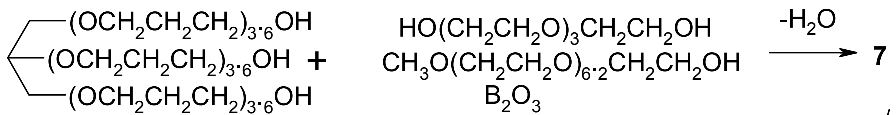


6 m=7.6, n=2



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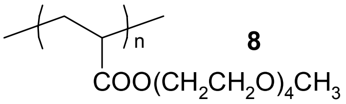

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As the addition of **4** resulted in a significant conductivity enhancement, it was used as one of components of the PEO-based composite electrolyte. The $Li/LiCo_{0.2}Ni_{0.8}O_2$ battery exhibited good cyclability but relatively low specific capacity (below 100 mAh/g) [283]. The role of the anion receptor in this system, however, was not discussed deeper.

3a was also studied as an additive for the PAMPSLi-EC/PC-**3a** gelly polyelectrolyte. The addition resulted in an enhancement of the lithium cation mobility (confirmed by ^{7}Li NMR measurements and a conductivity increase). It turns out be the result of combined composite plasticization and anion receptor complex formation (confirmed by ^{11}B NMR studies). Also in this case, several problems with compatibility between matrix and receptor occurred e.g. for EC:**3a** molar ratio lower than 12:1, phase separation was observed. The highest conductivity achieved for PAMPSLi-EC-**3a** was equal to $2.5*10^{-4}$ S/cm [285]. Even higher conductivity values, up to $8*10^{-4}$ S cm^{-1} at RT were observed when the effect of addition of **3a** to gel based on AMPSLi- dimethylacrylamide copolymer and EC was studied [286].

2.3.2 Polymer networks with built-in boroxine ring

As synthesis of the boroxine ring receptors is based on direct reaction between B_2O_3 and alcohols, it was also interesting to determine if materials obtained by means of analogous reaction with diols can yield a linear polymer or polymeric network. Such a system should be stable (against high temperature, hydrolysis and electrochemical oxidation and reduction), and, due to interactions with the cation and the anion, exhibit higher conductivity and lithium transference number in comparison with the pristine PEO based system. Indeed, conductivity of **6**-salt systems was slightly less than 10^{-5} S cm^{-1} at RT and 10^{-3} S cm^{-1} at 60ºC [279, 276]. These values, however, strongly depend on the density of matrix cross-linking (and resulting viscosity), the salt used and the molar ratio between salt and the boron atoms [276, 281]. The mechanisms of conductivity in the system presented are suspected to be similar to these typical for PEO. The only difference was that PEO interacts mainly with the cation whereas matrices presented in this paragraph interact with both cation and anion (confirmed by ^{11}B NMR studies). In consequence, a salt addition results in an increase of T_g for about 32ºC [277] which is also a proof for strong matrix-salt interactions.

This polymer matrix was studied also in *semi*-IPN consisting of PEO and **6**, due to good compatibility of both matrix constituents and a similar mechanism of the cationic transport. Such a system exhibits lower crystallinity than PEO, higher lithium transference number (about 0.4) and enhanced conductivity (more than one order of magnitude at RT) [280, 281]. Moreover, the T_g of obtained *semi*-IPN was lower than that of PEO, suggesting a higher mobility of poly(oxyethylene) chains. The application of this blend also lowered the interfacial resistivity and stabilized the electrode-electrolyte interface. Thus, no significant lowering of the discharge capacity of the $Li/LiCo_{0.2}Ni_{0.8}O_2$ battery after 50 charge-discharge cycles was observed.

Easy synthesis of the system studied and promising results of battery tests show that this *semi*-IPN matrix can be an interesting material for commercial applications [282].

2.4 Receptors with single boron atom interacting with anion

2.4.1 $B(C_6F_5)_3$

The $B(C_6F_5)_3$ receptor was widely studied as an electrolyte additive [265, 287-292, 294, 295], due to the fact that it is commercially available, stable up to 5 V vs. Li/Li^+ in several solutions, e.g. in DMC-EC-PC 3:1:1 [288], DMC-EC 2:1 [289], DMC-EC 2.5:1 [287], DMC [289]; whereas the stability decrease down to 4.3 V vs. Li/Li^+ for the DME-based system [288, 289] should be attributed to the solvent, not the receptor oxidation). Moreover, this receptor is characterized by good thermal stability [288] and strong acceptor properties.

As it was previously described in chapter 1.4, there is a difference in the mechanism of receptor activity between well and weakly dissociated systems. In systems, in which the salt is **well-dissociated**, such as $LiClO_4$ in organic carbonates, the receptor addition resulted in a conductivity decrease. This lowering has two possible explanations. Firstly, complex formation reduces the mobility of the anion excluding it partially from charge transportation. This mechanism is confirmed by parallel lowering of conductivity and lithium cation transference number enhancement. Secondly, the addition of the receptor raises viscosity of the system due to the interactions between the receptor and the solvent (the presence of anion-receptor and solvent-receptor interactions was confirmed by FTIR studies [287]). Interestingly, when a well-dissociated electrolyte was used for soaking porous PE separator, conductivity enhancement upon the receptor addition was observed. The authors ascribed this phenomenon to the higher electrolyte uptake into the porous separator structure in the case of systems containing the receptor. In systems in which the salt is **weakly-dissociated**, such as LiF, LiCl, LiBr, LiI, $LiCF_3COO$ and LiC_2F_5COO [288, 293] in DME or mixtures of organic carbonates, adding the receptor enhances salt dissociation. It is due to lower Lewis basicity of the “complexed” anion in comparison with the “uncomplexed” one. In consequence, adding the receptor to such systems leads to the enhancement of conductivity to values high enough for applications in lithium batteries (up to $6 \cdot 10^{-3}$ S cm^{-1}). It is also worth noting that the salt dissociation enhancement and the lowering of Lewis basicity of the “complexed” anion results in significant solubility improvement for these salts.

Anion-receptor interactions in systems containing LiCl and LiI were examined by means of the NEXAFS studies. A split of the K line of chlorine (2835 eV) and $L_{||}$ line of iodine (5190 eV) was observed as an effect of anion-receptor complex formation.

Basing on these results, electrolytes containing 1 M of this receptor and 1 M of the salt (LiF or $LiCF_3COO$, LiC_2F_5COO), were tested in a Li/$LiMn_2O_4$ battery. Such systems, when compared with a commercial $LiPF_6$-based electrolyte, exhibited lower but stable in time discharge capacity and higher Coulombic efficiency (CE). Contrary to the commercial electrolyte, such stability was observed not only at RT but also at elevated temperatures in which commercially available system is unstable [288, 294].

"Solubilization" of the LiF after adding $B(C_6F_5)_3$ was also used for another purpose. The addition of small amounts (usually 0.1 M in the case of 1M $LiPF_6$ solution in organic carbonates) of the receptor was tested in several lithium battery systems to reduce the growth of the passive layer on electrodes. These layers contain mainly LiF, which is the decomposition product of $LiPF_6$. As a result of the formation of the complex between the fluoride anion and the receptor and the fact that the lithium salt of this "complexed" anion is (contrary to LiF) soluble in several solvents (e.g. in mixtures of cyclic carbonates or DME), a slower growth of passive layers was observed. Consequently, a higher amount of the cathode material was active after several charge-discharge cycles [265]. Thus, the receptor-modified electrolyte, when used in batteries with Li/$LiMn_2O_4$, "Li-ion"/$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, or "Li-ion"/$Li_{1+x}[Ni_{0.3}Co_{0.3}Mn_{0.3}]O_2$ [290, 291, 295] electrodes as well as in a symmetrical "Li-ion"/"Li-ion" design (in this case, $LiBF_4$-organic carbonates-receptor solution was used as the electrolyte) was characterized by higher capacity than commercial $LiPF_6$-based, receptor-free electrolyte. Moreover, this capacity was stable during cycling. The batteries containing electrolyte with an addition of the receptor (contrary to receptor-free ones) exhibited good stability and good cyclability (both CE and capacity) up to 55ºC for both Li/$LiMn_2O_4$ battery [290] and symmetrical "Li-ion"/"Li-ion" system [292].

However, it is worth noting that too high a concentration of the anion receptor can induce creation of PF_5 and passivation of the lithium anode because of the triggering of the $LiPF_6$ decomposition to LiF and PF_5 [291]. Also the application of this receptor to salt-DME systems (DME is more stable in terms of degradation in contact with Lewis acids or bases) failed owing to poor electrochemical stability of DME and, thus, oxidation of DME in contact with the cathode [289].

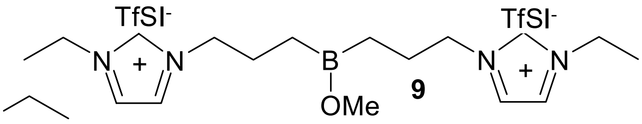
$B(C_6F_5)_3$ was tested also as an additive to the SPE consisting of PEO, PEODME and LiTf. The addition of the receptor, when the receptor concentration was 10 times lower than that of salt, resulted in the enhancement of the lithium transference number of the system and, in elevated temperatures, in conductivity improvement. Bigger amounts of the receptor resulted in lowering the conductivity at temperatures lower than 50ºC and in a conductivity increase above this temperature [296]. An opposite tendency was observed for SPE consisting of PEO, PEODME and LiF. In this case, a monotonic increase of conductivity in function of receptor concentration was observed. The system with the receptor to LiF ratio 1:1 exhibited conductivity even higher than respective SPE containing LiTf. Also in this case, the lithium transference number was higher for systems containing the receptor [296].

2.4.2 Other low M_W trialkyl- and triarylboranes

Triarylboranes were studied by several authors because of their simple chemical structure, relatively good solubility, and commercial availability or, at least, simple synthesis. Thus, they were used as model anion trapping additives.

The effect of BPh_3 anion receptor in the PEODME-salt (LiI, LiTf, LiTfSI, $LiClO_4$, $LiBF_4$) systems was studied by Marcinek [297]. A slight conductivity improvement after the BPh_3 addition was observed for temperatures lower than RT. For higher temperatures, and especially for high (3 M) salt concentrations, the BPh_3 addition resulted in lowering the conductivity by 2 to 5 times or had no effect on this parameter. It was suggested that this conductivity lowering is related to the complex formation and in the case of higher salt concentration the effect of conductivity lowering should be attributed to a viscosity increase.

For a system containing LiTf, the presence of the anion-receptor complex was proved by means of FTIR spectroscopy. Effective anion complexation was observed at temperatures lower than RT. DSC studies revealed that addition of the receptor reduced the fraction of the PEODME crystalline phase at sub-ambient temperatures [297].



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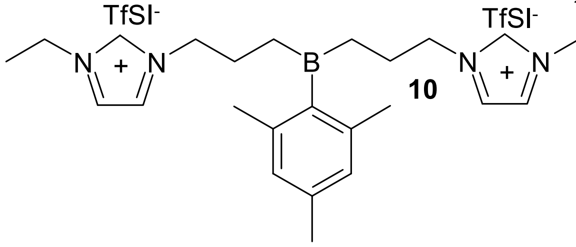

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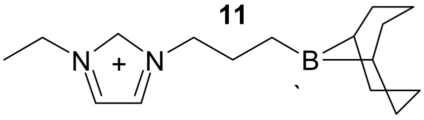

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Matsumi synthesized and characterized several molten salts containing the imidazole group (ionic liquids or soft solids at RT) **9-11**[1] with a borane or borinate group in their structure. The systems studied exhibited high lithium transference numbers (up to 0.7 for **10**-LiTf and **10**-LiTfSI) and conductivity lower than 10^{-4} S cm^{-1} at RT [298].

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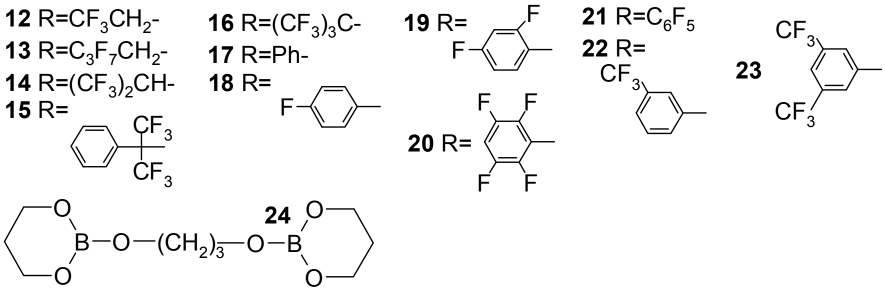
[1] From chemical point of view, **29** is not borane but borinate. However, as it is only one out of two borinate compounds presented in this review, and the effect of **29-31** receptors was studied by the authors in the same article, they were described in the “boranes” chapter.

2.4.3 Low M_W triesters of boric acid

Several triesters of boric acid **12-23** were synthesized and studied as anion receptors in various electrolytes [288, 293, 299, 300].

All aliphatic borates studied were highly fluorinated compounds and, thus, the strength of the receptor was high enough to complex the anion even in a strongly coordinating solvent. Hence, the addition of majority of these compounds resulted in similar conductivity enhancement (up to $9 \cdot 10^{-3}$ S cm^{-1} in the best conducting system). Thus, electrolytes containing electrochemically stable trialkylborates can be used in lithium batteries to reduce the growth of passive layers on electrodes and to obtain highly conducting electrolytes based on weakly or moderately dissociating salts such as LiF, LiBr or $LiCF_3COO$. A $Li/(CF_x)_n$ battery with such electrolyte exhibited 10% higher capacity and lower internal resistance in comparison with one with commercially available, receptor-free, $LiPF_6$-based electrolyte but a slightly lower cell voltage [300]. Also $Li/LiMn_2O_4$ and $Li/LiNi_{0.85}Co_{0.15}O_2$ batteries with such electrolyte exhibited stable discharge capacity and high CE [299].

12-23: $B(OR)_3$



In the case of aromatic borates, not only perfluorinated compounds but also several non- or partially fluorinated ones were tested. Thus, several of them were too weak to complex the anions in the systems studied. Consequently, the existence of the conductivity enhancement phenomenon depended on the chemical formula of the particular receptor used [293]. Moreover, aromatic borates are less stable than aliphatic ones. For example, “aliphatic” receptor **14** in organic carbonate mixture is stable up to 5.2 V vs. Li/Li^+, when “aromatic” **21** in the same solvent exhibits stability only up to 3.8…4.3 V, depending on the salt used and solvent composition [299]. This is too low for application of “aromatic” **21** in the lithium battery. Also thermal stability (77°C for **21**-LiF-solvent system and even lower for receptor itself) was too low for such applications [288]. The authors suggest that it is the result of possible easy loss of the electron by the oxygen atom connected to the aromatic ring. In consequence, batteries in which electrolytes containing aromatic borates were used were characterized by low stability of the discharge capacity during the charge-discharge cycling (50% specific capacity fade after 50 cycles was observed) [288].

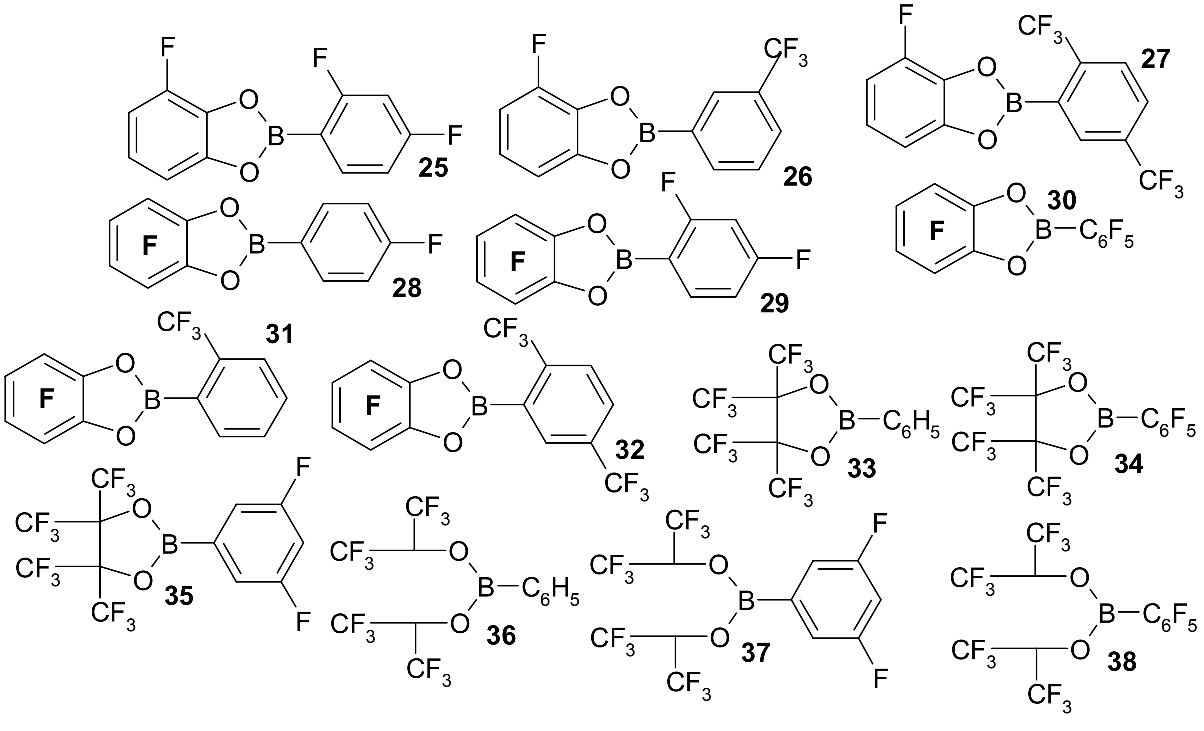
To compare the mechanism of anion receptor interactions for borates and to prove the presence of the anion-receptor interactions, several NEXAFS experiments were conducted. Similarly to the observations for systems containing $B(C_6F_5)_3$, a split of the chlorine K line (2835 eV) and iodine $L_{=}$ line (5190 eV) is observed, however, the split was weaker than in the systems containing $B(C_6F_5)_3$. Moreover, the strongest split was observed for aromatic borates (e.g. $B(OC_6F_5)_3$) which are not electrochemically stable. Fortunately, the fact that the interaction of the aliphatic borate and the anion is weaker (in terms of NEXAFS) than in the case of the anion and $B(C_6F_5)_3$ does not influence conductivity enhancement negatively. This result suggests that even receptors characterized by binding strength lower than $B(C_6F_5)_3$ are strong enough to complex the anions in polar solvents. Thus, the binding strength of the receptor, at least while in a particular range, does not play the crucial role in the enhancement of the charge transport. For instance, systems containing **14** exhibited the conductivity value higher than $B(C_6F_5)_3$-containing ones [295, 299].

Another approach to the synthesis of the electrolyte was presented by Zhang [301]. In this study, borate compound **24** was studied as an alternative for cation coordinating ethers or polyethers. LiTfSI and $LiClO_4$ solutions in **24** exhibited conductivity up to 10^{-4} S cm^{-1} at RT and above 10^{-2} S cm^{-1} at 100ºC. These values were significantly lower than those of systems based on alkyl carbonates (which are typically at the level of 10^{-2} S cm^{-1} at RT). It was due to the high viscosity of salt solutions in **24** as well as **24** itself. Conductivity values for salt solutions in **24** were significantly higher than those of salt solutions in poly(propylene glycol) M_W=4000, characterized by similar viscosity as pristine **24** itself. It proves that **24** exhibits relatively strong coordination properties. Application of **24**-EC or **24**-EC-PC instead of **24** itself resulted in higher conductivities. Unfortunately, the dielectric constant of these systems was not compared by the authors, thus, the conductivity cannot be unambiguously attributed to the difference in coordinating properties between the systems studied. Moreover, **24** exhibited brilliant stability versus oxidation (up to more than 5.5 V vs. Li/Li^+) and stabilized the electrode-electrolyte interface when added to the salt solutions in organic carbonates.

2.4.4 Dialkylboronates

Dialkylboronates (e.g. **25-38**) are diesters of boronic acid $RB(OH)_2$ (R - alkyl or aryl group). In consequence, receptors based on boronates exhibit properties similar to those of borates and boranes. The main difference is related to the fact that molecules of receptors of this type are characterized by significantly lower symmetry. Thus, they exhibit better solubility and a lower melting point in comparison with borates and boranes. This group of compounds was also studied as the potential electrolyte additives [302-305].

The mechanisms of the anion-receptor interactions (studied by NEXAFS [302]) as well as consequences of such interactions (e.g. salt solubility and conductivity enhancement) are very similar to these in boranes and borates. Moreover, optimal, in terms of conductivity, compositions containing boronate receptors are characterized by conductivity values similar to the best systems containing borane or borate (comparison based on ref. [303]). Similarly to the borate receptors, aromatic esters of boronate acids exhibit stability lower than their aliphatic analogues [304]. Also in this case, lithium batteries (Li/LiMn$_2$O$_4$, Li/LiNi$_{0.85}$Co$_{0.15}$O$_2$ and "Li-ion"/Li$_{1.1}$[Ni$_{0.3}$Co$_{0.3}$Mn$_{0.3}$]O$_2$ [305]) with various electrochemically stable receptor-poorly dissociating salt-organic carbonate systems as electrolytes exhibit high and stable capacity and high CE. DME-based systems exhibit low oxidation stability also in the case of this class of receptors.

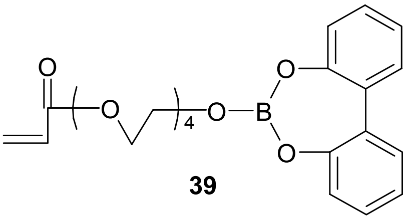


Apart from these several similarities, a very interesting exception can be observed. A Li/LiMn$_2$O$_4$ battery with LiF-**34**-DME electrolyte is characterized by stable capacity and high and stable CE [304]. This result is opposite to the results obtained for an analogue battery with LiF-DME-B(C$_6$F$_5$)$_3$ electrolyte [289] and for Li/LiNi$_{0.85}$Co$_{0.15}$O$_2$ battery with electrolyte containing the same dialkylboronate [304]. While the discrepancy between systems incorporating the same receptor and different cathode materials can be explained by means of higher OCV of Li/$LiNi_{0.85}Co_{0.15}O_2$ in comparison with $LiMn_2O_4$, it is problematic to explain the discrepancy between batteries containing **34** and $B(C_6F_5)_3$ with electrodes built of the same materials. Unfortunately, this interesting phenomenon is not discussed by the authors.

Receptor **30** was also tested as the bifunctional additive being simultaneously an overcharge protecting compound (redox shuttle) and the anion receptor. The activity of this receptor as the redox shuttle was confirmed during overcharge tests. Moreover, the battery with $LiPF_6$-organic carbonate-**30** electrolyte exhibited a higher discharge capacity during charge-discharge cell cycling [305].

Hirakimoto *et al.* studied the effect of the addition of borate receptors **39**-**41** to the solution of salts in various solvents [306-308]. In several cases, e.g. for all DME- or DMC-based solutions as well as for all the systems containing LiCl and $LiCF_3COO$, the addition of the receptor resulted in a conductivity increase. Contrastively, for relatively well dissociated $LiBF_4$/LiTf/LiTfSI solutions in PC or GBL, a conductivity lowering was observed. This decrease was ascribed to the increase of viscosity of the solution and not to partial immobilization of the anion (this is valid only with the combined assumption that Walden product is constant for both receptor-containing and receptor-free systems, and that a similar concentration of charge carriers is present in both systems). In the case of poorly dissociated systems, the effect of conductivity enhancement was ascribed to better salt dissociation (in these systems, this effect dominates over the effect of conductivity lowering due to a viscosity increase) through the complex formation [307]. This assumption was later confirmed by the author through determining the factors controlling ionic conductivity in such systems. For this purpose a possible relation between the conductivity of the system and its viscosity was examined. The authors declare it can be applied to determine the concentration of the charge carrier and to compare this parameter between a system containing the receptor and a receptor-free one. A product of system conductivity and its viscosity is used here as an indicative measure. Normalizing this value to be equal to 1 for pristine systems and comparing with those for systems containing the receptor, values in range of 3.3...4.4 for $LiCF_3COO$ and 0.9...1.1 for systems containing LiTfSI can be observed. This proves that the dissociation of the former is strongly affected while for the latter no important change is observed [308]. Moreover, the effect of solubility enhancement after adding the receptor to a system containing LiCl has the same origin [307].

The highest conductivity observed was equal $7 \cdot 10^{-3}$ S cm^{-1} (system: LiTfSI-DME-**39** [306]).



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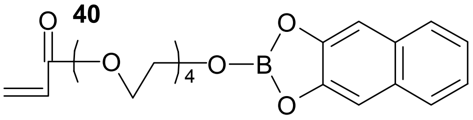

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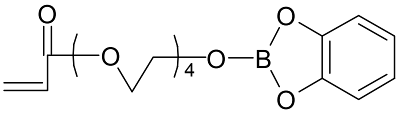

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PFG NMR studies were used to obtain molecular information on the salt dissociation process. As the NMR technique produces results being a weighted average of all sensitive nuclei present in the sample, in the case of poorly dissociated salts it is impossible to regard the diffusion coefficient as the value characteristic for particular charged species. The dissociation degree can be calculated by comparing the values measured with those calculated from Nernst-Einstein equation. In the case of the $LiCF_3COO$ salt the value obtained was two to three times higher for the systems containing receptor whereas no significant change for the LiTfSI system was observed upon the addition of the receptor.

In the receptor-free systems, diffusivity studies for $LiCF_3COO$ show that D_+ and D_- are equal indicating that ionic pairs are the predominant species in the system. This is, however, not the case for solution containing LiTfSI where anionic diffusivity is higher than cationic one. This points onto the fact that anion and cation movements are, at least partially, independent. In the case of a system containing $LiCF_3COO$, the diffusivity of both positively and negatively charged species was higher after adding the receptor. This increase suggests that the diffusivity change of dissociated ions, in comparison with ionic pairs, is high enough to overcome the phenomenon of viscosity increase after the receptor addition leading to the final improvement of ion transport properties of the system studied. In the case of a well-dissociated LiTfSI-containing system, a diffusivity decrease was observed. This phenomenon should be ascribed to the viscosity increase while no dissociation change is present.

To study the phenomenon of anion-receptor complex formation in these systems, ^{11}B NMR studies were conducted. In the ^{11}B NMR spectra of salt-free DME-**40** and DME-**41** systems two peaks are observed (the authors attribute one of them to the uncomplexed receptor molecule and the other to the receptor-solvent complex) while in **39** solution in DME a single peak in the spectrum was observed. This difference in the spectrum of **39** in comparison with those of **40** and **41** compounds is attributed by the authors to the fact that in the case of the solvent interacting compounds a boron atom belongs to a five-membered ring while in the case of **39** to a seven-membered one.

After the addition of a well-dissociated salt, such as LiTf or LiTfSI, to this system an additional peak in the spectra (relative chemical shift 5 ppm) was observed. In the case of addition of LiCl or $LiCF_3COO$ to the DME-**40** system, 0 and 6 ppm signals diminish and only the peak with a relative chemical shift of 5 ppm can be observed. In both cases, this behavior was ascribed to the phenomenon of anion-receptor complex formation [307]. Also upon the addition of $LiCF_3COO$ to the solution of **39** in DME, a similar behavior was observed. Moreover, when the amount of salt added was less than stoichiometric, peaks characteristic for both uncomplexed receptor and receptor-salt complex were observed [308].

2.4.5 $B(PEOME)_3$

Several publications were dedicated to $B(PEOME)_3$ as the ester of the poly(ethylene glycol) monomethyl ether and the boric acid.

One of the systems to which $B(PEOME)_3$ was introduced is the polymer network obtained from (poly(ethylene glycol) methyl ether) methacrylate ((PEGMEMac) and poly(ethylene glycol) dimethacrylate ($PEGMac_2$) as the plasticizer or coplasticizer. In this amorphous system, the mechanism of conductivity is similar to that observed in PEO-based systems and can be ascribed to the segmental motions of the polymeric chain. Thus, the introduction of $B(PEOME)_3$ to such a system improves the ion transport properties of the membrane due to both plasticization of the system (lowering of T_g [309, 310]) and better salt dissociation. Indeed, for nearly all the systems studied, independently of the salt used, a monotonic increase in conductivity with the increase of receptor concentration was observed [309, 311, 312]. The importance of the influence of the phenomenon of polymeric matrix plasticization on the conductivity values observed was confirmed by the fact that the addition of the receptors with shorter oligo(oxyethylene) chain produces systems characterized by higher conductivity (due to stronger plasticization). Moreover, systems with shorter oligo(oxyethylene) chains exhibited a higher lithium transference number due to higher concentration of borate groups [311].

Also in the case of $B(PEOME)_3$ the receptor addition, similarly to other systems presented, results in an increase of the lithium transference number from 0.05 to 0.1 in the case of LiTfSI- and from about 0.1 to 0.25 and 0.35 in the case of $LiClO_4$- and LiTf-based systems, respectively. Interestingly, the dependence of conductivity on the type of salt used is different in comparison with the observations for other PEO-based polymer architectures in which the conductivity of a composite doped with $LiClO_4$ is several times lower than for systems doped with LiTfSI and comparable with these doped with LiTf. In the case of $B(PEOME)_3$, the conductivity of the $LiClO_4$-based system is only slightly lower than one of containing LiTfSI and 3 times higher for a sample containing LiTf. These results suggest that boron esters interact stronger with Tf^- and ClO_4^- anions than with the $TfSI^-$ one [312, 313].

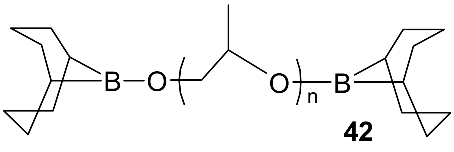
The polymer matrix containing the receptor is thermally stable up to 250ºC [313]. Moreover, the addition of the receptor resulted in an increase of membrane flash point [311]. The electrochemical stability of the membrane is moderate. The system is stable up to 4.5 V at RT and up to 4.2 V at 60ºC [311]. Interestingly, a PE sponge soaked with receptor-free PEODME-LiTfSI-$PEGMac_2$ exhibits stability up to 4.6 V vs. Li/Li+ and 5.2 V vs. Li/Li^+ after the addition of $B(PEOME)_3$ [314]. Unfortunately, the authors of this article did not account for this change.

To increase the conductivity of the polymeric matrix, $B(PEOME)_3$ was used as a coplasticizer together with PC being added simultaneously to the same polymer network. This approach combined the advantages of high conductivity (due to a higher dielectric constant upon PC addition) and high lithium transference number (due to the anion immobilization by $B(PEOME)_3$). The membranes obtained were characterized by higher lithium transference number than the pristine matrix-salt-PC composition (0.35 for $B(PEOME)_3$-containing and 0.1 for $B(PEOME)_3$-free system) and higher conductivity than the PC-free matrix-salt-$B(PEOME)_3$ system. Interestingly, there was no significant difference in the lithium transference number between the systems incorporating $B(PEOME)_3$ as the plasticizer and coplasticizer (PC: ester=1:1) [315].

Similar results, i.e. high lithium transference number (above 0.6), stability up to 4.5 V vs. Li/Li^+, were observed for a microporous PE sponge with Kynar coating soaked with EC-PC-1M $LiClO_4$ gelled system with 1,6-hexanediol diacrylate matrix and $B((OCH_2CH_2)_3OCH_3)_3$ additive [316].

$B((OCH_2CH_2)_3OCH_3)_3$-EC-PC-$LiClO_4$ gelled system with 1,6-hexanediol diacrylate matrix, when studied in a $Li/LiCo_{0.2}Mn_{1.8}O_4$ battery, exhibits stable discharge capacity (about 90 mAh g^{-1}). Storage tests revealed no growth of passive layer on the electrodes. This result was confirmed by a CV test in which the system was electrochemically stable up to 4.5 V vs. Li/Li^+ for the first cycle and to 5.0 V vs. Li/Li^+ for subsequent cycles. However, the main problem observed during the cell-cycling tests performed both at RT and 50ºC was high electrolyte resistivity and, thus, high capacity loss when high charging (and discharging) currents (0.2 C at RT and 2 C at 50ºC) were used [315, 318]. A very similar system (EC-PC-1M $LiClO_4$ with 1,6-hexanediol diacrylate and $B((OCH_2CH_2)_3OCH_3)_3$) exhibited very poor stability when used in a $Li/LiCoO_2$ battery (a charge capacity fade during the 1st discharge was observed). Similarly to other oxyethylene unit-based electrolytes the instability of ether groups versus oxidation plays the dominant role here [316].

In other studies, a borate ester added to the PEO-$LiClO_4$ solid polymer electrolyte enhanced the initial discharge capacity when used in a Li/$LiCoO_2$ battery (0.1 C at 60ºC). The application of this receptor to rechargeable systems is impossible due to its high capacity fade (over 50% after 8 cycles) being the consequence of instability of the polymer matrix versus the cathode. The application of the PEO-$LiClO_4$-B(PEOME)$_3$ electrolyte in the Li/$LiFePO_4$ battery resulted in lowering the discharge capacity of the battery in comparison with the receptor-free system when low (0.1 C at 60ºC) current density was applied and its increase when a higher current charge rate (0.5 C at 60ºC) was used. It is due to the fact that in a battery containing a borate additive the system is characterized by faster growth of the passive layer on the electrolyte-lithium anode surface but higher conductivity. The faster growth of the passive layer can be ascribed to the weaker chemical resistivity of B(PEOME)$_3$ in comparison with high M_W PEO (or, alternatively, not the B(PEOME)$_3$ itself but rather its impurities, such as PEOME). Higher conductivity can be, in this case, ascribed to both plasticization of the polymer matrix and improvement of dissociation. The discharge capacity of a battery with the electrolyte containing receptor was relatively stable in time (8% fade between 5th and 20th cycle). This can be explained by the fact that after the first cycles the passive layer on the electrode-electrolyte interface was formed, playing the protective role and self-limiting its own further growth [270].



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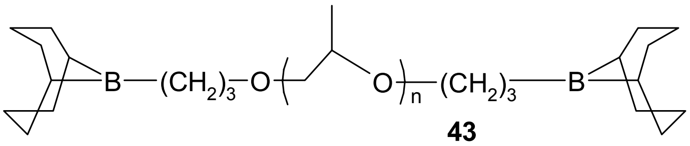
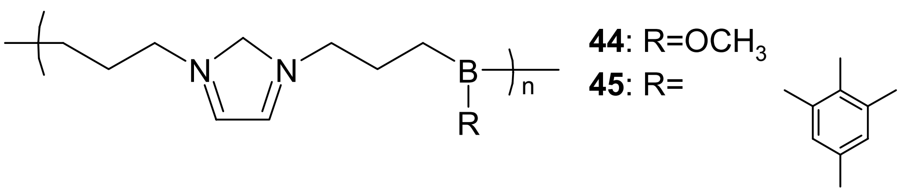


43

2.4.6 Other olygomeric receptors

Receptors **42** with boronate and **43** with borane group covalently linked to the oligomeric, PPG-based chain were studied by Mizumo. The **42**-LiTf system was characterized by conductivity lower about 3-4 times than PPG-LiTf, but also 3 times higher lithium transference number. The increase of the lithium transference number was independent of average number of the propylene oxide units linked to the receptor. The **42**-LiTfSI system exhibited higher ionic conductivity but a lower lithium transference number and the **42**-LiBr/$LiCF_3COO$ systems exhibited a lithium transference number similar to the **42**-LiTf but lower conductivity and T_g (due to poor dissociation of these salts). Conductivity and the lithium transference number for best conducting systems containing LiTf were similar to those consisting of *pseudo*-polyelectrolytes (oligoethers capped with $–CH_2SO_2N^-SO_2CF_3$ anionic group at the end of the oligoether chain) [318, 319].



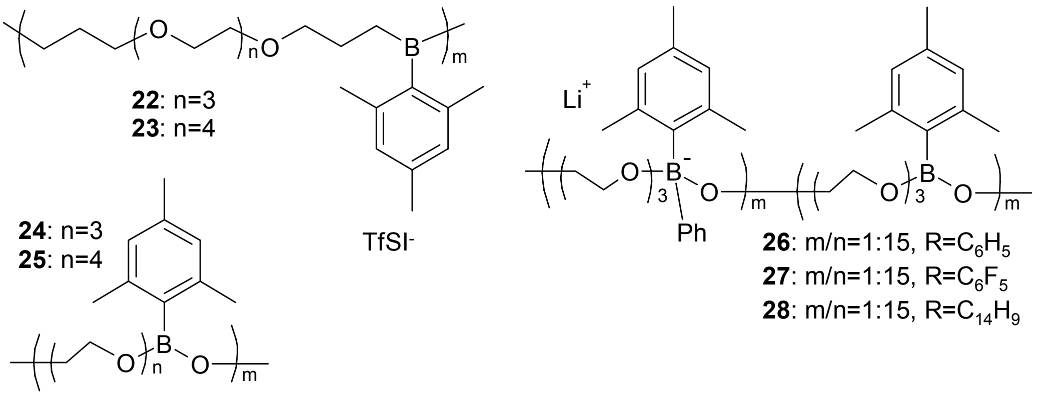
44: $R=OCH_3$
45: R=

Oligomers **44-45** (M_W=4,000-9,000) of chemical structure similar to ionic liquids were also studied. They exhibited lithium transference numbers higher than similar molten salts and similar ionic conductivity. In ^{11}B NMR spectra of the presented oligomers changes of the chemical shifts upon various salts addition were observed. Those changes depended on the anion of the salt, suggesting the presence of anion-receptor interactions [320].

2.4.7 Linear polymers with the boron group covalently linked to the polymeric chain

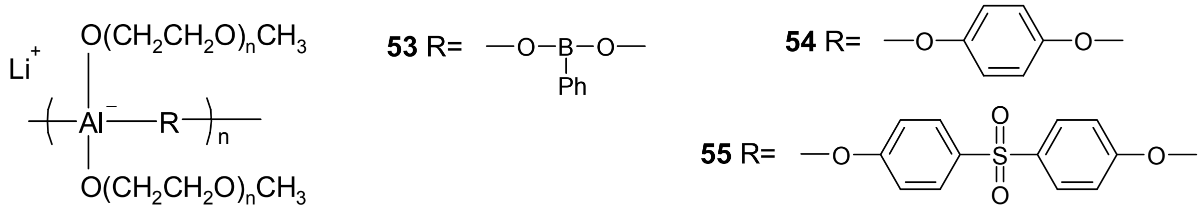
Borane receptors built into the polymeric chain **46-47** [321, 322] were examined by Matsumi. The system studied exhibited a lithium transference number in a 0.3-0.4 range (slightly higher than PEO-salt systems) and conductivity lower than for systems containing respective boronate receptors built in the polymeric chain (**48-49**).

Synthesis of polyelectrolytes **50** resulted in a conductivity lowering (in comparison to **46-49**-containing systems) by more than one order of magnitude (partially because of the lowering of the number of charge carriers), correlated with an increase of the lithium transference number values to about 0.8 [322]. However, the values of conductivity were still about one order of magnitude higher than in respective polymers incorporating $-SiPh_2-$ instead of -BPh-moiety [323].



22: n=3
23: n=4
24: n=3
25: n=4
26: m/n=1:15, $R=C_6H_5$
27: m/n=1:15, $R=C_6F_5$
28: m/n=1:15, $R=C_{14}H_9$

The application of polyelectrolytes of a similar formula, as **51** or **52**, resulted in much higher conductivities. Unfortunately, the lithium transference numbers for these systems were not measured [322]. In another publication, also poly(organoboron halide) polymer was studied by the same research group [324].

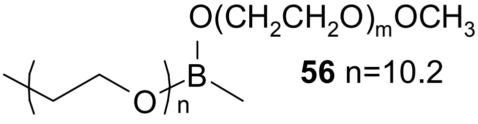


53 R=

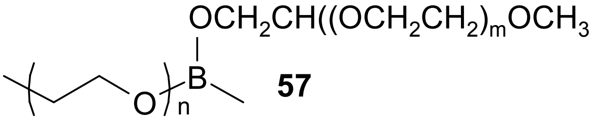
54 R=

55 R=

Another similar polymeric system **53** was applied by Matsushita [325] and Fujinami [326]. In their studies, an aluminate anion was incorporated in the polymeric chain and -OBPhO-moiety was covalently linked to the aluminum atom. The systems studied containing the receptor exhibited higher conductivities in comparison with **54** or **55** systems incorporating into the chain chemical moieties not being capable of forming complexes with anions.



56 n=10.2



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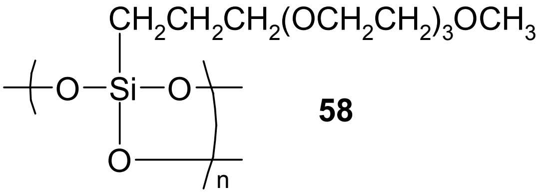
Linear polymers **56**-**57** were studied by Kato. These linear polymers exhibited slightly lower conductivity than the networks described before (up to $1.5 \cdot 10^{-4}$ S cm^{-1} at 60ºC and 10^{-5} S cm^{-1} at RT for **56**-LiTfSI) and a lithium transference number up to 0.38 for the LiTf-**56** system [327].

2.4.8 Polymer networks based on PEG-B_2O_3

Several networks being chemically borate esters of poly(ethylene glycols) were synthesized in order to obtain an amorphous, highly conducting, PEO-like and thermally stable polymer network. As in the case of $B(PEOME)_3$ receptors, this class of polymer networks exhibits moderate electrochemical (4.5 V vs. Li/Li^+ at RT) and brilliant thermal stability (up to 200ºC) [328].

Also in the case of this class of composites, a lithium transference number enhancement was observed in comparison with the respective PEO-salt system. Moreover, the lithium transference number grew when the concentration of boron atoms increased, i.e. in the case of shorter poly(oxyethylene) chains. For instance, when LiTfSI was used, it was equal to 0.64 and 0.44 for PEG M_W=150 and 250, respectively, and 0.16 for PEG M_W=400 and 600. Systems containing $LiClO_4$ and LiTf exhibit higher lithium transference numbers in comparison with analogous ones containing LiTfSI, due to the higher affinity of these anions to the borate groups [329].

Similarly to the majority of other oxyethylene-based systems, this one also exhibits the mechanism of conductivity based on segmental motions of the polymeric chain and, in consequence, VTF thermal dependency on conductivity. The best-conducting systems exhibit conductivity equal to $6 \cdot 10^{-5}$ S cm^{-1} at RT and 10^{-3} S cm^{-1} at 110ºC [328, 329]. In the case of shorter PEG bridges, conductivity was, in general, lower, due to higher cross-linking density of the polymer matrix. This explanation is confirmed by the DSC studies i.e. systems of lower PEG M_W are characterized by higher T_g [329-331]. These effects were independent of the salt used, however, no significant difference between the systems with PEG M_W=600 and PEG M_W=1000 (long poly(oxyethylene) chains) was observed.



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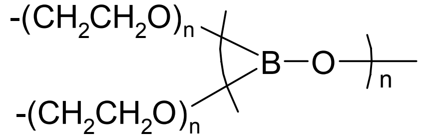
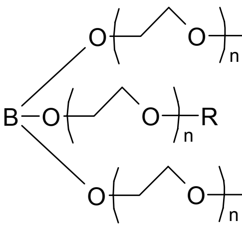


59

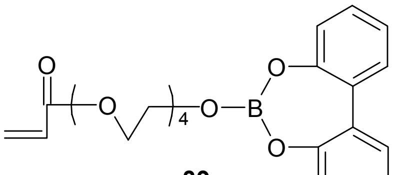
B_2O_3-PEG containing polymer network **58**-**59**, containing not only boron but also siloxane units, was synthesized by Kurono. Such a composite doped with LiTf was characterized by conductivity at the level of 10^{-4} S cm^{-1} at 100ºC and 10^{-5} S cm^{-1} at RT. Slightly higher conductivity was observed for polymers of lower concentration of the borate groups [332]. *Semi*-IPN obtained by blending of these polymer networks with PEO exhibited slightly lower conductivity.

2.4.9 Other systems with boron-based receptors covalently immobilized in the polymeric network

The previously described monomeric boronates (see Chapter 2.4.4) were used in the synthesis of **62**-based polymer matrices for polymer-solvent-salt gel electrolytes [306, 307, 333] as well as polymer-salt solid polymer electrolytes [308]. Systems containing **39**-**62** and **40**-**62** polymer networks were compared to the receptor-free system, obtained from **62** and (poly(ethylene glycol) methyl ether) methacrylate. The modified systems exhibited higher conductivity with the exception of the **40**-**62**-$LiBF_4$-GBL system [306, 307]. For polymer-salt SPEs with **41**-**62** matrices, a higher lithium transference number and higher conductivity for systems containing LiCl and $LiCF_3COO$ in comparison with the receptor-free **62**-based network were observed. An opposite effect on conductivity was observed for the system containing LiTfSI. It was mainly due to higher T_g of **41**-**62** matrix in comparison with its receptor-free analog.



60: R= $C(O)CH{=}CH_2$
61: R=CH_3 or R= $C(O)CH{=}CH_2$



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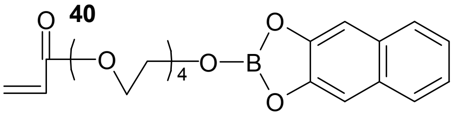
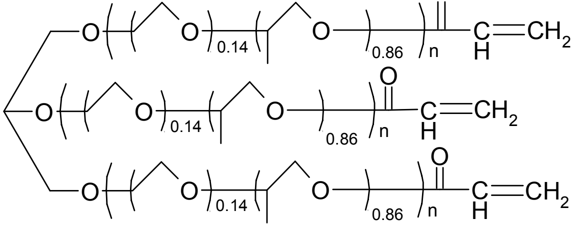
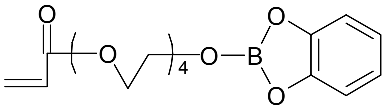




62



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Polymer networks consisting of **60** or **61**, based on the borate group containing a macromonomer, were studied by Aihara. Both networks exhibited higher lithium transference numbers and conductivity in comparison with similar polymer networks based on **62** macromonomer. The **61**-based network which is characterized by lower cross-linking density in comparison with **60** (due to lower content of unsaturated moieties in the macromonomer) exhibited higher conductivity than the **60**-based one. The **61**-based network had higher T_g which stands in contrast with the lower density of chemical cross-linking. To account for this phenomenon one must take into consideration that the stiffening effect can be a combination of chemical cross-linking and physical one resulting from salt-polymer interactions. The observed discrepancy indicates that the effect of physical cross-linking (being the result of a higher number of free ions) dominates in the overall stiffness of the polymeric matrix in comparison with the chemical one. Unfortunately, both **60**- and **61**-based networks, when used as electrolytes in Li/$LiCoO_2$ batteries, do not improve their performance during charge-discharge cell cycling; the **61**-based one has the initial capacity similar to the boron-free systems, however, its discharge capacity decreases in time whereas the **60**-based electrolyte has discharge capacity stable but lower than the boron-free systems. Due to its elevated conductivity, the battery containing the **61**-based electrolyte exhibited lower inner resistance during the cell-cycling tests in comparison with **62**-based systems (which was important for overall battery characteristics) only when cell cycling in higher discharge rates (1 C) were applied [334].

Contestabile *et al.* performed several tests on the electrolyte containing $LiPF_6$, organic carbonates and a borate anion receptor. The addition of the receptor resulted in higher discharge capacity for a wide range of temperatures and discharge currents and for more than 120 charge-discharge cycles in comparison with the receptor-free system [335].

Chapter 3

Non Lewis Acid-Based Anion Receptors

In the previous chapter applications of several groups of compounds being anion receptors as the electrolyte additives were described. The majority of these studies were conducted on liquid lithium cation conducting systems utilizing receptors interacting with anions by means of **Lewis acid-Lewis base** interactions. It was due to the fact that receptors interacting with the anion by means of other than Lewis acid-Lewis base were in general regarded to be non-applicable in liquid electrolytes. The main reasons are presented in Table 2.

Type of anion receptor interaction	Typical receptors	Why possibly non-applicable
ion-ion	Protonated and other positively charged aromatic and aliphatic amines, receptors containing guanidine group, pyrrolic receptors such as porphyrine derivatives	Complex formation resulted in the formation of a positively charged or electrically neutral anion-receptor entity. As such complex is expected to be cation counterion, such class of receptors is non-applicable (see Chapter 1.4.1).
hydrophobic effect	β-cyclodextrin	Receptor molecules contain several hydroxyl groups and, thus, are unstable against the anode (in liquid systems). Very strong cation coordination.
ion-dipole	Aza-ethers, cryptands containing $N^{+}\cdots B^{-}R_3$ groups, receptors containing sulfoxide and phosphoroxide groups	Several problems in synthesis of the receptors, relatively weak single interaction between the anion and the receptor application - a need of designing a receptor oriented for a number of parallel anion-receptor interactions.
hydrogen bond	Receptor containing: urea, urethane, amide, pyrrole, hydroxyl groups	Relatively weak single interaction between the anion and the receptor – a need of designing a receptor oriented for a number of parallel anion-receptor interactions. The receptor contains several mobile protons and is regarded unstable against the anode.

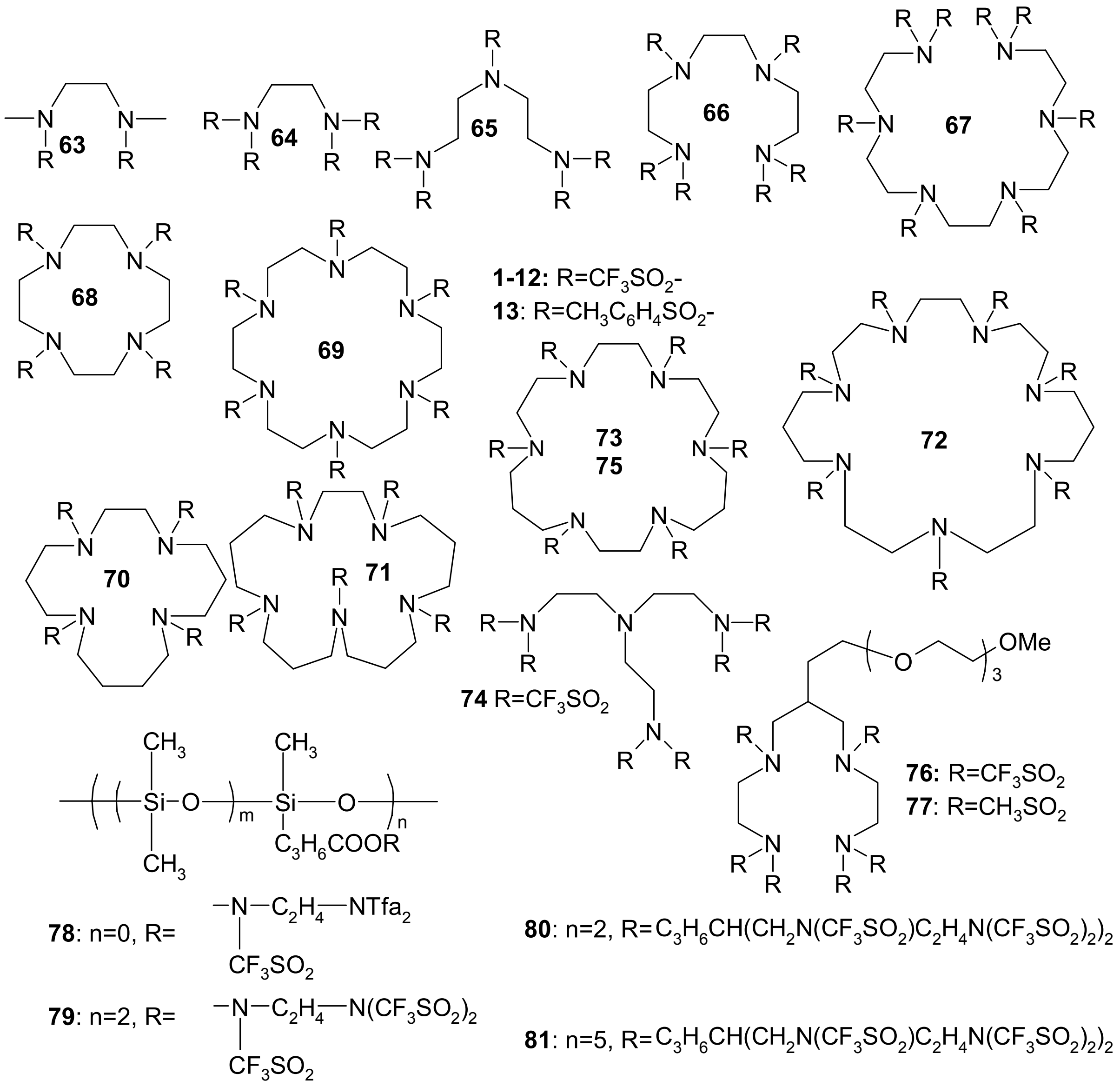
Table 2. Comparison of different possible anion-receptor interactions in terms of their applicability in the electrolyte systems.

The first two groups of the receptors (interacting with the anion by means of the **ion-ion** and **hydrophobic effect** interactions) reveal chemical properties which absolutely eliminate them from any lithium-oriented applications. This situation is different for other classes where rather technical matters (in the case of receptors interacting with the anion by means of the **ion-dipole** interaction) and negative assumptions (in the case of receptors interacting with the anion by **hydrogen bonds**) were taken into consideration.

3.1 Aza-ether receptors

A third class of receptors interacting with the anion by means of forces other than Lewis acid-Lewis base was proposed and practically realized by the McBreen group. It was initially suspected that such a receptor should interact with the anion by means of the ion-dipole interaction. Computer molecular dynamics simulations showed that in this case the interaction between the anion and receptor is not only due to the ion-dipole electrostatic forces but is also related to the hydrogen bond formation [336].

Several aza-ethers (**63-81**) were synthesized in the Brookhaven National Laboratory by the McBreen research group. This type of receptors interacts with the anion by means of the ion-dipole interaction i.e. nitrogen atoms covalently bonded to the CF_3SO_2- group have partially positive charge and they can interact with the negatively charged ion [255, 337-341]. Alternatively, the receptor can interact with the anion via hydrogen atoms of CH_2 groups [342]. Aza-ethers, due to their chemical structure, are mostly selective on anions characterized by high surface charge density, namely, fluorides and chlorides, but they also interact with larger anions such as iodides, bromides or perchlorates. Because of that, the receptor addition resulted in good solubility of LiCl anf LiF in THF. High ionic conductivity, up to $1.7 \cdot 10^{-3}$ S/cm was observed for the **74**-THF-LiCl system (it is about 1000 times higher than for the corresponding, receptor-free LiCl solution in THF) [255]. The addition of the receptor to the solutions of other salts in THF also resulted in conductivity enhancement. The effectiveness of the anion-receptor interaction strongly depends on the structure of its polyamine "core". The receptor **74**, based on tris(2-aminoethyl)amine exhibited (in comparison with other receptors) the highest affinity to the majority of the anions studied being interesting counterions for lithium salts. The affinities of the receptors based on linear polyamines were lower and the lowest for these based on cyclic polyamines. In the case of linear and cyclic polyamines, the strength of the anion-receptor interactions increases with the number of -CH_2CH_2NTfa- units present in one molecule of the compound studied. It might be due to the number of the interacting centers in the receptor molecule [255, 339]. Such dependency between the receptor binding strength and the structure of the receptor was confirmed by conductivity measurements (**74**-containing systems were characterized by highest conductivity) and the spectroscopic studies.



1-12: R=CF_3SO_2-

13: R=$CH_3C_6H_4SO_2$-

74 R=CF_3SO_2

76: R=CF_3SO_2

77: R=CH_3SO_2

78: n=0, R= $-N(CF_3SO_2)-C_2H_4-NTfa_2$

79: n=2, R= $-N(CF_3SO_2)-C_2H_4-N(CF_3SO_2)_2$

80: n=2, R=$C_3H_6CH(CH_2N(CF_3SO_2)C_2H_4N(CF_3SO_2)_2)_2$

81: n=5, R=$C_3H_6CH(CH_2N(CF_3SO_2)C_2H_4N(CF_3SO_2)_2)_2$

NEXAFS studies of LiBr-receptor-THF systems showed a splitting of the bromide K line (13475 eV) into two separate ones. A similar splitting of the chloride K line (2835 eV) was observed when LiCl-receptor-THF systems were studied. In this case, the most intensive split was observed for systems in which the highest conductivity enhancement was observed [255, 339]. Contrary to this, such a split was not observed for several receptors whose addition did not result in conductivity enhancement such as e.g. polyamines [338]). The NEXAFS results for the chloride anion were confirmed by ^{35}Cl NMR study i.e. the addition of the receptor resulted in a broadening of the observed peak [343].

The anion-**68**-solvent interactions were studied quantitatively by D'Aprano [341]. He calculated several ion pair association constants (cation-"free" anion and cation-"complexed" anion) as well as anion-receptor complex formation constants by means of conductivity measurements and calculations based on the Lee-Wheaton theory. He proved that in well-dissociated solutions such as $LiClO_4$-PC (cation-"free" anion association constant equal to 4 M^{-1}) or $LiClO_4$-CH_3CN (cation-"free" anion association constant equal to 18 M^{-1}) upon the addition of the receptor the overall conductivity was slightly reduced but lithium transference number t_{Li+} increased. In poorly-dissociated systems such as $LiClO_4$-THF (cation-"free" anion association constant above 10^7 M^{-1}), both overall conductivity and lithium transference number increased due to better dissociation of the salt (as cation-"free" anion ion pair formation constant is significantly higher than the cation-"complexed" anion one). The detailed values of equilibrium constants characterizing the process of complex formation, as well as the formation of ionic pairs incorporating the cation and the complexed anion or the cation and the uncomplexed anion ion pairs are given in Table 3.

Solvent	K_1, [dm^3 mol^{-1}]	K_2, [dm^3 mol^{-1}]	K_3, [dm^3 mol^{-1}]
CH_3NO_2	40	91	375
PC	10.3	3	4.4
CH_3CN	34.2	11	18.4
THF	$9*10^6$	$9*10^6$	$1.7*10^7$

Table 3. Formation constants: of anion-anion receptor complex (K_1), of an ionic pair consisting of a cation and anion-anion receptor complex (K_2) and of a ionic pair consisting of cation and uncomplexed anion (K_3) in $LiClO_4$-**68**-solvent system. After [341].

The presented receptors are, to the best knowledge of the author of this dissertation, the strongest coordinating agents which base on the dipole-ion interactions. The exchange of the Tfa electron-withdrawing group for tosyl or methanesulfonyl one resulted in significant lowering of the binding properties of the receptors [338].

Solid polymer electrolytes **78**-**81** with aza-ether groups covalently linked to the polymeric chain were also studied. Similarly to the liquid systems containing aza-ethers, NEXAFS studies revealed a split of the chloride K line. Conductivity enhancement in receptor-containing matrices [337] is also observed. Such phenomena suggest strong non-covalent interaction between the receptor built in polymeric chain and the anion. Unfortunately, the ionic conductivities of the best conducting systems (polymers **79** and **80**, about $4 \cdot 10^{-6}$ S/cm in RT and about 10^{-4} S/cm in 85°C) were comparable with the PEO-based systems. Thus, practical application of this material, much more expensive and complicated in synthesis, is limited.

3.2 Hydrogen bond based receptors – the question of applicability

Successful incorporation of aza-ether compounds into both liquid and polymeric electrolytes together with knowledge upon their mixed type of interaction with the anion incorporating both ion-dipole and hydrogen bond-type forces attracted the interest of scientists to other classes of compounds being capable of forming hydrogen bonds with anions.

In the first estimation the application of compounds incorporating relatively mobile protons should be impossible in lithium battery systems. It is due to thermodynamic instability of these compounds against both metallic lithium and lithium-intercalating anodes. On the other hand, considering polymeric systems in which diffusion limits the reactivity at the interfaces, one should remember that i) the stability of the anode-electrolyte is, at least partially, the result of SEI formation, thus, the receptor after the SEI formation may not be in direct contact with the anode and/or the kinetics of the reaction between the anode and the receptor might be too slow to influence properties of the electrolyte negatively and ii) acidic properties of hydrogen can be tailored to the system. Thus, one can consider some hydrogen bond forming compounds even not being thermodynamically stable against the electrode material as possible SPE additives being capable of complexing anions and, thus, promoting salt dissociation (all SPEs must be treated as weakly dissociated systems), leading, in consequence, to an increase of lithium transference number and/or conductivity. The possibility of the application of the "mobile hydrogen" compounds is additionally confirmed by the successful use of some polymer matrices or additives which do not affect system stability.

In solid polymeric electrolytes application of "hydrogen bond-type" anion receptors can be conducted successfully, even if their application in liquid system is disputable, as several systems (e.g. polymeric matrices) containing mobile protons were studied and exhibited good stability. The best example of such systems are electrolytes based on poly(ethylene imine), in which the concentration of mobile protons is higher than 23 mol (kg of the polymer)$^{-1}$ (see Chapters 1.1 and 1.4.3). Another good example is the addition of polysugars such as cellulose [344-347] and chitosan [348-351] (both contain OH groups in their structure) as well as acrylamide and methacrylamide (both contain mobile NH protons, presented in Chapter 1.3.1) to PEO resulting in obtaining a stable system.

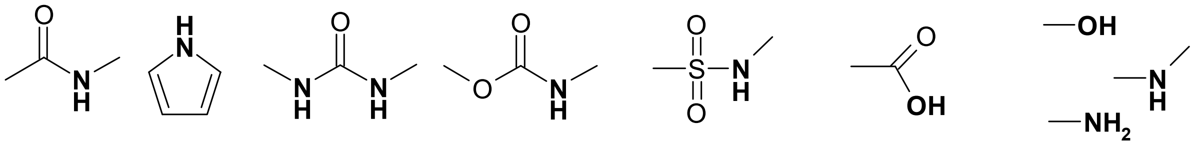


Figure 2. Groups capable of forming the hydrogen bond with the anion.

Taking all these facts into account, it is interesting to focus attention on electrically neutral receptors interacting with anion by means of the hydrogen bond.

3.3 Macrocyclic receptors interacting with the anion by means of the hydrogen bond

The majority of the groups capable interacting with the anion by means of the hydrogen bond are presented in Figure 2. As it was pointed in Chapter 1.4.3, when designing such a hydrogen-bond-interacting receptor i) the number of (identical or different) groups active in hydrogen bond-type interactions should be kept as high as possible due to the fact that a single interaction usually does not result in the formation of the complex; ii) active groups and their arrangement should be tailored in order to maintain good geometric fitting for more effective interaction with the anion, iii) the enthalpic effects of interaction can be supported by the entropic ones, thus, the receptor alone should be characterized by low, and the anion-receptor complex by high configurational entropy of the molecule. It is also worth noting that the majority of anions and, especially, ones applied to polymeric electrolytes, are multiatomic species[2]. Taking all these facts into account, macrocyclic molecules are among the most interesting ones when one considers receptors capable of forming complexes with anions such as ClO_4^-, BF_4^-, PF_6^-, Tf^- or $TfSI^-$ [352]. Macrocycles are in general characterized by low configurational entropy themselves. Moreover, in such molecules, the distances between groups active in the anion complexation can be easily tailored in order to form structures which are characterized by good receptor-anion geometric fitting.

The main problem here is of the synthetic matter and is related to the fact that the closing of the macrocyclic ring is complicated as the number of all the possible conformations of the receptor precursor grows with the ring size. Thus, the probability of "ends-of-chain-meet" spatial arrangement needed for the ring closing reaction is low. In the last years, the chemistry of the macrocycles is one of the most widely studied topics of supramolecular chemistry in general [353]. It was shown that a reaction yield can be optimized by means of alteration of the structure of the molecule (e.g. introduction of a heteroatom [354-356], aromatic [357-361] or geminal methyl [362, 363] fragments acting as molecular structure stiffeners into the chemical compound being a substrate in a ring closing reaction). This can also be achieved by optimization of reaction conditions, e.g. lowering substrate concentration in the reaction mixture [364-366], choice of the solvent [367] and the reaction temperature [368, 369].

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[2] The consequence of these facts is that among the most "easy-to-complex" anions one can include fluoride (F^-) and chloride (Cl^-) which are small and characterized by high density of the negative current. The complexation of the iodide (I^-) is much more complicated. Among other relatively easy to complex anions one can include carboxylates ($RCOO^-$) due to well-oriented charge density. Especially the interaction between the urea groups of the receptor and the carboxylate group of the anion is preferred as the consequence of very good geometric fitting between these groups. Unfortunately, the anions presented here cannot be applied in commercial electrolytes due to their very poor dissociation.

Addition of compounds being molecular templates [370-374] and the condensation processes leading to reactions other than ring closing, such as depolymerization of polymers, were also tested [375-378]. Unfortunately, most of these studies were conducted on polyethers or polyesters, which are not capable of coordinating anions. The chemistry of macrocycles which contain groups active in anion coordination as cyclic oligoamides [379-384] or calixpyrroles [385, 385] is less than 20% of the overall literature related to this topic but, on the other hand, there are still more than 2.000 publications (see e.g. books cited in Chapter 1.4.1). Only several macrocycles such as e.g. calix[n]arenes or resorcinol[4]arenes can play the role of the typical "building blocks" in the design of anion receptors as the rings of these molecules contain groups which can be substitutes. Hence, derivatives of such macrocycles can be successfully applied as anion receptors [387-393], being tailored to particular needs by the functional group choice.

Anion	Ionic radius, [Å]
F^-	1.33
Cl^-	1.81
Br^-	1.96
I^-	2,06

Table 4. Effective ionic radius of halogenides. Coordination number equal to 6. After [394]

3.4 Receptors selective on anions being weak Lewis basis

Contrary to the huge number of publications concerning topics of receptor design oriented on the complexation of biologically important anions such as phosphates (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$), sulfates (SO_4^{2-}, HSO_4^-), nitrates (NO_3^-), and halogenides (F^-, Cl^-, Br^-, I^-), the design of the receptors capable of coordinating anions such as ClO_4^-, BF_4^-, PF_6^-, Tf^- or $TfSI^-$ is rather of rare interest for the specialists in the field of supramolecular chemistry. It is mostly due to the following facts: i) the anions for battery applications have no importance in biological (biochemical) systems, ii) owing to their large size and complicated geometry, the design and synthesis of the receptors interacting with such anions is significantly more complicated than e.g. halogenide-sensitive receptors, iii) interactions between the receptor and the anions dedicated for electrolyte applications are weaker than in the case of anions usually applied in biological systems because of their low surface charge density in such anions (resulting from their large size, see Table 4) and poor coordinating properties (see Table 5) resulting from the fact that the charge is dispersed over several atoms [395].

Another factor limiting the application of the anion receptors is the cost of the synthesis. At least three factors should be taken here into account: the cost of commercially available substrates, the number, degree of complication and yield of reactions leading to obtaining the final product as well as the cost and difficulty of its purification. It is worth stressing that most of the receptors reported in the literature were synthesized in amounts smaller than 100 mg, and such an amount of the receptor (also due to its high M_W, usually above 500 g mol^{-1}) is not high enough for the casting of one typical SPE membrane (100 µm thick, containing about 20% m/m of the receptor, area 20 cm^2) and, consequently, for battery tests.

Another important factor limiting the number of potentially useful structures is related to self-association of the receptors. This tendency can be observed not only in case of calixarene derivatives containing urea groups [396] but also several other molecules [397-401].

Anion	DN	Anion	DN
PF_6^-	2.50	$CF_3SO_3^-$	16.90
AsF_6^-	2.50	NO_3^-	21.1
SbF_6^-	2.50	CN^-	27.1
BF_4^-	6.03	I^-	28.9
ClO_4^-	8.44	CH_3COO^-	29.5
$(CF_3SO_2)_3C^-$	2.50	SCN^-	31.9
$(CF_3SO_2)_2CH^-$	7.80	Br^-	33.7
$(CF_3SO_2)_2N^-$	5.40	Cl^-	36.2

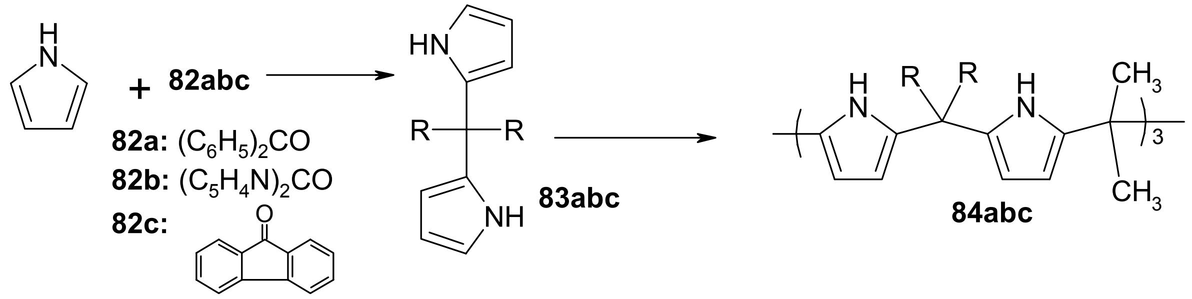
Table 5. Donor numbers (on the same scale as Guttman Donor Numbers for solvents of various anions). After [402, 403].

Taking the above presented facts into account, it was decided to limit the interest to the two classes of receptors, namely calix[6]pyrrole and calix[4]arene derivatives.

3.5 Calix[6]pyrroles

Calix[6]pyrroles are characterized by a large macrocyclic hole and C_3 symmetry which is identical to that of several anions such as e.g. Tf^-, ClO_4^- and BF_4^-. Thus a good geometrical fitting is achieved between the above-mentioned anions and calix[6]pyrroles. Moreover, they can be synthesized in the multigram scale (over 10 g) which is needed for practical application. What is additionally worth noting, the donor properties of the pyrrole ring are weaker than those of other group being the hydrogen-bond donor (e.g. amide, urea and urethane) and, due to this, the interaction of the receptor containing the pyrrole group with cations is significantly weaker than in the case of the other anion receptors (see Chapter 1.4.3). This property is also important when taking into account slowing down of the irreversible reaction between the anode material and the receptor.

Calix[6]pyrroles, contrary to calix[4]pyrroles, are products not thermodynamically stable in terms of configurational entropy. Therefore, the number of publications in which the synthesis of calix[6]pyrroles was described is more than 10 times lower that for calix[4]pyrroles. In general, five receptors being calix[6]pyrrole derivatives were synthesized thanks to three different strategies.



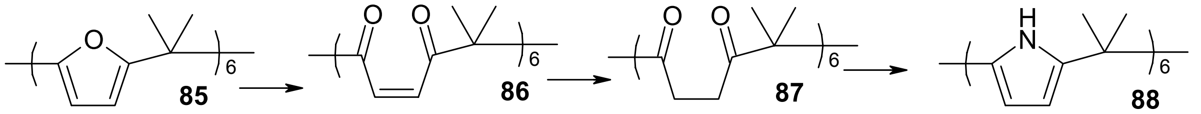
Turner et al. synthesized two different receptors being calix[6]pyrrole derivatives from dipyrrolic intermediates such as **83ab**. These compounds can be obtained by the condensation of pyrrole and ketone **82a** or **82b** in molar ratio equal to 2:1 with $BF_3{\cdot}Et_2O$ as the condensation catalyst. The next synthetic step of the synthesis incorporates the ring-closing reaction of the intermediate product with the acetone. Such a strategy led to obtaining receptors from commercially available compounds in two steps. One could note, however, that only the compound **84a** (C6P) was synthesized with high yield (above 50% as it comes to the intermediate product and above 20% as it comes to pyrrole; the respective yield of the synthesis of **84b** was lower than 5%) and the synthesis of the intermediates was possible only in the case of three ketones (substrates) i.e. benzophenone (**82a**), di(2-pirydyl)ketone (**82b**) and 9-fluorenone (**82c**) condensate with pyrrole effectively [404].

In the above mentioned studies on the synthesis of **84ab**, trifluoroacetic acid CF_3COOH was used as catalyst. To study its role in the mechanism of reactions, dipyrrolic intermediates with acetone, several other catalysts including $BF_3{\cdot}Et_2O$, methanesulfonic CH_3SO_3H and toluenosulfonic and trihalogenoacetic (CF_3COOH, CCl_3COOH or CBr_3COOH) acids were tested. Interestingly, only the application of trihalogenoacetic acids led to obtaining calix[6]pyrrole derivatives whereas other compounds resulted in obtaining the receptor containing four pyrollic rings. It might be a consequence of the template (matrix) effect of the catalytic compound due to the relatively strong hydrogen bond-like interaction between the protons from the aromatic ring of benzene and halogens from the acid molecule. As the symmetry of the CX_3 group is identical as that of calix[6]pyrrole, such interaction can promote ring closing. This hypothesis is supported by the fact that the application of dual 2,2,2-trichloroethanol-methanesulfonic acid catalyst resulted in obtaining calix[6]pyrrole, contrary to the previously mentioned system in which only CH_3SO_3H was used as catalyst [405].

Receptor **84a** (1,1,3,3,5,5-*meso*-hexaphenyl-2,2,4,4,6,6-*meso*-hexamethyl-calix[6]pyrrole, C6P) exhibits strong anion coordination properties and forms stable complexes with several anions in solution. Interestingly, when comparing various halogenides, it is selective on the iodide anion - the selectivity order is (K_a in CD_3CN-CH_2Cl_2 1:9 mixture in brackets): I^- ($6600M^{-1}$)>F^-($1080M^{-1}$)>Cl^-($650M^{-1}$)>Br^-($150M^{-1}$) in solution. For a typical anion receptor the interaction strength between the ion and the receptor changes in order $F^->Cl^->Br^->I^-$, resulting from stronger coordinating properties of smaller anions due to their higher surface charge density. This untypical order was explained by very good geometric fitting of the anion and the receptor in the case of the iodide anion. Stable complexes with trihalogenoacetates and (CF_3COO^-, K_a=1150 M^{-1}) tetrafluoroborate anion (BF_4^-, K_a=2350M^{-1}) were also reported. What is also worth noting is that the receptor is not selective on acetate (CH_3COO^-) anions. Also electrically neutral trichloroethanol can interact with this receptor (K_a=60M^{-1}) due to good geometric fitting of the CCl_3- moiety in the macrocyclic hole of the receptor [406]**.**

Several X-ray diffraction experiments on monocrystals containing C6P reveal that this receptor is capable of forming complexes not only with molecules containing CF_3 or CCl_3 groups but also several other molecules such as chlorobenzene, acetonitrile or nitrobenzene [407]. Unfortunately, anion-receptor complexes in the solid state were not reported.

Cafeo *et al.* synthesized *meso*-dodekamethylcalix[6]pyrrole **88** from *meso*-dodekamethylcalix[6]furan **85** by oxidative opening of furan rings to enodione (**85→86**), then hydratation of the carbon-carbon double bonds (**86→87**) followed by condensation with application of ammonia acetate (**87→88**) [408]. In the synthesis of **88**, chromatographic purification of intermediate products was not needed as in the case of C6P.



Receptor **88**, like C6P, forms stable complexes with halogenide anions, however, the highest selectivity was reached for the chloride anion (selectivity changes in order $Cl^->Br^->F^->I^-$ and is the result of both good anion-receptor geometric fitting and appropriate Lewis basicity of the anions). The exact values of the complex formation constant are presented in Table 6.

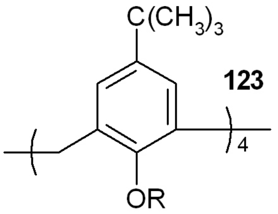
ion	K_a, [$mol^{-1}dm^3$]	ion	K_a, [$mol^{-1}dm^3$]	ion	K_a, [$mol^{-1}dm^3$]	ion	K_a, [$mol^{-1}dm^3$]

ion	K_a, [$mol^{-1}dm^3$]	ion	K_a, [$mol^{-1}dm^3$]	ion	K_a, [$mol^{-1}dm^3$]	ion	K_a, [$mol^{-1}dm^3$]
F^-	33[3]	NO_3^-	16	Br^-	710	CN^-	100
Cl^-	5500[4]	HSO_4^-	10	I^-	<10	$H_2PO_4^-$	n.a.[5]

Table 6. Constants of anion-**8** complex formation measured by means of NMR titration. After [409].

The results of complex formation constant estimation are confirmed by the crystallographic structures, i.e. in the case of **88**-Cl^-, nearly flat conformation of the receptor is observed while the receptor in **88**-Br^- complex is in "flowered" conformation and the anion is located about 0.7 Å above the surface of the pyrrole rings [409]. In solid-state complexes with neutral species such as water, studied by means of X-ray diffraction of monocrystals, interactions between the pyrrole NH moiety and oxygen originating from the water as well as those of the complete pyrrole ring and OH group are observed.

The effect of anion complexation was also confirmed by extraction of tetrabutylammonium salts from their water solution to the organic phase. The addition of the receptor resulted in extraction improvement by 50% in the case of the bromide salt and about 20 times in the case of the chloride. These results are consistent with the measurements of the complex formation constant [410].



123

a: $R=CH_3$
b: $R=CH_2C_6H_5$
c: $R=CH_2COOC(CH_3)_3$

This receptor was also used in a binary composition containing both an anion receptor and a cation receptor (modified cyclodextrin) in order to extract paraquat dichloride ($((CH_3NC_5H_4)_2)Cl_2$) from the water phase to the organic one (paraquat dichloride is widely used in the production of herbicides and is highly toxic). Due to chloride anion complexation, the binary system was much more effective in the transport of this compound to the organic phase in comparison with the system without any anion receptor [411]. Similar studies were also conducted on other **88**-cation receptor binary systems, such as **88**-18-crown-6 and **88**-calix[5]arene derivatives **89abc** in CH_2Cl_2 solution. In these systems, stable cation (usually,

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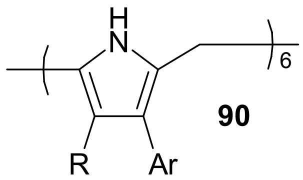
[3] In the mixture of 500:1, measured by means of the Cram method (see in: E. P. Kyba, R. C. Hengelson, K. Madan, G. W. Gokel, T. L. Tarnowsky, S. S. More, D. J. Cram, J. Am. Chem. Soc, 99 (1977) 2564)

[4] As above.

[5] NMR titration was impossible due to broadening after the addition of the salt.

linear alkylammonium)-cation receptor as well as anion-anion receptor complexes were observed [412].

Interestingly, it is (at least theoretically) possible to synthesize also *meso*-oktadekamethylcalix[9]pyrrole, characterized by a larger macrocyclic hole, and, thus, capable of complexing large anions effectively, using the same synthetic strategy as was successfully used for the synthesis of *meso*-oktadekamethylcalix[9]furan [413, 414].



90

a: R=$COOC_2H_5$, Ar=mesityl
b: R=$COOC_2H_5$, Ar=2,6-dichlorophenyl
c: R=$COOC_2H_5$, Ar=C_6H_5
d: R=CF_3, Ar=C_6H_5

Uno *et al.* synthesized several *meso*-unsubstituted calix[6]pyrroles **90** by oligocyclization of 2-hydroksymehtyl-3,4-disubstituted pyrroles utilizing different acids as condensation catalysts. The reaction yields were in range of 2 and 20% and depended on the catalyst and the substrate used in reaction. The authors measured NMR and mass spectra of the products obtained in order to confirm their chemical structure [415]. Crystallic structures of the synthesized compounds showed that the receptor in the solid state exists in the 1,3,5-alternate conformation. An additional observation to be made was the formation of intramolecular hydrogen bonds between the NH group of the pyrrole rings and the oxygens of the ester groups.

It is also worth stressing that the obtained receptors are resistive against oxidation. Unfortunately, their application is limited due to fact that their synthesis requires obtaining substrates untypical and complicated derivatives of pyrrole, and the yield of the synthesis of the macrocycle is relatively low [416].

3.6 Calixarene derivatives

Calixarenes are ones of the most intensively studied macrocycles in the last 20 years - the literature concerning them can be estimated at over 5,000 publications. Hence, only few examples of calix[4]arenes and calix[6]arenes being anion receptors are presented here - this chapter is not intended as a complete review of all studied calix[n]arene derivatives capable of coordinating anions. For instance, several receptors with sulfonamide groups in the wide rim, which were successfully synthesized in the last years, are not presented here.

Calixarene receptors are also among the most interesting when potential application in a technical scale system is taken into account. It is mainly due to simplicity and low cost of their synthesis which, in turn, is the result of both easy and cheap one-step synthesis of the macrocycle core and easiness of its modification. Moreover, calix[4]arene derivatives are characterized by stable and easy to control conformations, namely 1,3-alternate and cone. Thus, calix[4]arene is an efficient and versatile building block for anion receptors.

In the case of calix[4]arenes, two different strategies leading to obtaining electrically neutral receptors were applied. One is related to introduction of substituents containing hydrogen bond donors (or, in other words, amide, sulfonamide or urea groups) to the narrow rim. The complexation mechanism in this case is similar to that observed for linear and other macrocyclic receptors containing such donor moieties in their structure. The other one is based on the exchange of the *tert*-butyl groups for other (e.g. urea, sulfonic or alkyl) groups by *ipso*-nitration, sulfonation or transalkylation. This strategy is dedicated to designing receptors selective on bigger anions (e.g. $H_2PO_4^-$, HSO_4^-). Unfortunately, several receptors obtained through this technique exhibited strong self-association or were also selective on ionic pairs (not only free anions). Hence, their applicability as electrolyte additives was rather limited.

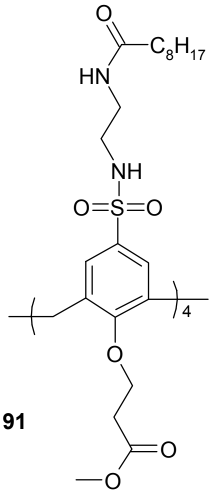
3.6.1 Calix[4]arene based anion receptors with hydrogen bond donors in the wide rim

Receptor **91** interacts with anions by sulfonamide and amide groups. As the majority of such systems, it is selective on HSO_4^- much better than on Cl^- and NO_3^- [417].

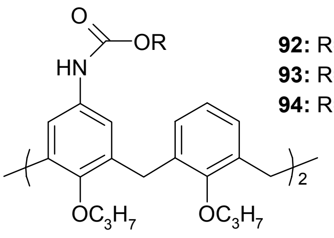
Several bidentate amide receptors **92-94** were also successfully synthesized [418]. Such receptors complex anions of tetraedric geometry (e.g. K_a=27 dm^3mol^{-1} for **92**-HSO_4^- complex in $CDCl_3$) and carboxylates (K_a=5000 dm^3 mol^{-1} for **93**-$C_6H_5COO^-$ complex in $CDCl_3$). Low values of the complex formation constant are related to weak interaction being the result of self-association of the receptors.

Surprisingly, diurea receptor **95** does not interact with anions [419] in $CDCl_3$. It is mainly due to strong self-association of the urea groups [420] being the result of poor coordinating and dielectric properties of the solvent. In contrast, receptors **96-99** do interact with the anions despite the fact that the same groups were able to complex them [341]. In these receptors, however, the urea groups are linked to the macrocyclic ring by CH_2 bridges. Because of this, self-association can be weaker (e.g. K_a=300 dm^3mol^{-1} for **96** in DMSO). Anion complexation in the same solvent is in range of 100-300 dm^3mol^{-1} in the case of anions of aromatic carboxylic acids such as benzoate and 2000 dm^3mol^{-1} in the case of acetate anion.

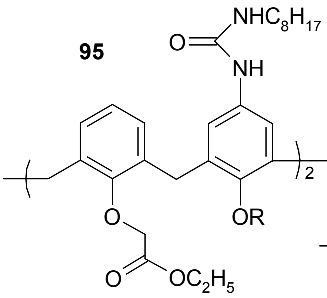
Also tetraurea molecules **100-108** were synthesized. The main aim in these studies, however, was not anion complexation but research of inter- and intramolecular hydrogen bonds between urea groups as such molecules were easy in synthesis and representative as a model of the process of self-organization [421].



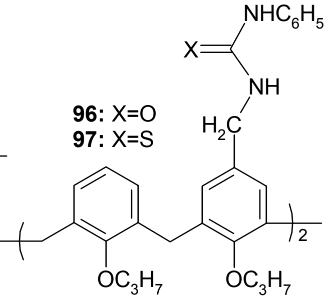
91



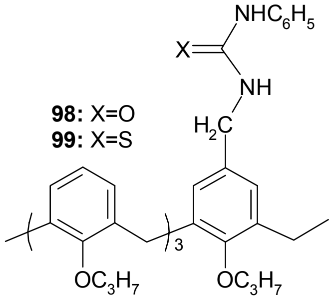
92: R=CH_2Cl
93: R=$CHCl_2$
94: R=CCl_3



95

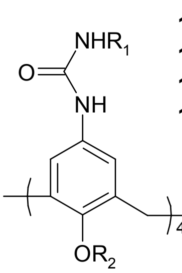


96: X=O
97: X=S

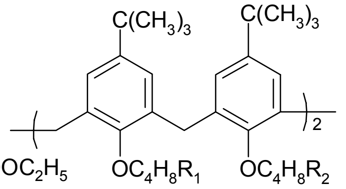


98: X=O
99: X=S

Several other calixarene-based receptors were studied as potential ditopic receptors capable of complexing ionic pairs. In this case, ester groups capable of complexing cations are placed in the narrow rim and urea groups in the wide one. Cation complexation results in a change of the macrocyclic ring conformation and weakening of the self-association process. Hence, interactions with anion are significantly stronger.



100: $R_1=C_4H_9$, $R_2=C_5H_{11}$
101: $R_1=C_6H_5$, $R_2=C_5H_{11}$
102: $R_1=C_6H_4OCH_3$, $R_2=C_5H_{11}$
103: $R_1=C_6H_4CH_3$, $R_2=C_5H_{11}$
104: $R_1=C_6H_4NO_2$, $R_2=C_5H_{11}$
105: $R_1=C_6H_4CH_3$, $R_2=CH_2COOC_2H_5$
106: $R_1=C_6H_4OCH_3$, $R_2=CH_2COOC_2H_5$
107: $R_1=CH_2C_6H_5$, $R_2=C_6H_5$
108: $R_1=C_6H_4CH_3$, $R_2=CH_3$



109: $R_1=R_2=$ $NHC(O)NHC_6H_5$
110: $R_1=R_2=$ $NHC(O)NHC_3H_7$
111: $R_1=R_2=$ $NHC(O)NHC_8H_{15}$
112: $R_1=R_2=$ $NHC(O)NHC(CH_3)_3$
113: $R_1=R_2=$ $NHC(S)NHC_6H_5$
114: $R_1=C_3H_7$, $R_2=$ $NHC(O)NHC_6H_5$

Com pound	Cl^-	Br^-	I^-	CN^-	SCN^-	Com pound	Cl^-	Br^-	I^-	CN^-	SCN^-
109	2660	1735	<25	855	<25	**112**	2015	1225	-	80	-
110	<25	<25	<25	<25	<25	**113**	335	575	<25	855	<25
111	285	450	-	550	-	**<u>114</u>**	**7105**	**2555**	**605**	**1115**	**<25**

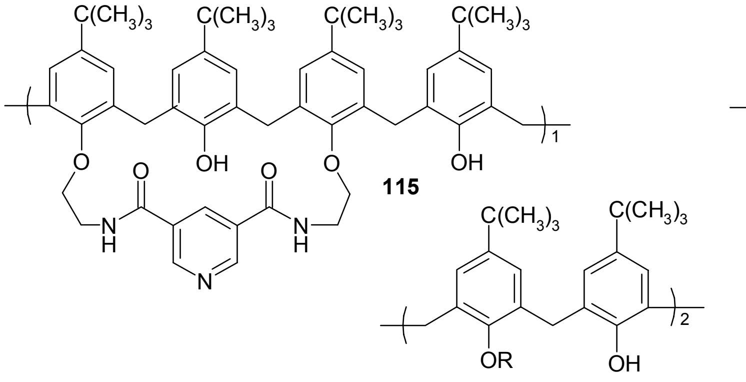
Table 7. Anion coordinating properties of receptors **109-114**. After [422].

3.6.2 Calix[4]arene-based anion receptors with hydrogen bond donors in the narrow rim.

The synthesis of calixarene derivatives with hydrogen bond donors in the narrow rim is based on a multi-step process. It begins with substitution of hydrogen of the phenolic OH groups by various moieties. In the next modification steps, these moieties are further processed in order to generate groups being hydrogen bond donors such as amide or urea groups. For instance, the Reinhoudt group synthesized several receptors containing two or four urea groups **109-114** [422]. Receptor **114** exhibited interesting coordination properties, e.g. it was able to complex iodides (lithium iodide is one of the salts interesting from the point of view of its application as an electrolyte additive). The anion coordinating properties of several anions and receptors are presented in Table 7.

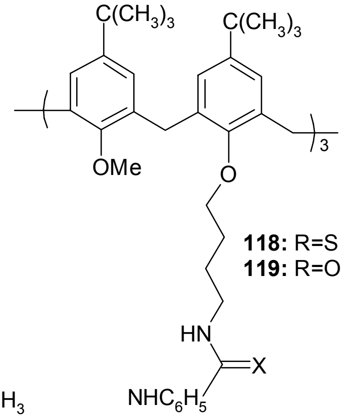
These stronger coordinating properties of **114** in comparison with molecules containing four urea groups in their structure result from its weaker pre-organization (or in other words self-association). Thus, the tendency observed is opposite to the one expected during the receptor design (lower number of urea groups should result *a priori* in weaker anion coordination). These results are confirmed by computer simulations [423].

Other calix[4]arene derivatives capable of coordinating anion by hydrogen bonds are **115-117** [424]. The presented receptors can form 1:1 (**115**) and 2:1 (**116-117**) complexes with several anions. Unfortunately, these molecules are positively charged and contain very acidic phenolic protons. Due to this, they cannot be applied as electrolyte additives.



115

116: R=$CH_2C(O)NHCH_2(C_5H_4N)CH_3$
117: R=$(CH_2)_2NHC(O)(C_5H_4N)CH_3$



118: R=S
119: R=O

3.4.2 Calix[6]arene-based anion receptors

Calix[6]arene based anion receptors are characterized by a bigger size of the macrocyclic hole and, thus, they should be interesting as building blocks in the design of receptors interacting with large anions. Unfortunately, the number of conformations in which calix[6]arene derivatives exist and their easy change of conformation result in the possibility of inter- and intramolecular hydrogen bond formation and, in consequence, in worse anion coordination properties of the receptor [425, 426] in comparison with one being e.g. calix[4]arene derivative. Despite that, it is possible to synthesize receptors i.e. calix[6]arene derivatives **118** and **119** with every second phenol group substituted with methyl and capable of being stable in 1,3,5-alternate conformation [427, 428]. Due to their symmetry, such receptors coordinated anions of tricarboxylic acids and halogenides (in this case, selectivity changed in order $Br^- > Cl^- > I^-$, unfortunately). Complex formation constants of **118** and **119** were lower than in the case of receptor **114** i.e. calix[4]arene derivative). Unfortunately, the formation constants of the **118**-NO_3^- and **119**- NO_3^- complexes were too low to be measured. The only proof of **118**-NO_3^- complex formation was that IR studies of the solution showed a shift of the NH stretching band to lower energies after the salt addition, suggesting hydrogen bond interaction with the anion.

Chapter 4

Summary of the Literature Review. Goals of the Work

In Chapter 1, a short introduction to electrolytes dedicated to lithium batteries i.e. ones with the anode consisting of metallic lithium or lithium intercalated in carbon is made. The main features of all the main classes of electrolytes, including ceramic (glassy), solid polymeric, gelled, liquid, and molten salt-type ones are discussed. The main stress in this Chapter was put on the Solid Polymer Electrolyte class. It is due to fact that this particular class of the electrolytes has a very high potential in several battery systems but its relatively low conductivity and lithium transference numbers limit the range of possible commercial applications. Various methods of conductivity enhancement of SPE including addition of the ceramic filler, changing the architecture of the polymer matrix, polymer blend formation, addition of electrically neutral plasticizer as well as plasticizing salts and anion receptor addition are discussed. As it comes to the last case, the addition of the anion receptors can change the conducting properties of the ions due to anion-receptor complex formation.

In Chapter 2, the influence of anion receptors interacting with anions by means of Lewis acid-Lewis base interactions on properties of electrolyte dedicated for the lithium battery was presented. This class of anion receptors was most widely studied because of commercial availability of several low molecular weight acid Lewis-type receptors such as $B(C_6H_5)_3$ and $B(C_6F_5)_3$. Also the majority of molecular and built-in polymeric matrix anion receptors containing borate and boroxine group are easy in synthesis. Unfortunately, the majority of studies presented in this review were made on liquid or gelled systems. Moreover, several polymeric systems with anion receptors built in the polymeric chain or used as an additive proved unstable in contact with anode materials. Thus, cell cycling tests often revealed deterioration of discharge capacity of the battery with electrolyte containing anion receptors. What is also worth stressing, several anion Lewis-type receptors can decompose a liquid or a polymeric matrix as they are strongly electrophilic. In consequence, it could be more effective to use a receptor interacting with the anion by a number of relatively weak, independent and parallel interactions rather than one interacting with the anion by one strong “supramolecular bond”.

In Chapter 3 a somehow limited study of supramolecular compounds interacting with anions by means of ion-dipole and hydrogen bond-type interactions showed that at least some of these compounds fulfill the criteria for potential application in Solid Polymer Electrolyte systems. When a choice is made, the main limitations are related to: i) easiness of synthesis, also on the multigram scale, ii) lack of protons acidic enough to form a strong hydrogen bond with the anion and stable enough not to react with anode materials, iii) complex formation with anions of salts applicable in the lithium battery (characterized by the dispersed negative current and low Lewis basicity), iv) relative neutrality towards cations and cation-anion ionic pairs as well as weak self-agglomeration. Thus, the author limits here his interest to compounds belonging to calix[4]arene and calix[6]pyrrole families. Their properties, including electrochemical stability, compatibility with the poly(ethylene oxide)-based polymeric matrix, influence of ionic equilibriums present in the electrolyte system as well as influence of thermal, physicochemical, morphological, mechanical and dielectric properties of the polymeric host will be the main topic of the later presented research activities.

Chapter 5

Experimental

5.1 Receptor synthesis

5.1.1. Synthesis of 1,1,3,3, 5,5-*meso*-hexaphenyl-2,2,4,4,6,6-*meso*-hexamethylcalix[6] pyrrole (C6P)

A two-step synthesis of C6P was conducted in the ¼ technical scale. The synthesis scheme was depicted previously in Chapter 3.3 (compound **84a**). As this synthesis was adapted to this scale and improved, it is presented in Chapter 6 of this work.

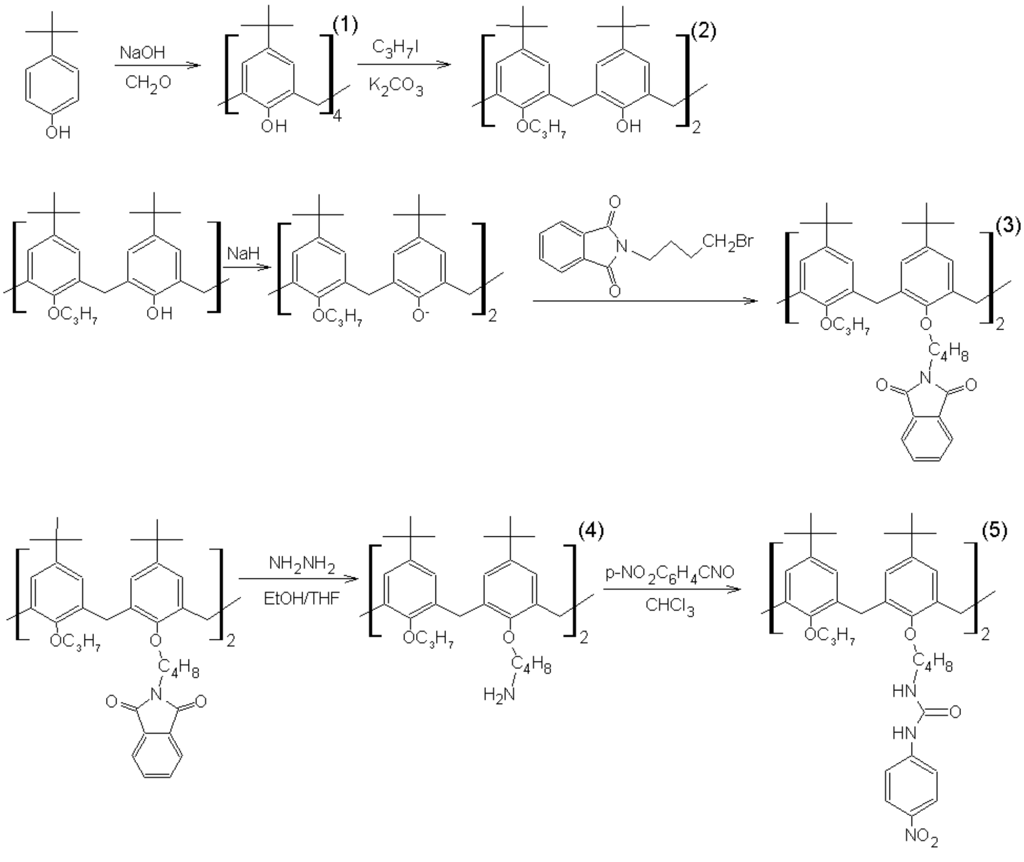


Figure 3. Cx2 receptor synthetic scheme. After [429]

5.1.2. Syntheses of 5,11,17,23-tetra-*p*-*tert*-butyl-25,27-bis(*N*-*p*-nitrophenylureidobutoxy)-26,28-dipropoxycalix[4]arene (Cx2) and a calix[4]arene derivative of coordination sphere identical to Cx2 but modified with two oligo(oxyethylene) chains in the wide rim (Cxg)

Multi-step syntheses of Cx2 and Cxg receptors were conducted on the laboratory scale as in [257, 429, 430] and [431], respectively. The synthesis schemes are depicted in Figures 3-5. The author stresses here that the synthesis of the Cxg receptor was proposed and conducted by prof. Rokicki's research team. The Cx2 receptor was proposed by Błażejczyk. Consequently, the syntheses of the receptors are not part of this dissertation.

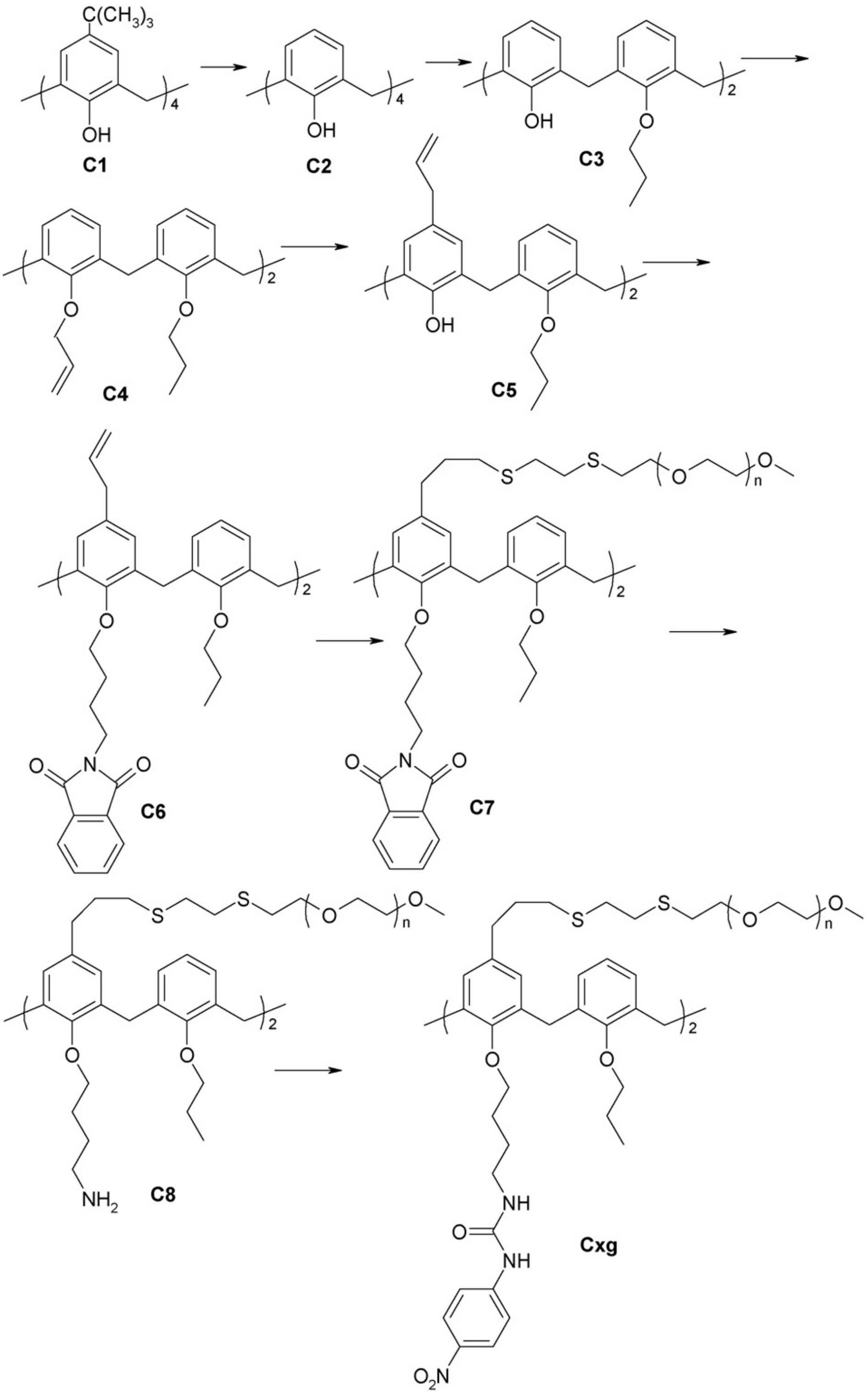


Figure 4. Cxg synthetic scheme, part 1: main synthetic route. After [431]

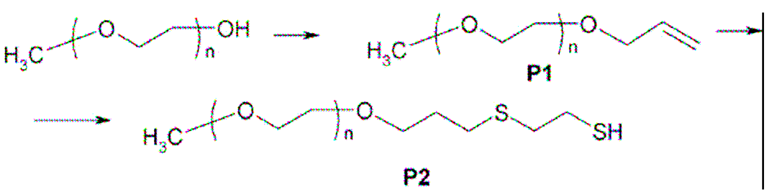


Figure 5. Cxg synthetic scheme, part 2: intermediate oligo(oxyethylene) compounds. After [431].

5.1.3. Synthesis of C4A

The synthesis of C4A was conducted as a one-step synthesis (Figure 6) according to the literature [432]. After the synthesis, C4A was dried for over 300 hours at temperature up to 100°C under high vacuum (diffusion pump). How this synthesis was adapted to this scale and improved is presented in Chapter 6 of this work.

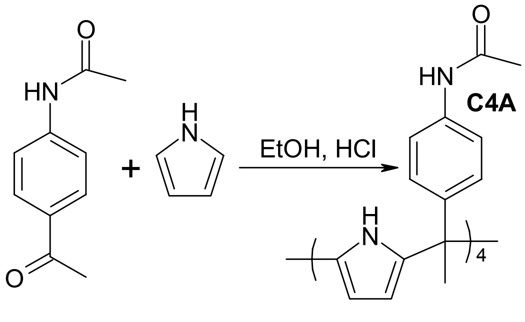


Figure 6. C4A synthetic scheme.

5.2 Sample preparation

All preparative operations were performed in an argon glove-box with humidity level under 3 ppm. The samples were either closed hermetically in appropriate vessels or left inside with the measurement devices connected to the glove-box. PEO, PEODME (both supplied by Aldrich), receptors and lithium salts (LiTf, LiI, $LiBF_4$, all Aldrich) were dried under high vacuum (diffusion pump) for over 150 hours at temperature elevated gradually to 50 (PEO), 80 (PEODME), 100 (receptors) and 120 ºC (lithium salts). PVdF-HFP copolymer (Kynar, supplied by Atofina), battery grade PC (Aldrich, both used in synthesis of gelled electrolytes), anhydrous CH_3CN, CH_2Cl_2 (POCH) and deuterated solvents (Armar Chemicals, used in ^1H NMR studies) were used as received.

5.2.1 Liquid samples

The concentrated salt and receptor solutions (salt concentration above 0.1 mol dm^{-3} in the case of salt and 0.02 mol dm^{-3} in the case of the receptor) were prepared by dissolving an appropriate amount of salt and/or receptor in the appropriate amount of solvent. The samples of low salt and receptor concentration were prepared by dilution of more concentrated solutions.

5.2.2 Gelled samples

Two methods were applied to synthesize the gel electrolytes: one-step (casting of the polymer material together with the electrolyte solution) and two-step (preparation of PVdF matrix and soaking in the electrolyte), giving similar results of ionic conductivity and mechanical strength. As the C6P additive did not solve completely in typical organic electrolytes such as PC, the gels contained a suspension of C6P in the polymeric matrix and in the liquid phase.

5.2.3 Solid polymeric electrolytes - the casting technique

The preparation of the samples of electrolyte was conducted as in [433]. The electrolyte was obtained by casting the mixture of two separately prepared solutions i.e. salt and PEO in CH_3CN and the receptor (C6P, Cx2 or Cxg) in CH_2Cl_2 and dried using the procedure described in the Reference above. For ones containing Cxg, the oligo(ethylene oxide) chains present in the receptor were counted in the total number of the ether oxygen atoms present in the sample.

5.2.4 Solid polymeric electrolytes - the hot-pressing technique

The preparation of the samples was conducted as in [434]. The electrolyte components were carefully sieved and the lowest particle size fraction (i.e. particle size of about 50 μm) was selected. The components were then put in their correct proportion inside sealed, polyethylene bottles and thoroughly mixed by soft milling for at least 24 hours to obtain a homogeneous mixture of the powders. Next, the powder mixtures were hot-pressed in an aluminum mold by applying a 3 ton pressure at 80-100°C for 20-30 minutes.

5.3 DSC

DSC data were collected using a Perkin-Elmer Pyris 1 DSC at the heating rate of 20ºC min^{-1} at 0 to 250ºC temperature range (crystallinity measurements) and, after this measurement, at the heating rate 5ºC min^{-1} at −120 to 0ºC temperature range (glass transition temperature measurements). The degree of the crystallinity measured by means of DSC was calculated according to the equation $X_c = Q_m (Q^{PEO}_m)^{-1}$, where Q_m is the latent melting heat of the polyether used and Q^{PEO}_m is that for the crystalline PEO phase. According to the literature, $Q^{PEO}_m = 213.7\ J\ g^{-1}$ [433, 435].

5.4 XRD studies

X-ray powder diffraction patterns were recorded on a Seifert HZG-4 automated diffractometer using Cu Kα radiation (λ= 1.5418 Å). The data were collected in a Bragg-Brentano (θ/2θ) horizontal geometry (flat reflection mode) between 5º and 60º (2θ) in 0.04º steps, at 2 or 3 s $step^{-1}$. The optics of the HZG-4 diffractometer was the system of primary Soller slits between the X-ray tube and the fixed aperture slit of 2.0 mm. One scattered-radiation slit of 2 mm was placed after the sample, followed by the detector slit of 0.35 mm. All samples were placed on a glass support and kept sealed during the experiment with a self-adhesive tape. The data collected were baseline corrected. The signal intensity was normalized taking into consideration different sample thickness and sweeping velocity.

5.5 SEM images

SEM images were taken using a FEI Quanta 200 microscope with an EDAX EDS analyzer. To preserve the properties and crystalline structure of the membranes tested all the operations of sample preparation were performed in a dry-box and the beam current was minimized to avoid the thermal effect of the beam (sample melting). The low vacuum mode was used for both image gathering and the EDS analysis.

5.6 Raman spectroscopy

Raman spectra were collected using a Nicolet Almega Raman dispersive spectrometer, equipped with a confocal Raman microscope, a 1800 lines mm^{-1} holographic grating and a CCD camera. A diode laser operating at 780 nm was used as the excitation source and spectral resolution was about 2 cm^{-1} for high resolution spectra. In order to avoid contact with air during the measurements, the samples were kept in sealed glass containers. All the spectra were recorded at 25ºC. For mapping experiments, the spectra were collected using a 360 lines mm^{-1} holographic grating and resolution was about 10 cm^{-1}. The exposure time was typically 15–20 s for mapping experiments and 60–120 s for high resolution spectra.

5.7 FTIR spectroscopy

Infrared absorption spectra were recorded on a computer interfaced Perkin-Elmer 2000 FT-IR system with a wavenumber resolution of 2 cm^{-1}. All the spectra were registered for samples placed in a cuvette with a fixed length between the KBr plates at 25°C. The FTIR spectra were analyzed using a Galactic Grams Research software package using the Gaussian-Lorentzian function.

5.8 NMR spectroscopy

^{1}H NMR spectra were recorded on a computer interfaced Varian Gemini 200 NMR spectrometer at 200 MHz. ^{19}F NMR spectra were recorded on the same spectrometer at 188

MHz. All the measurements were performed at 25°C. The spectra were analyzed using Mestrec 2.3 software.

5.9 Solvent-receptor complex formation constant estimation using the NMR titration technique.

For the H+G→H-G (H - host molecule, G - guest molecule, H-G - complex) reversible reaction, the chemical shift of one of host molecule atoms should be theoretically calculated as follows:

$$\delta = \delta_{HG} + (\delta_H - \delta_{HG})\frac{\sqrt{(1+K_a c_H(r-1))^2 + 4K_a c_H} - 1 - K_a c_H(r-1)}{2K_a c_H}$$

[1]

Where δ - is chemical shift calculated, δ_H - chemical shift of the “free” host, δ_{HG} - chemical shift of the “complexed” host, r - guest:host molar ratio, K_a - association constant, c_H - host concentration. In one series of measurements we need to estimate three values: δ_H, δ_{HG} and K_a. Using the least square method, for given K_a, δ_H and δ_{HG} can be calculated from equations as follows [436]:

$$\delta_{HG} = \frac{1}{W}\Big(\sum_i (x_H^i)^2 \sum_i x_{HG}^i \delta_{\exp}^i - \sum_i x_{HG}^i x_H^i \sum_i x_H^i \delta_{\exp}^i\Big)$$
$$\delta_H = \frac{1}{W}\Big(\sum_i x_{HG}^i x_H^i \sum_i \delta_{\exp}^i x_{HG}^i - \sum_i (x_{HG}^i)^2 \sum_i \delta_{\exp}^i x_H^i\Big)$$
$$W = \sum_i (x_{HG}^i)^2 \sum_i (x_H^i)^2 - \Big(\sum_i x_{HG}^i x_H^i\Big)^2$$

[2]

where x_H - molar fraction of the host, x_{HG} - molar fraction of the complex, $\delta_{\exp}$ - experimentally measured δ. K_a can be numerically calculated using this method. The following equation should be approximated to 0 using the bubbling algorithm:

$$0 = \sum_i (\delta_{HG} + (\delta_H - \delta_{HG})x_H^i - \delta_{\exp}^i)((\delta_H - \delta_{HG})x_H^i),$$
$$x_H^i = \frac{\sqrt{(1+K_a c_H(r^i-1))^2 + 4K_a c_H} - 1 - K_a c_H(r^i-1)}{2K_a c_H}$$

[3]

The author emphasizes here that all the parameters in this equation are the function of K_a, host and guest concentration. The values of the other can be calculated using equations given above.

5.10 PFG NMR experiments

The PFG NMR measurements were performed on a Chemagnetics CMX-300 spectrometer used in conjunction with a Japan Magnet Technology 7.1 T superconducting magnet. In this field the ^{1}H (I= 1/2), ^{7}Li (I= 3/2), and ^{19}F (I= 1/2) resonances occur at $\omega_0/2\pi$ = 301.0, 117.0, and 283.2 MHz, respectively. The pulse gradient spin echo (PGSE) NMR measurements were performed using a 5 mm dual broad band gradient PGSE probe and a current amplifier provided by Nalorac. The multinuclear measurements were made using a multiply-tuned Nalorac Z-Spec NMR probe. Experimental details are described elsewhere [437]. The NMR self-diffusion measurements used the Hahn spin-echo pulse sequence [438] with a pair of square-shaped gradient field pulses of magnitude g and duration δ. One is applied between the two rf pulses and the other identical gradient pulse is applied following the π pulse at a time Δ after the first gradient pulse. The echo amplitude is attenuated by an value depending on how much the position of the spins has changed by the process of self-diffusion in the time interval Δ. It can be shown that the attenuation of the spin-echo amplitude is given by:

$$A(g) = \exp\left[-(\gamma g \delta)^2 D \left(\Delta - \frac{\delta}{3}\right)\right]$$

where D is the self-diffusion coefficient and γ is the magnetogyric ratio of the spin. The diffusion coefficient D is determined by fitting this equation to the echo amplitudes for a series of gradient strengths g (0.2–1.2 T/m). The typical reproducibility of the diffusion coefficient measurements is about ±3%. Thin films of the electrolyte were sealed under Ar (<5 ppm water) in 5mm NMR tubes.

5.11 Estimation of the lithium ion transference number – the polarization technique

The experiments were performed on a PAR 273 (EG&G)–1255 FRA (Schlumberger) set. The lithium ion transference number (t_{Li+}) of the membrane samples were measured at the fixed temperature (between 50 and 120ºC). The steady state (polarization) technique, which involves a combination of ac and dc measurements, was applied [439-441]. The impedance response of the Li|electrolyte|Li cell was measured prior to the dc polarization run, in which a small voltage pulse (ΔV) was applied to the cell until the polarization current reached the steady-state I_{ss}. Various voltage pulses (3–30 mV) were applied in order to test the experimental error. The relative estimation error did not exceed 10%. Finally, the impedance response of the cell was measured again. The double ac test is required to determine electrolyte resistance (R_e) as well as the solid electrolyte interphase (SEI) resistance before

(R_0) and after (R_{ss}) dc polarization. That allowed the evaluation of the initial current (I_0) arising immediately (~10μs at 50ºC) after the application of the voltage, since, along with the Ohm's law, $I_0 = \Delta V/(R_e+R_0)$. According to this method, the transference number t_{Li+} of lithium ions, as the carriers of charge flowing through the Li|solid electrolyte|Li cell, could be calculated with the following equation:

$$t_+ = \frac{I_{ss}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{ss} R_{ss})} = \frac{R_e}{(\Delta V/I_{ss}) - R_{ss}}$$

where R_0 - initial SEI resistance of passive layers formed on both lithium electrodes; R_{ss} - secondary passive layer resistance (as the steady state polarization current is reached).

5.12 Determination of the lithium transference number through the Newman Technique

For transference number determination in low PEODME-based electrolytes the procedure originally proposed by J. Newman's group [442] and introduced by Ciosek *et al.* [443] to liquid systems was applied. Three independent series of experiments were conducted: restricted diffusion (mean salt diffusion coefficient determination), concentration cell OCV measurements and the symmetric cell polarization experiment. All the operations were performed in an argon-filled glove-box.

5.13 Conductivity measurements

Ionic conductivity was determined by means of impedance spectroscopy. The electrolytes were pressed between stainless-steel blocking electrodes. An Atlas 98HI Frequency Response Analyzer was used in 1Hz to 100 kHz frequency range. The cell was immersed in a HAAKE DC 50 cryostat to control the measurement temperature at 273–338 K range. A Bernard Boukamp EQ software [444] was used to analyze the obtained impedance data. The thermal dependency of conductivity for all the samples studied was described by the Arrhenius type equation: $\sigma=\sigma_0 \exp(-E_a R^{-1} T^{-1})$

5.14 Cyclic voltammetry

CV experiments were performed on a PAR 273 (EG&G)–1255 FRA (Schlumberger) set and the results analyzed with a Power Suite (EG&G). The electrochemical stability of the electrolytes was studied by means of the CV technique. Three electrode cells with platinum working, tantalum counter and quasi-reference electrodes were filled either with liquid solutions or with PVdF gel prepared as soft jelly in order to establish good electrical contact.

Chapter 6

Results

6.1 Previous results

Receptor	t [°C]	O:Li	receptor:Li	t_{Li+}
114	90	100	0.00	0.14
	90	100	0.25	0.15
	90	100	0.50	0.18
	50	20	0.00	0.35
	50	20	0.30	0.59
	50	20	1.00	0.36
120	75	7	0.00	0.56
	75	7	0.30	0.70
121	60	20	0.00	0.26
	60	20	1.00	0.90
	90	7	0.30	0.69
	75	7	0.30	0.74
	55	20	0.30	0.51
	90	20	1.00	0.80
	75	20	1.00	0.93
	50	20	1.00	1.00

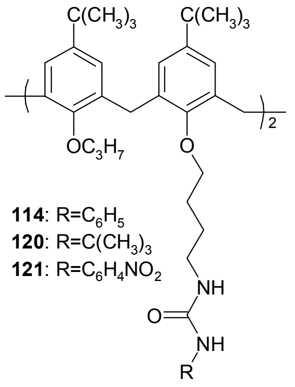


Table 8. Lithium transference number of calixarene-doped membranes. After [429] and [450].

Chapter 1 addresses several important problems related to poor ionic transport properties in PEO-based or PEO-originating systems. It also introduces the idea of application of anion receptors as conductivity enhancers. Also the properties of an "ideal" anion receptor in the electrolyte (and SPE in particular) were defined. Chapter 2 presents state-of-the-art addition of anion receptors to all types of the systems, liquid, solid and gelled which were tested as potential electrolytes in lithium batteries. In Chapter 3, the detailed solutions for hydrogen bond-type anion receptors possible to be used in SPEs were given. It is, however, obligatory to stress here that application of hydrogen bond-type receptors was the approach not uniquely proposed (or practically realized) by the author of this dissertation but constituted the aim of several previous dissertations, i.e.: Ph.D. thesis of Aurelia Błażejczyk [430], part of Raya Kovarsky's (University of Tel Aviv) MSc. thesis [445], and MSc. thesis of Magdalena Szczupak [446]. Also two papers [257, 447] regarding this topic were published. In the works of Błażejczyk and Szczupak as well as articles cited, it was shown that various anion receptors, being the calix[4]arene derivatives, can influence the ion transport properties of the PEO-based electrolytic membrane. One of the most interesting changes observed was the enhancement of the lithium transference number (Table 8) [257]. Unfortunately in the systems presented, the addition of the anion receptor resulted, in several cases, in the lowering of conductivity by more than one order of magnitude. One of the explanations for this phenomenon, proposed by the authors of the previously mentioned papers, is based on the assumption that the lowering of conductivity in systems containing the anion receptor is a result of partial immobilization of anions leading to lowering of anionic, and, in consequence, overall conductivity. In the opinion of the author of this dissertation, this mechanism is partially valid; however, it does not fully explain the role of the anion receptor. It is worth noting that the receptor addition results not only in the reduction of anionic conductivity but also in lowering cationic conductivity - as lithium cation conductivity (product of overall conductivity and the lithium transference number) was more than two times lower in the systems containing the anion receptor than in respective receptor-free ones. Two explanations of this lowering are possible. Firstly, the receptor addition can result in a higher degree of physical cross-linking of PEO matrix. Secondly, the conductivity lowering can be attributed to interactions between the oxygen or nitrogen atoms of the anion receptor molecules and cations.

salt	N \ X	0	0.125	0.25	0.5	1.0
$LiBF_4$	20	0.32	0.78	0.81	0.85	
	50			0.72	0.53	0.68
	100			1.06	0.75	0.92
LiI	20	0.24	0.56		0.78	
	50			0.75		
	100			0.49		

84a

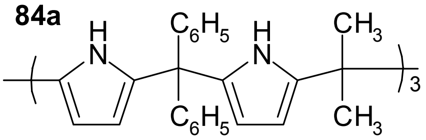


Table 9. Lithium transference numbers of the $P(EO)_N(salt)_1(\mathbf{84a})_X$. After [429]

Thus, the interest was shifted from calix[4]arene derivatives to other classes of H-bond receptors, namely calix[n]pyrroles. In this case, the interactions between the anion receptor and the cations were minimized due to the fact that the only free electron pair (potential Lewis base which can interact with the cation) is engaged in the formation of the pyrrole aromatic ring. The author of this dissertation proved in his MSc. thesis that receptor **84a** (1,1,3,3,5,5-*meso*-hexaphenyl-2,2,4,4,6,6-*meso*-hexamethyl-calix[6]pyrrole, C6P) significantly improves the lithium transference number of several PEO-based SPEs (Table 9). The role of this receptor in solid PEO-based electrolytes will be presented in Chapter 6.3. In Chapter 6.2 the syntheses of anion receptors belonging to the calix[n]pyrrole family are described. Both syntheses were published previously, however, both were optimized and adapted by the author to the larger scale.

The author of this dissertation emphasizes here that the data published in this Chapter are the result of collaboration with several research teams. The detailed list of the collaborators and description of their activities which led to obtaining the data described in this Chapter was given in the "Acknowledgements" section at the beginning of this work.

6.2 Synthesis of the receptors

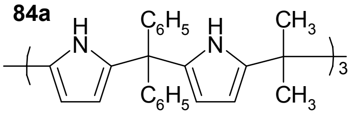
6.2.1 Synthesis of the 1,1,3,3,5,5-*meso*-hexaphenyl-2,2,4,4,6,6-*meso*-hexamethyl-calix[6]pyrrole (**84a**, C6P) in a ¼-technical (semi-pilot plant) scale

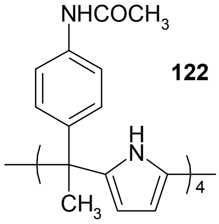
The main aim of conducting the reaction in a ¼-technical scale was obtaining a sufficient quantity of (1,1,3,3,5,5-*meso*-hexaphenyl-2,2,4,4,6,6-*meso*-hexamethyl-calix[6]pyrrole, C6P) needed for electrochemical investigations (ca. 250 g).

Another aim of this work was the investigation of

- synthesis repeatability,
- effect of the quantity of trifluoroacetic acid (CF_3COOH, TFA) on the synthesis - due to relatively high cost of this reagent,
- effect of the purity of the starting material (diphenyldi (pyrrol-2-yl)methane) on the total yield of calix[6]pyrrole - since during the diphenyldi(pyrrol-2-yl)methane purification, ca. 20% of the starting material is lost.

84a





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6.2.2 Synthesis of diphenyldi(pyrrol-2-yl)methane

The synthesis of diphenyldi(pyrrol-2-yl)methane was conducted according to the procedure proposed by Eichen *et al.* [406], improved [448] as follows: to the solution of 500 g (7.45 mol) of pyrrole and 500 g (2.75 mol) of benzophenone (both reagent grade, Aldrich) in 5000 g of ethanol (99.8%, Polmos Kutno), 500 g of the BF_3*Et_2O was added dropwise. The reaction mixture was stirred for 5 days at room temperature under argon. Then, the precipitate was filtered off and washed with 1000 ml of cold ethanol and dried, yielding 400 g (1.34 mol) of diphenyldi(pyrrol-2-yl)methane (a yield of 49%).

NMR and IR spectra confirmed obtaining the correct product.

6.2.3 C6P synthesis procedure

C6P was synthesized from diphenyldi(pyrrol-2-yl)methane (synthesis proposed by Eichen *et al.* [406], improved [448] and adapted to a ¼-technical scale) as follows: 400 g (1.34 mol) of diphenyldi(pyrrol-2-yl)methane (synthesized in the laboratory scale presented above) and 400 g of trifluoroacetic acid (Fluka) were dissolved in a mixture of 32 kg of 99.5% acetone (Brenntag) and 32 kg of 99.8% ethanol (Polmos Kutno). The reaction mixture was stirred for 5 days at room temperature under argon. Then, the reaction mixture was cooled down to

−5°C. After 12 hours the precipitate was filtered off and washed with 1000 ml of cold ethanol, and then dried, yielding 90 g (89 mmol) of 1,1,3,3,5,5-*meso*-hexaphenyl-2,2,4,4,6,6-*meso*-hexamethylcalix[6]pyrrole (a yield of 20%).

NMR and IR spectra confirmed obtaining the correct product. As no additional peaks in the ^{1}H NMR spectra of the final product were observed in the comparison with the literature data, the purity of the product should be higher than 95%.

Before application as an additive, the anion receptor was dried for over 200 hours under high vacuum (diffusion pump) at 80ºC.

6.2.4 Results

In the first two runs, the repeatability of the synthesis was estimated. In both cases, ca. 90 g of C6P crystallized from the reaction mixture was obtained.

In the next synthesis, the reaction was performed with a smaller (80% of the referred) amount of TFA. In this synthesis about 50 g of C6P were obtained. Thus, a smaller quantity of CF_3COOH resulted in lowering the yield of the C6P synthesis by ca. 50%. In consequence, from technological and economic points of view, it is necessary to control the quantity of CF_3COOH as the most important factor of high yield in C6P synthesis.

In the last run, the synthesis with diphenyldi(pyrrol-2-yl)methane with a higher amount of impurities was conducted. In this case, ca. 65 g of the product with a higher amount of impurities was obtained. As about 25% of the by-product is lost during the purification and the use of contaminated by-product resulted in lowering the yield of the C6P synthesis by over 35%, also using non-purified substrate is economically non-reasonable.

6.2.5 Laboratory scale synthesis of the 1,2,3,4-*meso*-tetramethyl-1,2,3,4-*meso*-tetra(p-acetamidophenyl)calix[4]pyrrole (C4A, **122**).

The laboratory-scale synthesis of the 1,2,3,4-*meso*-tetramethyl-1,2,3,4-*meso*-tetra(p-acetamidophenyl)calix[4]pyrrole was conducted on the basis of publication [449]. The yield of this synthesis was improved by replacing methanol used as in the original paper with ethanol. This resulted in an improvement of the yield from 20 to over 35%. The synthesis was conducted at ambient temperature (25°C) and in the atmosphere of nitrogen as follows. To the solution of the 70.9 g (0.4 mol) of p-acetamidoacetophenone in 1 l of ethanol (WIRASET), 26.8 g (0.4 mol) of pyrrole (Aldrich) was added. The mixture was stirred for about 30 minutes. Then, 8 ml of 36% aqueous hydrochloric acid were added. The reaction mixture was then stirred for 24 h. The pale pink powder precipitated from the mixture. The precipitate was filtered, washed twice with ca. 100 ml of methanol and dried. After drying, the powder was crystallized from dimethylformamide (DMF, POCH), yielding about 25 g (37 mmol, yield 37%) of the product. The ^1H NMR spectrum of the product was identical to the one in the publication on the basis of which the synthesis was conducted.

6.3 The effect of adding C6P on the properties of PEO-based electrolytes.

6.3.1 Introduction

In SPE systems (characterized by low conductivity and lithium transference number values) the addition of the supramolecular compound results not only in a change in these parameters but also influences the mechanism of transportation of charged species. Such changes are the result of changes in the morphology of the polymeric system, changes in its crystallinity and in the concentration of the charged species through the creation of “new” charged species such as anion-receptor complexes[6]. Thus, several research methods and techniques were used in order to study these changes.

6.3.2 The effect of addition of C6P on diffusion of ions in PEO-$LiBF_4$ membranes studied by means of PFG NMR.

One of the most important factors responsible for ion transport in electrolyte is diffusion of charged species. The PFG NMR technique yields averaged diffusion coefficients. Hence, this result can be used for the estimation of both conductivity and the lithium transference number.

Figure 7 presents the multinuclear spectra for PEO–$LiBF_4$ with and without C6P at 90ºC. The ^1H, ^7Li, and ^{19}F spectra appear as single lines without any structure. The ^7Li and ^{19}F spectra of the sample containing C6P appear to be slightly broader than without the additive. It can be attributed to heterogeneous broadening resulting from the homogeneous ionic environments due to the presence of C6P, rather than to a dynamic effect. That is, although decreasing the mobility of the anion (the desired result) can cause a similar broadening, it turns out that the Li^+ mobility increases, as will be discussed below.

The measurements were possible from 70ºC for ^{19}F diffusion and from 80ºC for the ^7Li and ^1H diffusion. Figure 8 shows a typical attenuation of the intensity of the ^{19}F PGSE NMR spin echo spectra at 90ºC of the sample with and without C6P. For a given set of experimental parameters (γ, g, δ, Δ), the slopes of these plots give the diffusion coefficients.

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[6] In Appendix A it will be presented how the changes in conductivity and concentration of various (electrically charged and neutral) species depend on values of association constants.

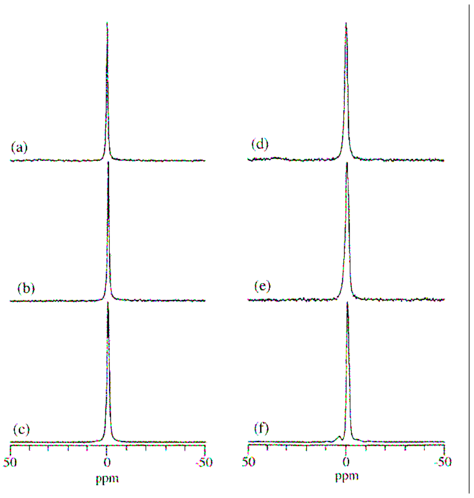


Figure 7. Lineshapes at 90ºC of 100:1 PEO–LiBF$_4$: (a) ^{19}F, no C6P, (b) ^{7}Li, no C6P, (c) ^{1}H, no C6P, (d) ^{19}F, with C6P, (e) ^{7}Li, with C6P, (f) ^{1}H, with C6P. The chemical shift scale is arbitrary.

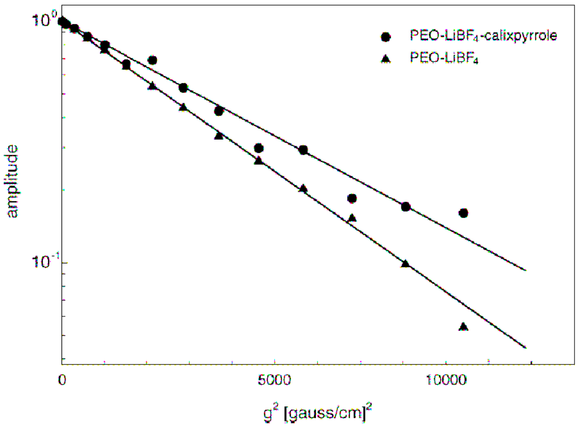


Figure 8. Signal attenuation plots of ^{19}F (anion) NMR spin-echo spectra as function of g^2 at 90ºC in 100:1 PEO–LiBF$_4$ with and without C6P.

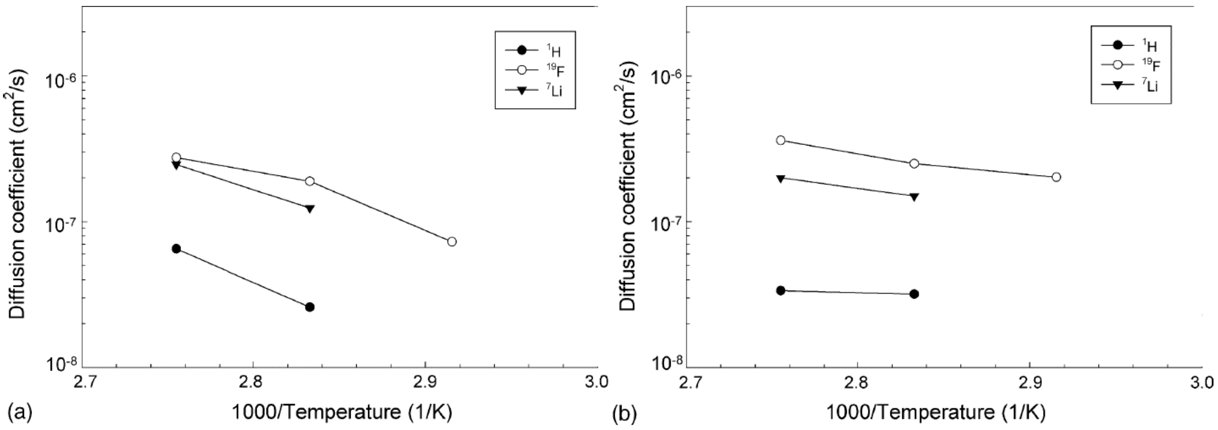
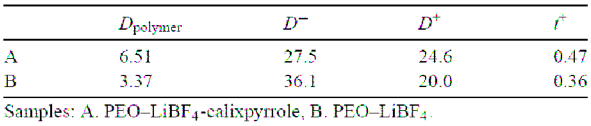


Figure 9. Arrhenius plots of self-diffusion coefficients for ^{1}H, ^{7}Li, and ^{19}F. (a) 100:1 PEO-LiBF$_4$-C6P (b) 100:1 PEO-LiBF$_4$.



	$D_{polymer}$	D^-	D^+	t^+
A	6.51	27.5	24.6	0.47
B	3.37	36.1	20.0	0.36

Samples: A. PEO–$LiBF_4$-calixpyrrole, B. PEO–$LiBF_4$.

Table 10. Self-diffusion coefficients D (10^{-8} cm^2/s) at 90ºC for the mobile species and the lithium transference number $t^{NMR}{}_{Li+}$.

The results of the diffusion measurements are summarized in an Arrhenius plot shown in Figure 9 and Table 10 which show the self-diffusion coefficients of the polymer (H), cation (Li), and anion (F) at 90ºC. For both samples, these coefficients follow the order anion>lithium>polymer. To obtain an approximate measurement of the cation transference number $t^{NMR}{}_{Li+}$ the following relation involving the diffusion coefficients was used:

$$t^+ = \frac{D^+}{D^+ + D^-}$$

It is believed that $t^{NMR}{}_{Li+}$ calculated directly from the cation and anion diffusivities is valid for relatively diluted salt concentrations where a minimal amount of ion pairing is expected. As it turns out, even if the absence of ion pairing is a valid assumption, there is a disagreement between the lithium cation transport number results measured with PFG NMR and those measured with the polarization technique and presented in subchapter 6.1. However, in both cases the lithium transport number is higher for samples containing the anion receptor than for the anion receptor-free ones. The diffusion data show i) that the anion (i.e. BF_4^-) has a bigger diffusion coefficient than the cation in both samples, ii) that the cation (i.e. Li^+) in the sample with C6P has faster diffusion than in the sample without C6P, iii) that the polymer diffusion (i.e. H) in the sample with C6P is faster than in the sample without C6P, iv) that the anion (i.e. BF_4^-) in the sample with C6P has a smaller diffusion than the anion in the sample without the agent. It can be noted here that proton diffusion is significant above the melting point (~76ºC), even in a PEO of high M_W (~10^6). The proton diffusion results coefficients are $6.5{\cdot}10^{-8}cm^2s^{-1}$ for electrolyte with and $3.4{\cdot}10^{-8}cm^2s^{-1}$ for one without C6P, respectively. This is consistent with the value measured for pure high M_W ($5{\cdot}10^6$) PEO, which was about $6{\cdot}10^{-8}cm^2s^{-1}$ at 90ºC. Note that the C6P seems to be a mild plasticizer (i.e. C6P addition results in an increase of the chain mobility). The lithium diffusion is $2.0{\cdot}10^{-7}$ and $2.5{\cdot}10^{-7}cm^2s^{-1}$ for samples without and with C6P, respectively. The lithium diffusion is, thus, 25% higher for system containing C6P than for the C6P-free one. This can be explained by the plasticizing effect mentioned previously or, alternatively, by the changes in the concentration of various charged species (see Appendix A). The anion diffusion data at 90ºC give some insight into the effect of C6P on polymer electrolytes. As noted in Table 10, the fluorine (anion) diffusion is $3.6{\cdot}10^{-7}$ and $2.75{\cdot}10^{-7}cm^2s^{-1}$, without and with C6P, respectively, about a 30% decrease when the anion trap is added to the polyether-salt system. Our experimental evidence shows that there is definitely significant anion transport, even with the trapping agent. However, it can be seen that the cation transference number does improve from 0.36 to 0.47 when the trapping agent is added to PEO–$LiBF_4$ system.

6.3.3 Role of C6P in changes of conductivity of the PEO-LiTf and PEO-LiTfSI electrolytes.

The presented proof of interaction of anionic receptor molecules with BF_4^- anions and (in Chapter 6.1) I^- anions is of rather conceptual character as lithium salts of these anions do not play an important role in practical battery applications. The reasons for this are relatively low conductivity of electrolytes containing both LiI or $LiBF_4$, poor electrochemical stability of the I^- anion and the tendency of the BF_4^- anion to decomposition resulting in poor ion transport properties of the SEI in the case of systems containing $LiBF_4$). On the other hand the previously presented systems constituted graceful test fields due to: i) relatively high affinity of I^- and BF_4^- to C6P being the result of relatively strong Lewis basicity of these anions as well as good geometric fitting between the electron pairs in these anions and H-bond donors of the C6P molecule; ii) high concentration of ionic pairs and higher ionic agglomerates. Hence, the PEO-LiTf and PEO-LiTfSI systems are much more interesting when practical application of the polymeric electrolyte is taken into consideration. In both systems, the SEI of both systems is characterized by relatively low resistance because of outstanding stability of both anions against electrochemical reduction/oxidation. Moreover, the latter is known to form complexes with PEO characterized by the melting point lower than PEO itself. What is also worth stressing, the $TfSI^-$ anion exhibits lower affinity to the formation of ionic pairs with cations. Thus, ionic conductivity and the lithium transference number of the PEO-LiTfSI system are uniquely high for a polymeric electrolyte, especially at temperatures below the PEO melting point. Unfortunately, lithium cation conductivity of this system still needs to be enhanced when its commercial application is regarded. Hence, there is a need to limit anionic conductivity and enhance ionic dissociation of the salt. This can be done by anion coordination.

$P(EO)_Y(LiTf)_1C6P_X$								
	X=1		X=0.5		X=0.25		X=0.125	
	E_{act} [kJ mol^{-1}]	σ_0 [S cm^{-1}]	E_{act} [kJ mol^{-1}]	σ_0 [S cm^{-1}]	E_{act} [kJ mol^{-1}]	σ_0 [S cm^{-1}]	E_{act} [kJ mol^{-1}]	σ_0 [S cm^{-1}]
Y=50			109.4	$4.67 \cdot 10^{11}$	97.1	$4.11 \cdot 10^{9}$	85.2	$2.94 \cdot 10^{7}$
Y=100	89.3	$2.64 \cdot 10^{8}$	88.3	$2.75 \cdot 10^{8}$	87.7	$2.22 \cdot 10^{8}$	73.2	$8.88 \cdot 10^{5}$
Y=200	79.4	$8.17 \cdot 10^{6}$	78.1	$2.56 \cdot 10^{6}$	76.9	$2.24 \cdot 10^{6}$		

Table 11. Arrhenius parameters of conductivity in PEO-LiTf-C6P systems.

The immobilization of the TfSI⁻ anion by anion receptors is very difficult (See e.g. Chapter 2). As C6P interacts with anions not by groups with high density of electrons but rather with CF_3 groups, there is a chance that C6P molecules will form complexes with these anions. The presence of two CF_3 groups in the TfSI⁻ makes possible the formation of complexes with anion: receptor 2:1 stoichiometry. This encourages the use of high receptor concentration in the systems containing LiTfSI.

The conductivity of the $P(EO)_X(LiTf)_1C6P_Y$ membranes (X=50, 100, 200; Y=1, 0.5, 0.25, 0.125) exhibits an Arrhenius type dependency on temperature $\sigma_{(T)}=\sigma_0 \exp(-E_{act}R^{-1}T^{-1})$. The detailed E_{act} and σ_0 values are given in Table 11. In general, the conductivity of electrolytes does not change significantly after the addition of the anion receptor. This situation is similar to the one observed for membranes of higher (e.g. P(EO):LiTf 20:1) salt concentration studied by Golodnitsky [450]. Also similarly to more concentrated systems, samples of higher receptor concentration exhibit lower conductivity at sub-ambient temperatures and comparable or even higher conductivity at elevated ones. Another tendency which can be observed is that samples of lower salt concentration are characterized by lower activation energies and lower values of σ_0 parameter. This suggests that in systems of higher salt concentration the number of charge carriers is higher but their mobility is lower.

$P(EO)_Y(LiTfSI)_1C6P_X$			Y=6	Y=10	Y=20	Y=50	Y=100
	X=1	E_{act} [kJ mol^{-1}]		119.1	114.1	17.9	
		σ_0 [S cm^{-1}]		$1.95E\cdot10^{15}$	$3.16\cdot10^{14}$	$8.82\cdot10^{-3}$	
	X=0.5	E_{act} [kJ mol^{-1}]		85.6	88.3	105.1	
		σ_0 [S cm^{-1}]		$3.35\cdot10^{10}$	$7.31\cdot10^{10}$	$7.29\cdot10^{12}$	
	X=0.33	E_{act} [kJ mol^{-1}]	136.7	84.6	95.4	96.8	136.7
		σ_0 [S cm^{-1}]	$3.08\cdot10^{17}$	$1.20\cdot10^{12}$	$1.18\cdot10^{13}$	$3.81\cdot10^{11}$	$8.89\cdot10^{17}$
	X=0.25	E_{act} [kJ mol^{-1}]	98.4		95.6		86.4
		σ_0 [S cm^{-1}]	$3.93\cdot10^{11}$		$1.01\cdot10^{11}$		$7.29\cdot10^{8}$
	X=0	E_{act} [kJ mol^{-1}]	120.2	80.9	108.9	87.1	87.2
		σ_0 [S cm^{-1}]	$9.64\cdot10^{15}$	$6.04\cdot10^{10}$	$1.30\cdot10^{15}$	$8.95E\cdot10^{10}$	$1.45E\cdot10^{10}$

Table 12. Arrhenius parameters of conductivity in PEO-LiTfSI-C6P systems.

The changes in the conductivity of PEO-LiTfSI-based electrolytes (Arrhenius parameters given in Table 12) after the addition of the receptor are of different character. In general, the receptor changes the conductivity of the membranes and they can be in the range of three orders of magnitude (see e.g. the difference between membranes of constitution $P(EO)_{100}(LiTfSI)_1C6P_{0.5}$ and $P(EO)_{100}(LiTfSI)_1C6P_{0.33}$). Unfortunately, these changes are hard to explain because they do not exhibit a monotonic tendency e.g. in the case of

$P(EO)_{100}(LiTfSI)_1C6P_X$ systems, conductivity decreases with the growth of receptor concentration for X=0.25 and 0.33, then the highest conducting system for X=0.5 is observed, then conductivity decreases for X=1.

Similar tendencies as for $P(EO)_{100}(LiTfSI)_1C6P_X$ systems can be observed when electrolytes in which salt concentration is higher are taken into consideration, i.e. P(EO):LiTfSI is equal to 50:1, 20:1 and 10:1 (Figure 10). The maximum of conductivity was in these cases observed for LiTfSI: receptor ratio equal to 4:1 or 3:1. There is a tendency easy to observe i.e. when the salt concentration is constant, the conductivity lowers monotonically in the following order: $P(EO)_Y(LiTfSI)_1C6P_{0.33}$> $P(EO)_Y(LiTfSI)_1C6P_{0.5}$> $P(EO)_Y(LiTfSI)_1C6P_1$. Unfortunately, contrary to systems containing LiTf the changes in σ_0 and E_{act} do not exhibit a tendency easy to interpret.

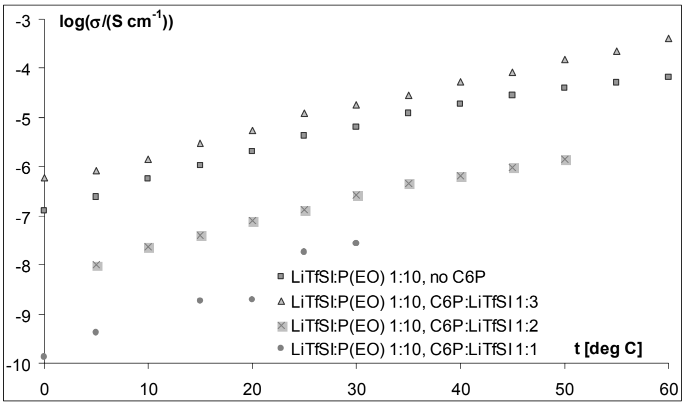


Figure 10. Thermal dependency of conductivity for $P(EO)_{10}(LiTfSI)_1C6P_X$ systems.

6.3.4 Role of C6P in the changes of physicochemical properties of PEO-LiTf and PEO-LiTfSI electrolytes studied by means of DSC.

As the conductivity studies showed interesting but not completely coherent results, a more detailed investigation of the studied systems was conducted. Firstly, the phase composition of the electrolytes and thermal properties of the phases present in the system were studied by means of the differential scanning calorimetry (DSC).

A typical DSC trace for the PEO-lithium salt system presents two signals: one (baseline shift) characteristic for the second order transition is observed between −80 and −20ºC and can be assigned to the glass transition while the other (endothermic peak) is located between 60 and 75ºC and can be attributed to melting of the PEO crystalline phase [451-453]. In contrast to previous results achieved by our group [257], no heat effect related to the crystalline PEO-salt complex melting was observed, suggesting that crystalline $P(EO)_n(LiX)_1$ domains are not present in the system studied.

C6P:LiTfSI ratio	LiTfSI:EO ratio	T_g, [°C]
1:4	1:100	-55
1:4	1:50	-44
1:4	1:10	-42
1:4	1:6	-32
0:1	1:50	-49
1:4	1:50	-54
1:3	1:50	-55
1:2	1:50	-57
1:1	1:50	-57

Table 13. Glass transition temperatures of PEO-LiTfSI-C6P systems.

In Table 13, glass transition temperatures for PEO-LiTfSI-C6P membranes are given. In the results obtained, two tendencies can be observed. When the receptor concentration to anion concentration ratio is fixed, glass transition temperature grows with rising salt concentration. This suggests lower dynamics of the segmental motions of polymeric chains for these samples. This effect can be easily related to the growing density of the physical cross-linking. It is the result of higher concentration of linking species, i.e. cations and positively charged ionic agglomerates.

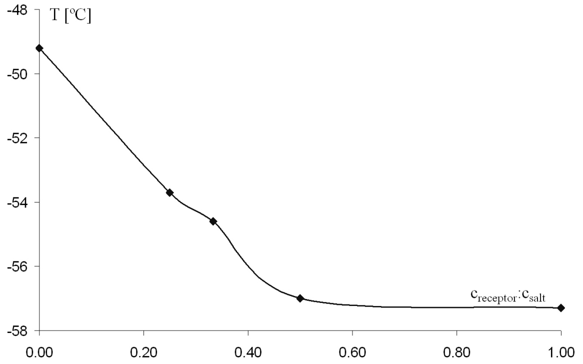


Figure 11. Dependency of the receptor concentration on T_g in PEO-LiTfSI-C6P systems.

Another tendency was observed when salt concentration was fixed for O:Li equal to 50:1 and the receptor concentration varied (Figure 11). Adding a small amount of the receptor resulted in an increase of concentration of free cations and positively charged triplets Li_2A^+ (see Appendix A). Thus, the density of physical cross-linking of the polymeric membrane is higher which results in lowering the T_g. When the receptor concentration is high, the plasticizing effect after the addition of the receptor dominates over the effect of cation concentration increase and, thus, T_g lowering is observed.

Table 14 presents glass transition temperatures for PEO-LiTf-C6P electrolytes characterized by low salt concentration. For the Li:O ratio not higher than 1:100 (corresponding to salt concentration at the level of 0.2 mol/kg) the glass transition temperature is independent of the receptor concentration. On the other hand, according to the literature data [454], in a receptor free $(PEO)_{100}(LiTf)_1$ system the glass transition at -72°C is observed. These data suggest that even for such low salt and receptor concentrations, the changes in T_g upon receptor addition can be observed. For higher salt concentration, e.g. the P(EO):salt ratio equal to 50:1, T_g is higher than for the samples of lower salt concentration. This phenomenon, as in the case of samples containing LiTfSI, should be related to higher concentration of cations and positively charged ionic agglomerates.

LiTf: EO ratio	C6P:LiTf ratio	T_g, [°C]
1:50	1:8	-40
1:50	1:2	-47
1:100	1:8	-58
1:100	1:4	-56
1:100	1:2	-57
1:100	1:1	-57
1:200	1:8	-55
1:200	1:4	-57
1:200	1:2	-57

Table 14. Glass transition temperatures for PEO-LiTf-C6P systems.

In Table 15, enthalpies of the PEO crystalline phase melting (endothermic peak between 50 and 80°C) are shown. This parameter can be used to calculate the degree of crystallinity: the enthalpy should be, then, divided by the value of the melting of the PEO crystalline phase (according to literature data, this is equal to 213.7 J/g [433]). The accuracy of this estimation is about 10% and is mainly related to the accuracy of baseline setting. When the results obtained are analyzed two tendencies can be easily observed. Firstly, a high degree of crystallinity is observed in membranes of low salt concentration,. This tendency can be related to either plasticizing properties of the salt or synergistic effect of plasticization coming from the anion and the anion receptor. Secondly, the crystallinity of the membrane does not depend (or, at least, depends in a way which cannot be easily explained by means of the model used) on receptor concentration, namely the changes of crystallinity of membranes of fixed salt concentration are not monotonic when the concentration of the receptor varies. This result is in good agreement with T_g and lithium transference number measurements (see Chapter 6.1) in which the t_{Li+} value was also independent of receptor concentration.

Similar studies were conducted for systems containing LiTfSI. Table 16 presents the values of enthalpy of PEO crystalline phase melting. In systems containing C6P, in which the salt: polymer ratio is higher than 1:20 (i.e. $P(EO)_6(LiTfSI)_1C6P_{0.25}$, $P(EO)_6(LiTfSI)_1C6P_{0.33}$, and

$P(EO)_{10}(LiTfSI)_{1}C6P_{0.25}$), the peak characteristic for the PEO crystalline phase melting practically cannot be observed. It can be due to the plasticizing properties of the salt. These results can be supported by the fact that a similar DSC trace was observed in the $P(EO)_{6}(LiTfSI)_{1}C6P_{0.33}$ system. When analyzing membrane crystallinity as a function of receptor concentration, no significant change is observed. The local minimum, observed for receptor: salt ratio equal to 1:4, should be rather attributed to the artifact and not to real changes in the system analyzed.

LiTf:EO ratio	C6P:LiTf ratio	ΔH, [J/g]	X^{C}_{DSC}, [%]
1:50	1:8	80	38
1:50	1:4	97	45
1:50	1:2	90	42
1:100	1:8	101	47
1:100	1:4	102	48
1:100	1:2	96	45
1:100	1:1	90	42
1:200	1:8	105	49
1:200	1:4	118	55
1:200	1:2	107	50

Table 15. Crystallinity of PEO-LiTf-C6P systems measured by means of DSC.

C6P:LiTfSI ratio	LiTfSI:EO ratio	ΔH, [J/g]	X^{C}_{DSC}, [%]
1:4	1:100	75	35
1:4	1:50	29	14
1:4	1:20	46	22
1:4	1:10	1	0
1:4	1:6	0	0
0:1	1:50	89	42
1:4	1:50	29	14
1:3	1:50	100	47
1:2	1:50	82	38
1:1	1:50	103	48
1:3	1:6	0	0

Table 16. Crystallinity of PEO-LiTfSI-C6P systems measured by means of DSC.

6.3.5 The role of C6P in crystallinity changes studied by means of X-ray diffraction studies.

The X-ray diffraction is usually used in the studies of SPE to estimate the crystallinity of the electrolyte. The results of crystallinity measurements, however, differ from those in which crystallinity was estimated through the DSC technique. In the case of X-ray diffraction measurements, the presence of defects in the PEO crystallites together with extremely low sizes of the crystalline domains results in lowering reflex intensities. Therefore, electrolyte exhibiting high crystallinity (by means of e.g. DSC) but with a high concentration of defects in the structure of the crystallites, should be characterized by low crystallinity measured by means of XRD. Hence, it is interesting to compare crystallinity data from these two methods in order to gain some additional information about the structure of the membrane.

In the case of heterogeneous systems, XRD can also prove that a particular phase is present. As nearly all the systems studied are, in various degree, heterogeneous (see Chapter 6.3.6), it was interesting to determine whether and which component of the membrane precipitates separately.

In Figure 12, a typical diffractogram of a PEO-LiTf-C6P membrane is shown. One can easily see a sharp peak located near 2θ =19° and a multiplet near 2θ =22…23° which should be attributed to the PEO crystalline phase. Apart from these peaks, there are two bumps: one in the region of 3…7° which can be attributed to amorphous areas containing the anion receptor and the other between 15 and 25° which can be attributed to amorphous, PEO-containing phases. The results of integration of these peaks are gathered in Table 17. In general, the intensities of the reflexes near 2θ =19° and 2θ =22…23° are much higher for PEO-LiTf-C6P membranes than for PEO-LiI ones. This result is quite surprising because membranes containing LiTf usually exhibit crystallinity lower than ones containing LiI. Thus, the intensities of the reflexes for the system containing C6P is about five times higher than in the case of the receptor-free PEO-LiTf membrane. This result is in disagreement with the values of electrolyte crystallinity measured using DSC which was at a similar level for receptor-free and receptor-containing systems. This might come from lower concentration of defects in PEO crystals for systems containing receptor. Alternatively, the diameter of the spherulites in systems containing the receptor can be higher than that of the receptor-free ones. This discussion will be continued when SEM images of these samples will be analyzed.

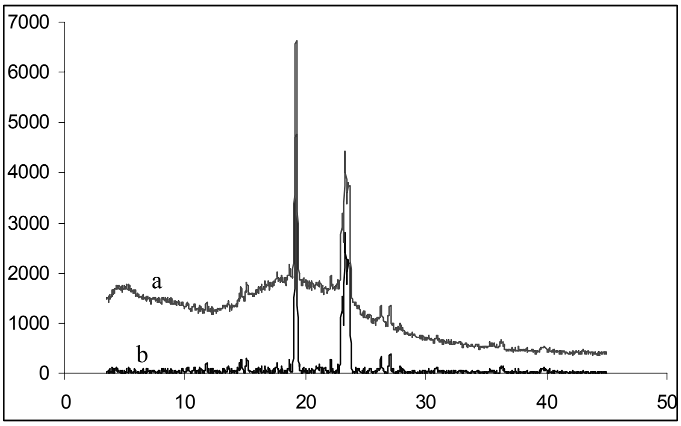


Figure 12. Typical diffractogram of the PEO-LiTf membrane- without (a) and with subtraction of the baseline.

	Sample	X	Y	19° intensity [a. u.]	22° intensity [a. u.]	Sample thickness [µm]	19° intensity normalized [a. u.]	22° intensity normalized [a. u.]
$P(EO)_{20}(LiI)_1$				87.0	144.6	120	0.73	1.21
$P(EO)_X(LiTf)_1C6P_{1/Y}$	1	50	8	202.5	334.4	120	1.69	2.79
	2	50	4	317.2	650.6	201	1.58	3.24
	3	50	2	166.1	333.2	133	1.25	2.51
	4	100	8	96.1	340.2	105	0.92	3.24
	5	100	4	142.2	446.8	101	1.41	4.42
	6	100	2	378.4	933.1	295	1.28	3.16
	7	100	1	217.0	495.6	153	1.42	3.24
	8	200	8	179.8	507.2	237	0.76	2.14
	9	200	4	158.2	681.0	190	0.83	3.58
	10	200	2	124.3	360.2	99	1.26	3.64
	11	200	1	362.3	802.6	286	1.27	2.81

Table 17. Areas of the peaks in the region of 19° (singlet) and 22° (multiplet).

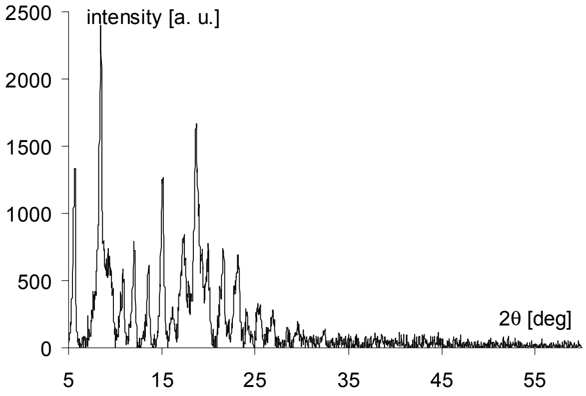


Figure 13. Diffractogram of C6P.

To determine if C6P exists in the form of micro- or nanosized crystals, diffractograms of PEO-salt-C6P electrolytes were compared with that of C6P (Figure 13). In case of C6P crystals, a sharp singlet at about 2θ=5.5° and a multiplet near 2θ=8.5° are present as well as a noticeable peak at about 2θ=18°. In the case of electrolytes, no such peaks were observed. The only change which can come from C6P is a bump near 2θ= 5°. Taking this result into account, one could state that either C6P agglomerates are not present in the system or contain not only C6P but also PEO matrix or salt in their structure.

6.3.6 Morphology of PEO-LiTf-C6P and PEO-LiTfSI-C6P electrolytes studied by means of Raman spectroscopy mapping, SEM and EDAX.

In the case of a linear PEO-based SPE, the material is always heterogeneous in terms of its phase structure. Firstly, crystalline domains of pure PEO are present. Secondly, one can observe crystals of PEO-salt complexes. Thirdly, several amorphous, inter- or intraspherulitic areas in the electrolyte can be observed. Each phase has (at least slightly) different constitution and ionic conductivity [455]. The problem of heterogeneity of the system is even more important in membranes containing additives. In this case, the number of phases grows. The overall conductivity of the electrolyte depends on the properties of the phases present in the electrolyte, their relative quantity and geometrical arrangement. Unfortunately, the local conductivity of the particular phase cannot be measured. Thus, studies on the morphology of the membrane and distribution of electrolyte constituents in the membrane can give some impact to the discussion on the changes in the conductivity mechanism.

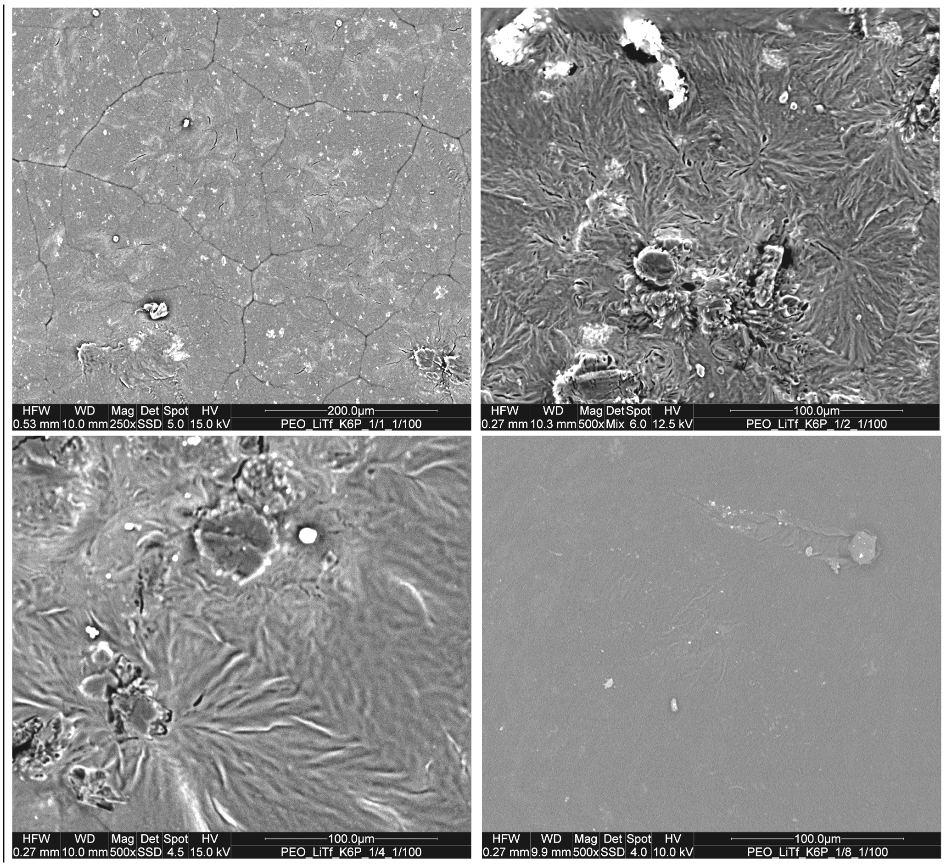


Figure 14. SEM images of $P(EO)_{100}(LiTf)_1C6P_X$ electrolytes: X=1 (a), 0.5 (b), 0.25 (c) and 0.125 (d).

The SEM images of $P(EO)_{100}(LiTf)_1C6P_X$ membranes are presented in Figure 14. As it is clearly seen, the membranes exhibit morphology typical for PEO-based solid polymer electrolytes with spherulites of diameter over 100 µm. Interestingly, the membranes with a higher receptor content (X at the range of 0.25 to 1) are characterized by rougher surface than those with the lower salt-receptor ratio. For the electrolyte with salt: receptor ratio equal to 8:1, the surface of the membrane is almost smooth. It can also be observed that the membranes studied are not fully homogeneous. Apart from the typical spherulites of the PEO crystalline phase and amorphous areas between them, one can also distinguish some agglomerates. Their diameter, when observed in the SEM images, is at the level of 10µm.

The SEM images of the PEO-LiTf-C6P membranes show that in the systems studied specific structures cannot be easily separated, yet the membrane morphology is typical for a PEO-based system, with typical spherulites. Moreover, also highly heterogeneous grains can be observed.

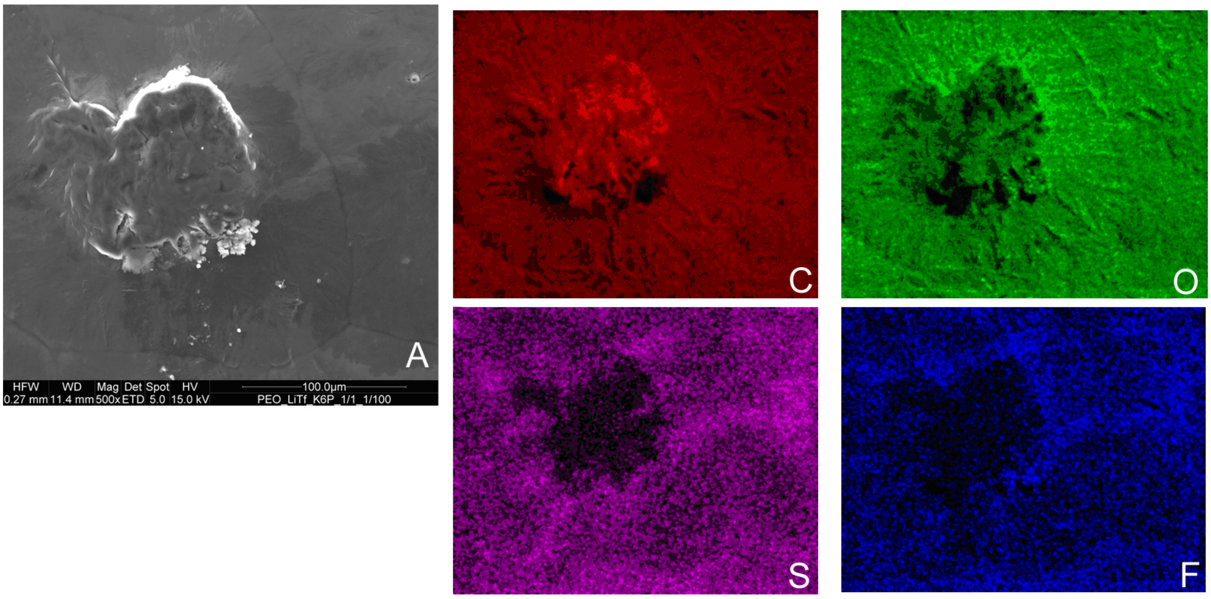


Figure 15. SEM (A) and EDAX images of carbon (C), oxygen (O), sulfur (S) and fluorine (F) elements in $P(EO)_{100}(LiTf)_1C6P_1$ membrane.

Figure 15 presents a SEM image and an EDAX map of one of such grains. As one can see, the area of the grain is rich in carbon, contains significantly less oxygen than the rest of the membrane and practically does not contain sulfur and fluorine atoms. Comparing these results with Table 18, in which the elementary composition of electrolyte constituents is given, it is clear that these grain areas contain mainly receptor molecules[7]. Moreover, one can see that the borders of the spherulites are richer in sulfur and fluorine atoms and relatively poor in carbon and oxygen in comparison with areas inside the spherulites. This phenomenon is similar to one observed in the samples containing calixarene-based anion receptor (see Chapter 6.4.4).

Element Compound	C,%	O,%	F,%	S,%
PEO	54	36	-	-
LiTf	5	58	23	13
C6P	85	-	-	-

Table 18. Elementary composition of electrolyte compounds.

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[7] As peaks characteristic for C6P were not observed in diffractogram of the membrane (see Chapter 6.3.5), and in the EDAX images the concentration of the sulfur in the carbon-rich areas is lower but not equal 0, the author suggest that it is "mainly receptor molecules" rather than "crystals of the precipitated receptor".

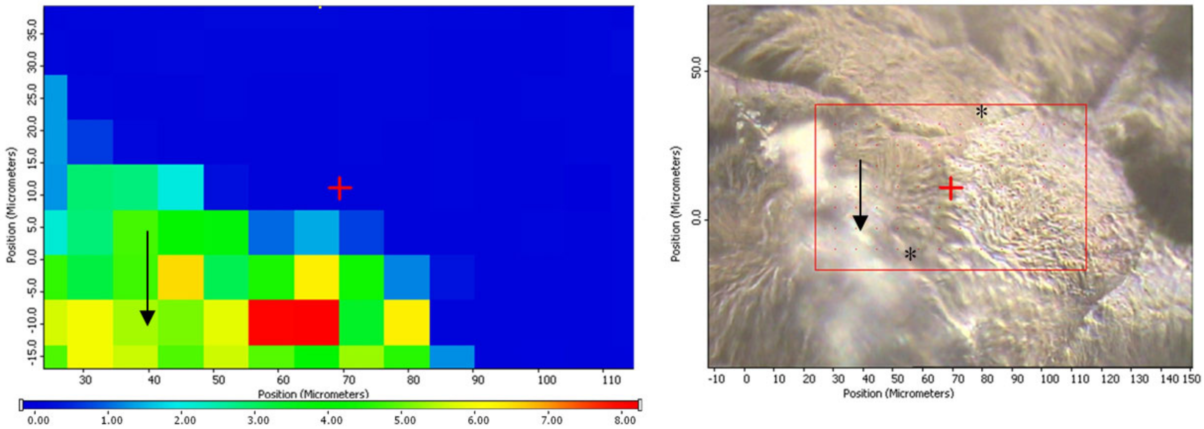

Figure 16. $P(EO)_{100}(LiTf)_1C6P_{0.5}$ membrane. Figure on the left: Raman map - ratio between intensity of 1004 cm^{-1} band (aromatic ring out-of-plane deformation band of C6P) and intensity of 1282 cm^{-1} band (CH_2 deformation band of PEO). Figure on the right: the picture of the same area from the CCD camera. C6P agglomerates in both figures marked by arrows. The points from which the Raman spectra were collected marked with asterisks.

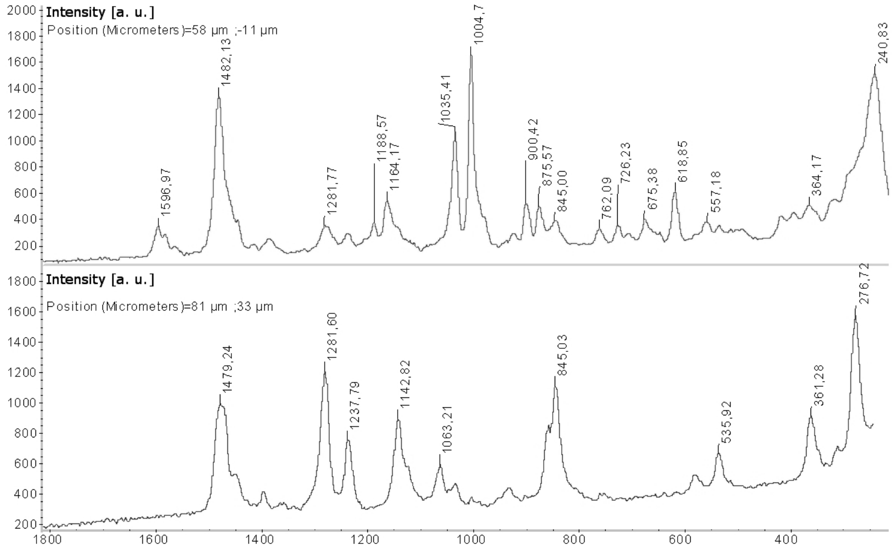

Figure 17. Spectra of the C6P agglomerates (upper spectrum) and other areas (lower spectrum).

Similar agglomerates were observed in Raman maps. Figure 16 presents the distribution of C6P on the surface of the membrane doped with C6P, obtained by comparison of relative intensities of peaks characteristic for C6P (γ_{CH}) and PEO (CH_2 deformation). The white "stain" on the membrane surface (marked with arrow) is characterized by spectra practically identical to calixpyrrole (Figure 17). On the other hand, there is practically no anion receptor in the areas of polymeric spherulites which contain mainly PEO and salt.

In the case of systems of very low receptor concentration, the membranes are much more homogeneous. In Figure 18, EDAX elemental maps of the $P(EO)_{100}(LiTf)_1C6P_{0.125}$ membrane are presented. The elements are distributed significantly more evenly than in the case of the $P(EO)_{100}(LiTf)_1C6P_1$ electrolyte. The single heterogeneity is located in the upper right part of the membrane and, following here the results of elemental analysis (lack of all elements present in the electrolyte membrane i.e. C, F, N, O), should be considered as an impurity on the electrolyte surface rather than agglomerate of the receptor. Such impurity can come from a particle of the molecular sieve used in the synthesis of the electrolyte.

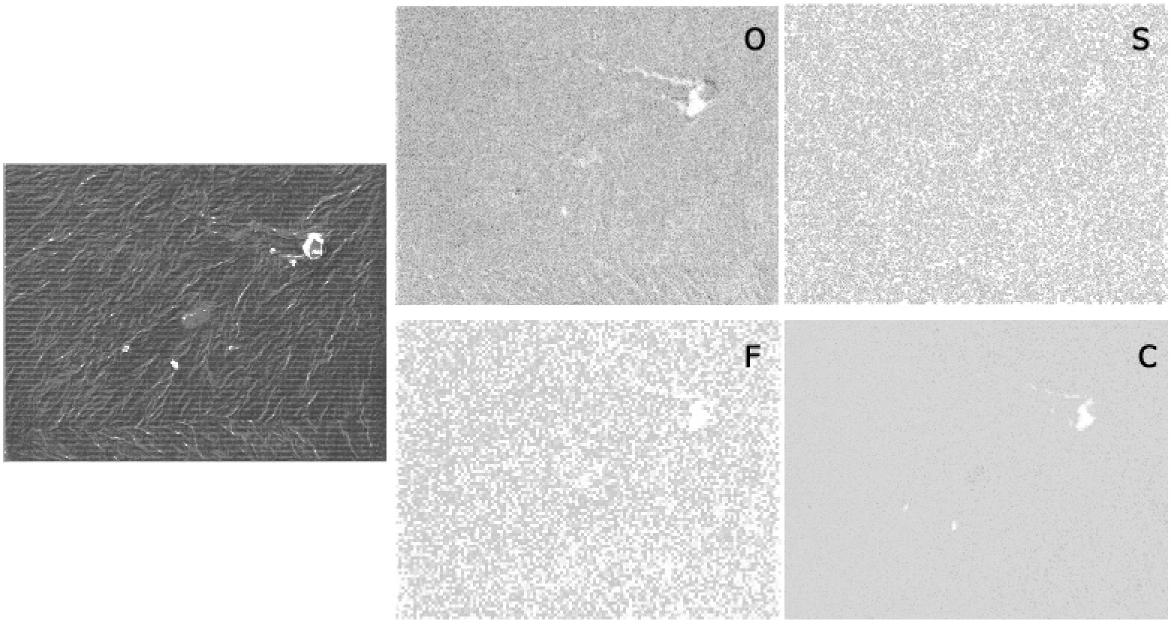

Figure 18. $(PEO)_{100}(LiTf)_1C6P_{0.125}$: SEM image and EDAX images of distribution of the carbon (C), oxygen (O), sulfur (S) and fluorine (F) elements in the membrane.

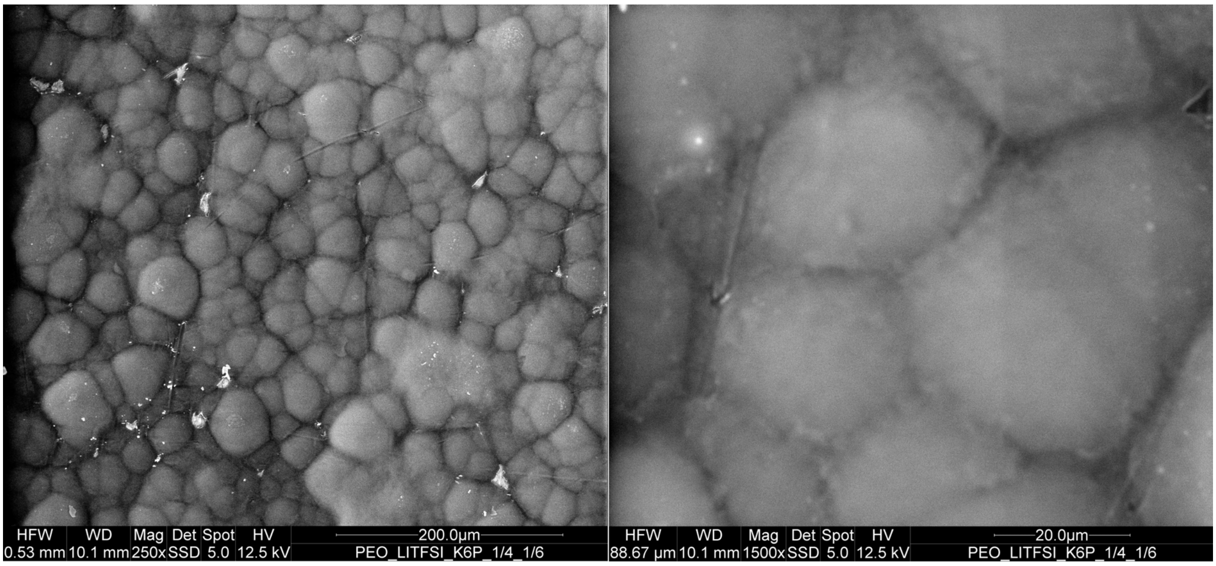

Figure 19. SEM images of $P(EO)_6(LiTfSI)_1C6P_{0.25}$ membrane.

As it was already mentioned, SEM images of the PEO-LiTfSI-C6P membranes show that their morphology is strongly affected by the salt and the additive content. In Figure 19, a membrane characterized by high salt and receptor concentrations is presented. In this case, a ball-like structure of the membrane morphology with spherulites of diameter in range of 20 to 50 µm can be observed. Different structures are observed for membranes of lower salt and receptor concentration, e.g. $P(EO)_{100}(LiTfSI)_1C6P_{0.25}$ (see Figure 20). In this case, also spherulitic areas are observed, however, they can be characterized by “brush-like” surface and a higher diameter of the spherulites. Also in contrast with the membrane of high concentrations of the salt and the receptor, deep cracks on the membrane surface are present.

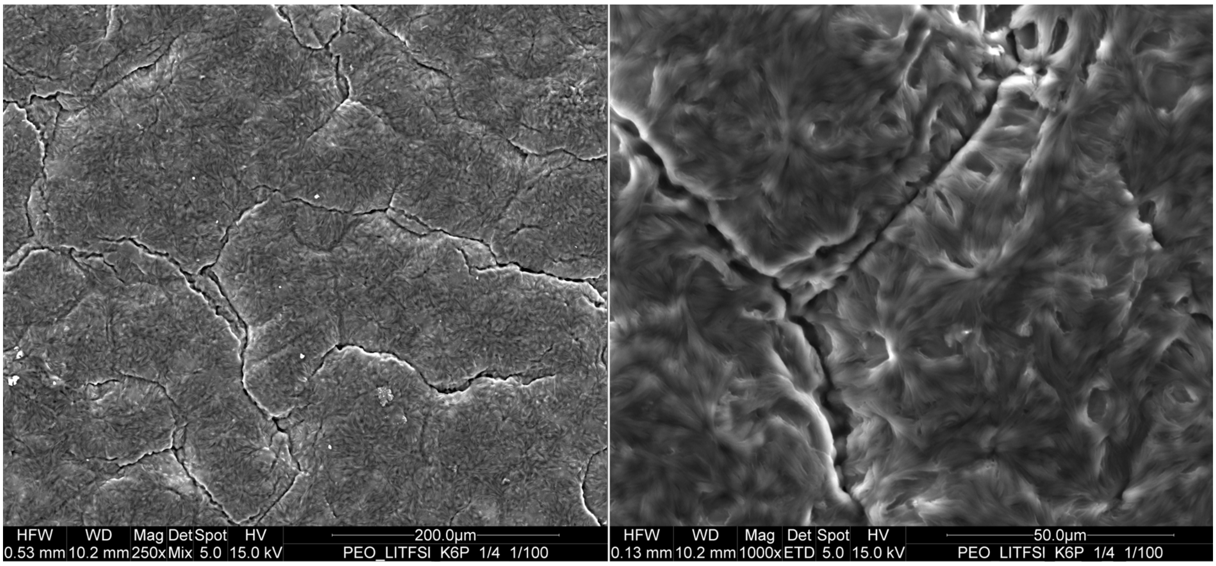

Figure 20. SEM images of $P(EO)_{100}(LiTfSI)_1C6P_{0.25}$ membrane.

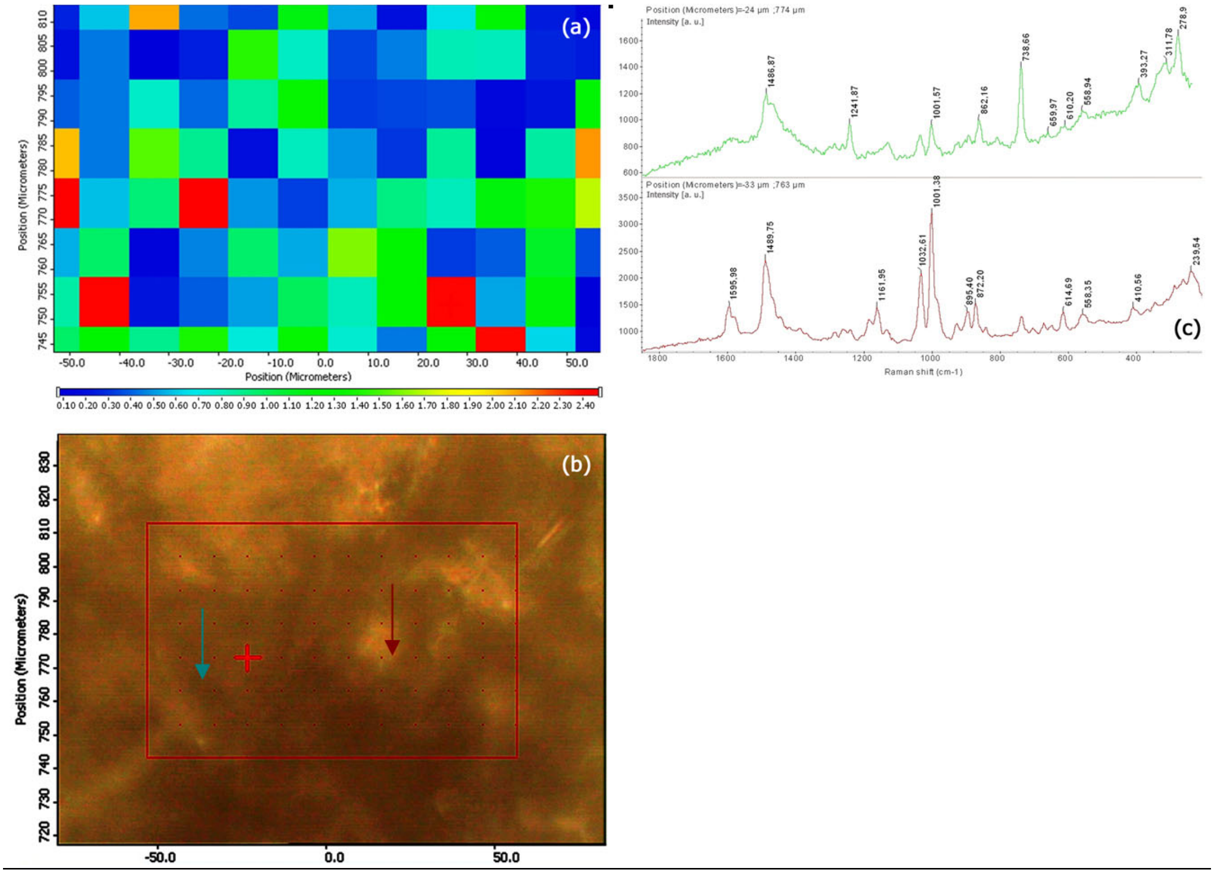

Figure 21. $P(EO)_6(LiTfSI)_1C6P_{0.25}$. Raman map - ratio between intensity of 739 cm^{-1} band (CF_3 deformation band of LiTfSI) and intensity of 1002 cm^{-1} band (C6P aromatic ring out-of-plane deformation band). (a). Picture from the CCD camera (b). Spectra from brighter and darker areas of the membrane (points with sample spectra marked with arrows in figure b) (c).

Raman mapping studies on the systems containing LiTfSI were also conducted. It was shown that all the membranes, as in the case of systems containing LiTf, are heterogeneous. However, even for higher salt and receptor concentrations, it is impossible to identify single big aggregates rich in receptor. In Figure 21, a Raman map of the $P(EO)_6(LiTfSI)_1C6P_{0.25}$ membrane is presented. One can easily see that the ratio between the salt and the receptor changes dramatically even in such small distances as 10 µm, however, this ratio is random. Moreover, contrary to the previous instance, there is no correlation between the relative Raman intensities and the relevant areas in the picture from the CCD camera.

Figure 22 presents a Raman map of the $P(EO)_{20}(LiTfSI)_1C6P_{0.25}$ membrane. The areas of the sample which are "brighter" in the optical image are in this case not enriched with C6P but characterized by even lower concentration of the receptor in comparison with the rest of the sample. Thus, in consequence, if the agglomerates are present, they are smaller or comparable to the method resolution (5 µm). It is contrary to the results obtained for samples containing LiTf when such agglomerates were of diameter bigger than 20-30 µm and their round-shape structure could be easily observed.

6.3.7 Discussion

As it was proved in Chapters 6.2 and 6.3, the addition of C6P significantly changes both the ion transport and physicochemical properties of PEO-based SPEs. It was also shown that the membrane containing C6P is heterogeneous.

Apparently the receptor addition (at least in the case of C6P) triggers the creation of new phases. If the receptor concentration is high, its precipitation is possible. Thus, the anion receptor, when used in PEO-based systems dedicated for application in the lithium battery, should be compatible with polymeric matrix in order not to precipitate from the system. As the dielectric constant of the polymeric matrix is below 6, the receptor should also be apolar. Contrary to that, oxygen atoms in a PEO macromolecule have very high donor numbers and, in consequence, high affinity to the polar species. Taking these opposite tendencies into consideration, the role of salt-anion receptor-polymer matrix compatibility in the membrane properties proved worth discussion.

As modified calix[6]pyrroles are very difficult to synthesize [456], in the studies of the role of the receptor-matrix compatibility, receptors being calix[4]arene derivatives were used. Cx2 receptor was synthesized and taken as the standard one,. This receptor was studied previously by Błażejczyk [257, 447]. As it was previously mentioned in Chapter 5, the compatibilization of the calix[4]arene derivative to the PEO and PEO-like matrices was achieved by the chemical linking of two oligo(oxyethylene) chains to the wide rim of this macrocyclic molecule by the Prof. Rokicki research team. This change does not affect the coordination properties of the receptor as the modification of the narrow rim in both (Cx2 and modified one) receptors were identical.

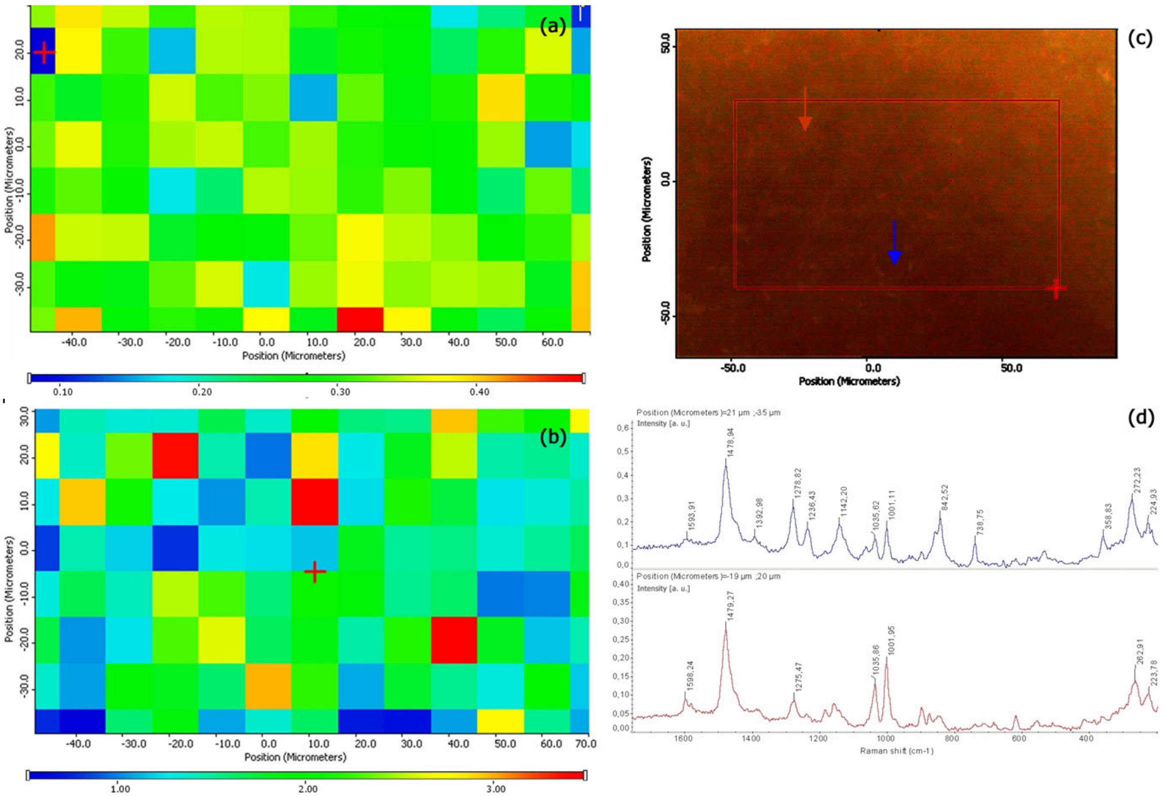

Figure 22. P(EO)$_{20}$(LiTfSI)$_1$C6P$_{0.25}$. Raman map - ratio between intensity of 739 cm^{-1} band (CF$_3$ deformation band of LiTfSI) and intensity of 1281 cm^{-1} band (CH$_2$ deformation band of PEO) (a). Raman map - ratio between intensity of 1002 cm^{-1} band (C6P aromatic ring out-of-plane deformation band) and intensity of 1281 cm^{-1} band (CH$_2$ deformation band of PEO) (b). Picture from the CCD camera (c). Spectra from brighter and darker areas of the membrane (points with sample spectra marked with arrows in figure b) (d).

6.4 Studies of receptor-matrix compatibility in terms of solid membrane microstructure.

6.4.1 Introduction

An addition of the anion receptor should not result in worse (mechanical, chemical or conducting) properties of the membrane. Such problems occur when receptor agglomeration or even precipitation is observed. Thus, the compatibility of the receptor with the polymer matrix is crucial to exclude these processes. Receptor-matrix compatibility results also in simpler synthesis of the membrane.

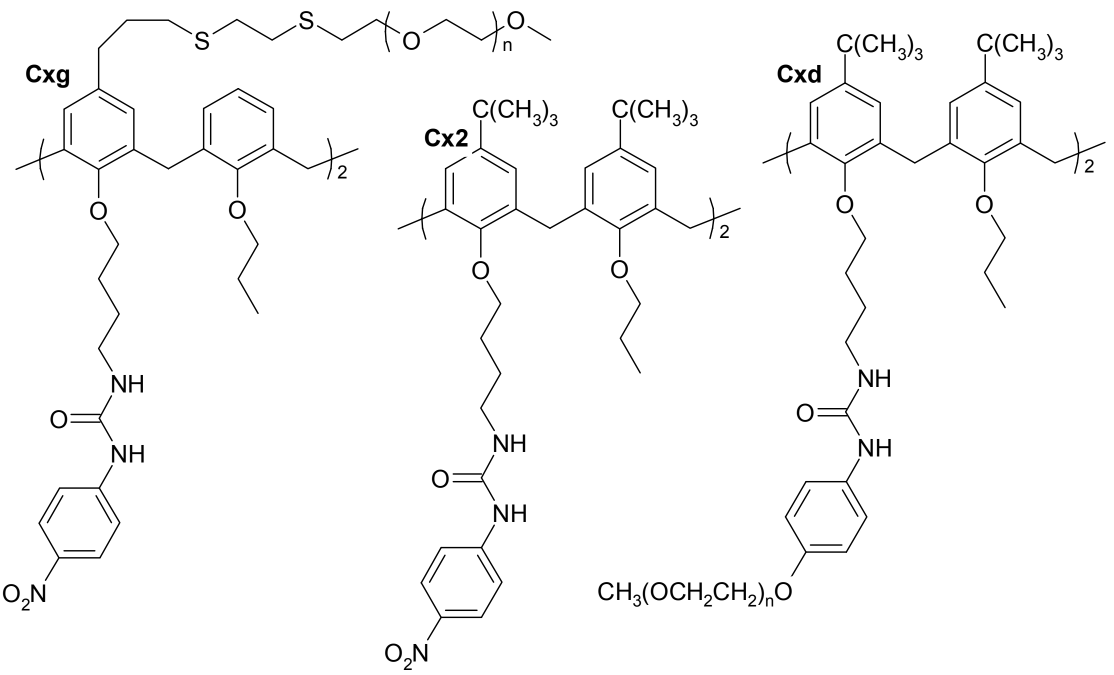

Figure 23. Structure of Cxg, Cx2 and Cxd.

In the studies conducted, an attempt was made to modify the Cx2 receptor by attaching poly(oxyethylene) chains to the receptor molecule. In the first approach (receptor Cxd), the Cx2 structure was modified by attaching two poly(oxyethylene) chains by replacing p-$OCNC_6H_4NO_2$ with p-$OCNC_6H_4(OCH_2CH_2)_nOCH_3$ in the last step of the synthesis [429]. Unfortunately, this synthetic path failed due to problems with isolation of the p-$NH_2C_6H_4(OCH_2CH_2)_nOCH_3$ compound (precursor of p-$OCNC_6H_4(OCH_2CH_2)_nOCH_3$) (Figure 23). In another approach, proposed [457] by Rokicki and realized by Pawłowska [431, 458], the broad rim of the calixarene ring was modified. The main disadvantage here was related to a much more complicated synthetic path while, as it was described previously, the coordinating properties remained unchanged.

It is worth noting here that the receptor-matrix compatibility is also an important factor in liquid systems as it was proved by the McBreen group [8]. Receptors containing boronate group were characterized by better compatibility with the liquid matrix due to their lower symmetry in comparison with other boron-based receptors (as ones containing borate and borane group). Thus, the boronate group containing receptors were characterized by e.g. higher solubility in the liquid matrix.

This subchapter is prepared on basis of publications [459] and [460].

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[8] See chapters „Triarylboranes”, “Dialkylboronates” and “Low molecular weight trialkylborates” in literature part of this work.

6.4.2 Conductivity results.

Thermal dependences of conductivities for $(PEO)_{20}LiTf$ and $(PEO)_{20}LiI$ composites with the addition of the anion receptors are depicted in Figures 24a and b, respectively. In both cases, it was observed that an addition of anion receptor results in lowering conductivity in temperatures lower than 50ºC. At higher temperatures, the conductivity of samples containing Cx2 is similar or even higher than those of systems which do not contain the anion receptor. The activation energy (Table 19) of conduction is the highest for systems containing Cx2. For samples containing LiI, the lowest value was observed for the system containing Cxg while for ones with LiTf, the pristine system is characterized by the lowest E_{act}. Despite the last fact the value of the E_{act} for samples containing Cxg was always far lower than for the ones with Cx2.

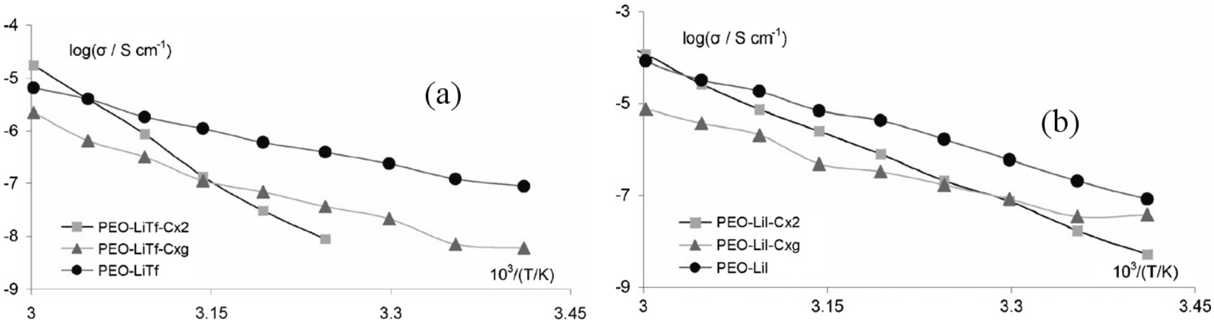

Figure 24. Thermal dependency on conductivity - systems containing LiTf (a) and LiI (b)

System	E_{act}, [kJ mol^{-1}]	System	E_{act}, [kJ mol^{-1}]
PEO-LiI	153	PEO-LiTf	89
PEO-LiI-Cx2	200	PEO-LiTf-Cx2	265
PEO-LiI-Cxg	115	PEO-LiTf-Cxg	118

Table 19. Activation energies of conductivity.

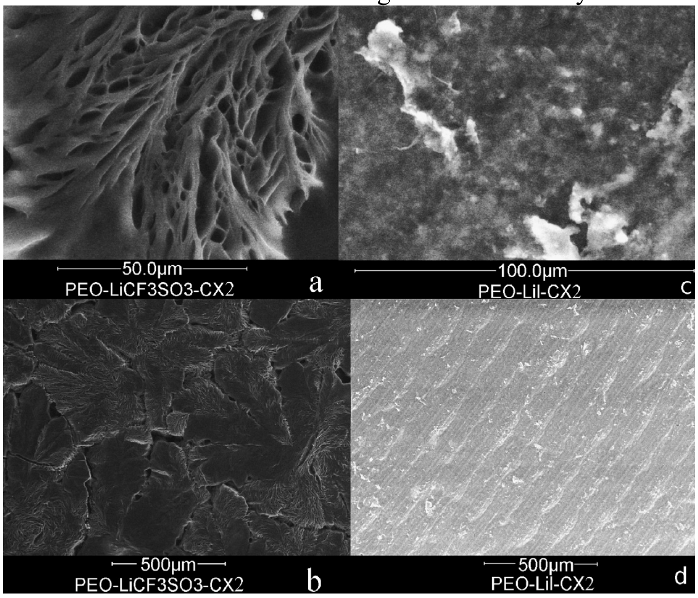

Figure 25. SEM images of PEO-LiTf-Cx2 and PEO-LiI-Cx2 systems.

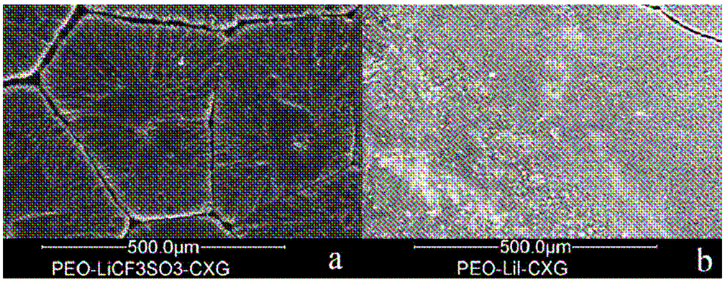

Figure 26. SEM images of PEO-LiTf-Cxg and PEO-LiI-Cxg systems.

6.4.3 Analysis of SEM images and EDS results.

The SEM images of the PEO-LiTf-Cx2 and Cxg composites are depicted in Figures 25abcd and 26ab, respectively. One can observe that the systems studied reveal different morphology: PEO-LiTf-Cx2 crystallizes forming ‘‘sponge-like’’ structures, while PEO-LiTf-Cxg forms large spherulites. In contrast, in systems containing LiI (Figures 25c and d and 26b) no separation of the specific structures can be observed with the spherulitic structure still maintained. It can be also observed that the volume of the interspherulitic amorphous phase for a sample containing Cx2 is significantly bigger than for one containing Cxg. Figure 27 shows the comparison of SEM images of the sample with EDS intensity mapping for two elements: carbon characteristic mainly for the receptor and, partially, for the polymer phase and sulfur which is present in the salt. Image 27a shows a well-defined boundary between the two spherulites. The carbon line intensity follows exactly the SEM image also revealing the phase boundary while the sulfur concentration profile is much more uniform. This observation proves that the salt is located evenly in both spherulites (being heterophase systems themselves) and in the inter-spherulitic amorphous phase whereas the receptor concentration is significantly higher in the interspherulitic areas than in spherulites.

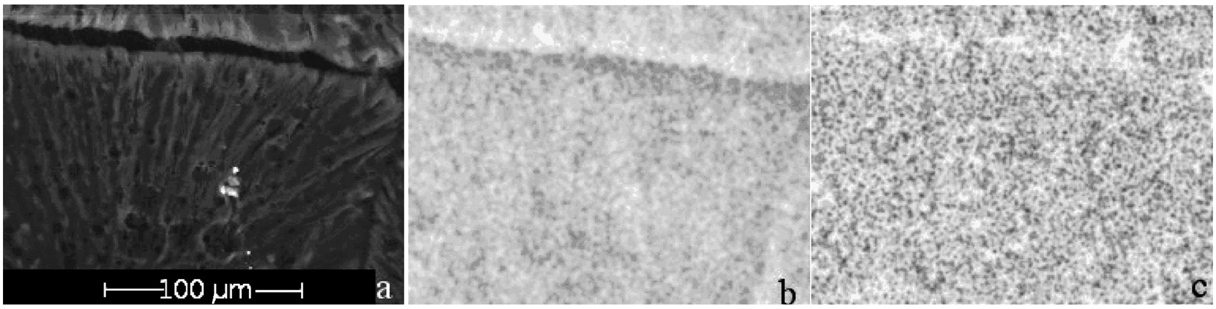

Figure 27. EDS images of the PEO-LiTf-Cxg sample. (a) SEM image of the area; (b) carbon K line intensity mapping; (c) sulfur K line intensity mapping.

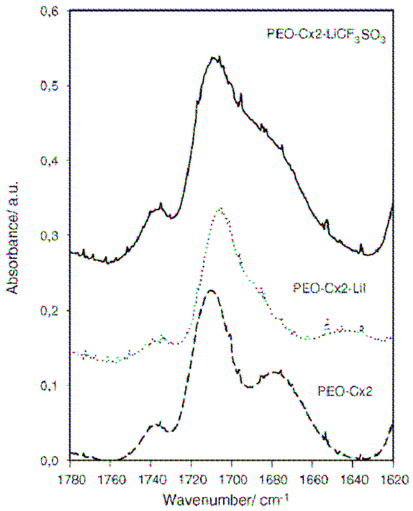

Figure 28. FT-IR spectra of PEO membranes doped with Cx2.

6.4.4 FTIR spectroscopy results.

The formation of a complexes of Cx2 receptor and anions were studied using FT-IR spectroscopy. The hydrogen bond formation between the amide group of the receptor and the anion (or polymer) results in a change of several bands characteristic for the amide group. The most pronounced changes are observed for bands of C=O stretching vibrations. Figure 28 shows a comparison of the carbonyl stretching region in the FT-IR spectra of PEO-Cx2, PEO-Cx2-LiI and PEO-Cx2-LiTf samples. In the spectrum of the PEO-Cx2 sample the band of C=O stretching vibration is split into a doublet with two distinct maxima, at 1710 and 1676 cm^{-1}. The peak at 1710 cm^{-1} corresponds to the free carbonyl group and that at 1676 cm^{-1} can be a superposition of peaks attributed to weakly and strongly associated carbonyl groups, with maxima respectively at ~1680 and 1640 cm^{-1}. In the spectra of samples containing the lithium salt the maximum of the peak is slightly shifted towards lower wavenumbers (1707 and 1705 cm^{-1} for LiTf and LiI, respectively) and the bands of free and associated carbonyl groups are highly overlapped.

It should be stressed here that the band is much broader for the PEO-Cx2-LiTf sample than for PEO-Cx2-LiI one. Additionally, the low frequency shoulder which appears at ~1675 cm^{-1} for the LiTf-doped electrolyte shifts to ~1690 cm^{-1} for the one containing iodide. The described effect may indicate that salt addition results in breaking stronger hydrogen bonds linking Cx2 molecules as well as formation of weaker ones between the anions and Cx2. The broadening of the band in spectra of lithium salt-doped membranes may also indicate some interactions between the lithium cation and the carbonyl group of the receptor.

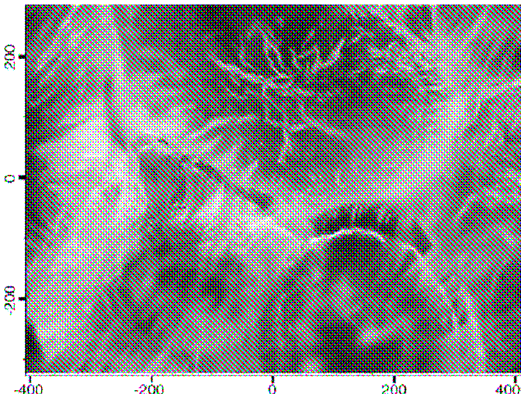

Figure 29. Polarized light optical microphotograph of the PEO-Cx2 film (distances in µm).

6.4.5 Results - Raman spectroscopy, Raman mapping and optical polarized light microscope images

The obtained membranes doped with Cx2 were all heterogeneous and highly crystalline. Optical polarized-light microscope images (see Figure 29) show that the diameter of the spherulites is between 50 and 200 µm.

Figure 30 presents the distribution of calixarene in the PEO-Cx2 matrix. It can be seen that the amorphous domains of membrane are richer in calixarene than the crystalline ones.

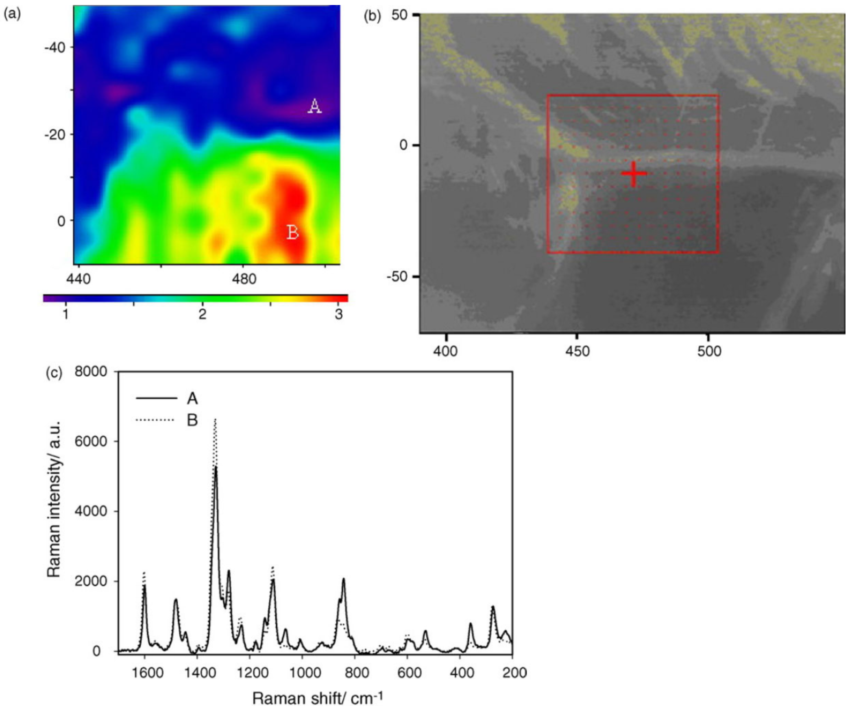

Figure 30. (a) Map of intensity ratio of characteristic peaks of Cx2 (ring stretching, 1600 cm^{-1}) and of the crystalline phase of PEO (CH_2 rocking, 842 cm^{-1}) for PEO-Cx2. (b) Photo of the mapped membrane from the CCD camera. (c) Raman spectra recorded in A and B areas. The scale of both maps in µm.

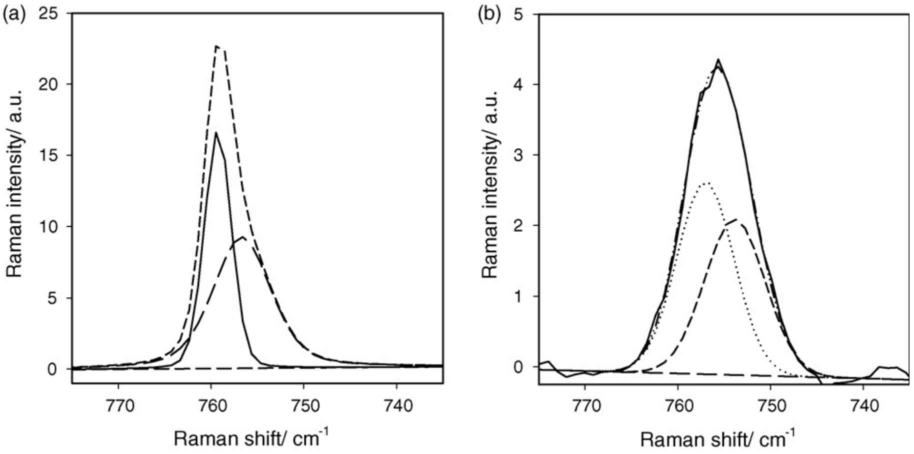

Figure 31. Deconvolution of the δ_{sCF3} band in Raman spectrum of amorphous (a) and crystalline (b) domains of PEO-LiTf membrane.

In order to study the complexation of salt both by calixarene and the polymer matrix, the Raman spectra recorded in crystalline and amorphous parts of membranes were analyzed. The band of the δ_{sCF3} vibration of Tf$^-$ anion is particularly useful to study complex formation. Figure 31a and b shows deconvolution of the δ_{sCF3} band for a spectrum taken in the crystalline and amorphous parts of the PEO-LiTf membrane. In the crystalline phase the maximum of this band is centered at 755 cm^{-1} while in the amorphous domains it is shifted to 759 cm^{-1} and is much more intense. According to the literature, various ionic species should give bands at ~753, ~758 and ~763 cm^{-1} ascribed to free anions, ionic pairs and triplets, respectively. In the spectrum taken in the crystalline domains, the peak can be resolved using two contributions, with maxima at 757 and 753 cm^{-1}. The share of the former is between 50 and 70%. For the amorphous domain, the band was split into contributes peaking at 759 and 756 cm^{-1}. The share of the former is 42% and of the latter 58%.

Different results were obtained using the band of the ν_{sSO3} vibration. In this case, for the amorphous domain the deconvolution gives three bands with maxima at 1054 cm^{-1} (triplets, 14%), 1043 cm^{-1} (ionic pairs, 62%) and 1031 cm^{-1} (free ions, 24%). For the crystalline phase, it was possible to resolve this band into two contributions with maxima at 1040 cm^{-1} (ionic pairs, 32%) and 1030 cm^{-1} (free ions, 68%). Similar results were obtained for the PEO-Cx2-LiTf membranes.

Deconvolution of the δ_{sCF3} peak gave 62% of ionic pairs and 38% of free anions for the crystalline phase, and 68% of ionic pairs and 32% of free anions for the amorphous phase. For the band of ν_{sSO3} vibration mode in the amorphous phase the same fraction of ionic pairs (68%) and free anions (32%) as for membrane without Cx2 can be achieved. In the crystalline phase, the content of free ions was lower than in the PEO-LiTf sample and equal to 60% while the share of ion pairs was almost the same (34%).

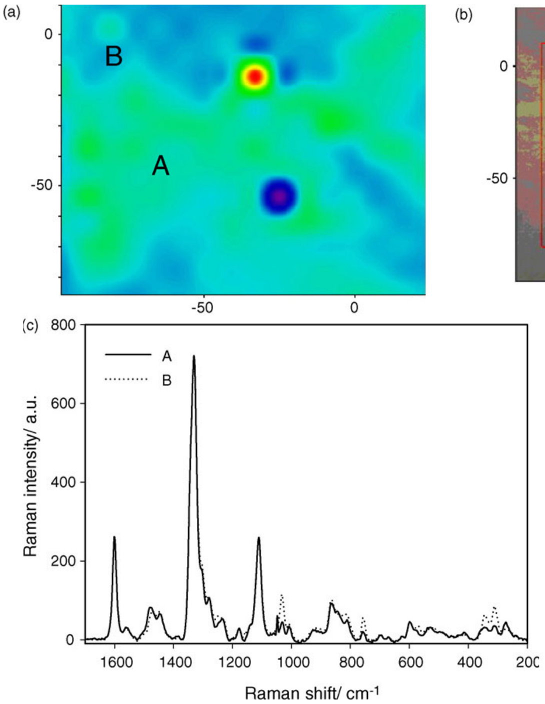

Figure 32. (a) Map of intensity ratio of characteristic peaks of Cx2 (ring stretching, 1600 cm^{-1}) and of LiTf (δ_{sCF3}, 758 cm^{-1}) for PEO-Cx2-LiTf. (b) Photo of the mapped membrane from the CCD camera. (c) Raman spectra recorded in areas A and B. Scale of both maps in micrometers (μm).

However, it must be stressed that the membranes studied were heterogeneous and the estimated values of the ionic species depend on the degree of crystallinity. Comparing the spectra normalized against the intensity of the δ_{sCF3} peak of LiTf it was also observed that the intensity ratios of ring stretching vibration of Cx2 (maximum at 1598 cm^{-1}) and of δ_{sCF3} are much higher in the amorphous phase (see Figure 32). These observations are confirmed by Raman mapping. Figure 32 presents a Raman map for PEO-Cx2-LiTf obtained by comparing intensities of peaks of ν_{ring} (Cx2) and δ_{sCF3} (salt). The Cx2/salt concentration ratio is higher in the amorphous domains of the sample and lower in the crystalline ones. These results correspond to those obtained for the PEO-Cx2 membrane (without salt), where, as seen in the Raman map shown in Figure 30, Cx2 was aggregated in the amorphous domains. A similar effect, i.e. a relatively higher content of free ions in the crystalline phase and a higher content of calixarene in the amorphous phase was found for the membrane containing Cxg.

Both membranes without the macrocyclic compound, PEO-LiTf and PEO-LiI, were crystalline but the crystallinity was higher for the iodide doped sample. Figure 33 shows a comparison of Raman spectra for PEO-LiTf, PEO-LiI, PEO-LiTf-Cx2 and PEO-LiI-Cx2, recorded in the crystalline areas of samples. It can be seen that the intensity of peaks at 1272 and 835 cm^{-1}, which are characteristic for the crystalline phase, is the strongest for the PEO-LiI sample. The addition of receptors resulted in a decrease in crystallinity for all the systems studied but this effect was more pronounced for iodide-doped samples. The crystallinity also decreased for the sample without the lithium salt which is consistent with FTIR data, indicating the formation of hydrogen bonds between ether oxygen of PEO and urea moieties of the receptor. The application of substituted calixarene as the anion receptor improves the homogeneity of the membrane. Figure 34 shows a comparison of Raman spectra extracted from the Raman map of the PEO-LiI-Cxg membrane. Only slight differences can be found for spectra recorded in various areas of the sample.

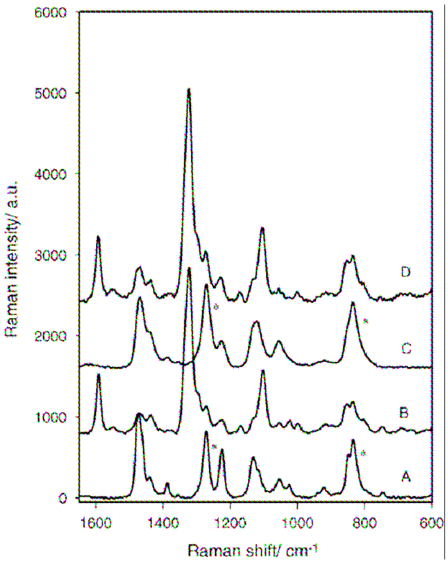

Figure 33. Raman spectra of (A) PEO-LiTf; (B) PEO-LiTf-Cx2; (C) PEO-LiI; (D) PEO-LiI-Cx2. Bands characteristic for the crystalline phase are indicated by asterisks.

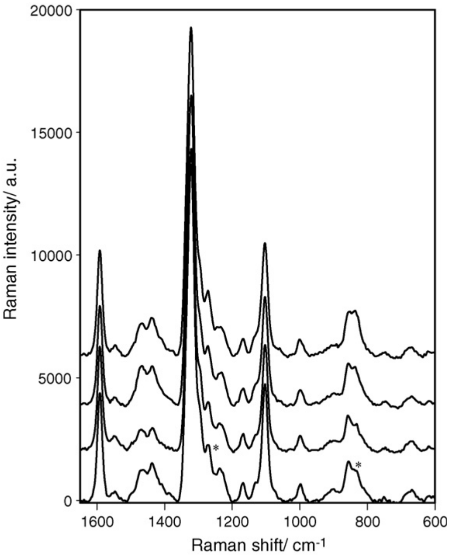

Figure 34. Raman spectra recorded in different areas PEO-LiI-Cxg membrane. Bands characteristic for the crystalline phase are indicated by asterisks.

6.4.6 Results - XRD diffractograms

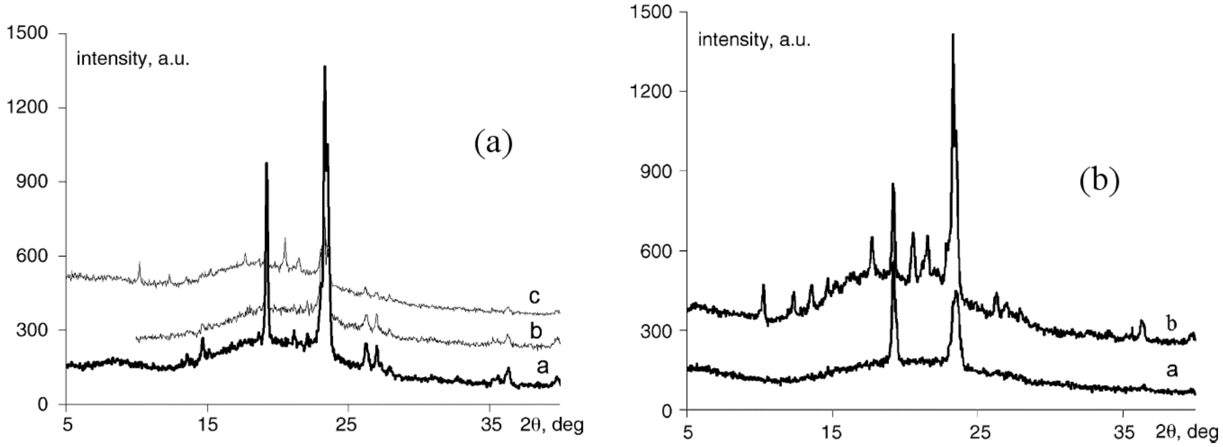

Figure 35. Figure a: Diffractograms of the samples containing Cx2: (a) no salt; (b) LiI; (c) LiTf. Figure b: diffractograms of the pristine samples. (a) $(PEO)_{20}$LiI; (b)$(PEO)_{20}$LiTf (b).

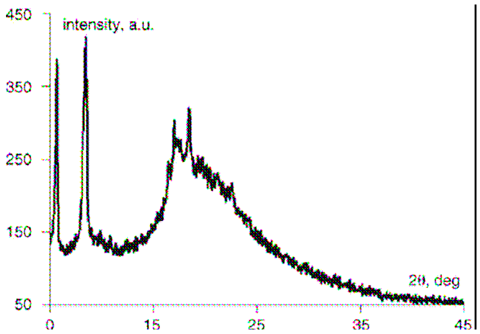

Figure 36. Diffractogram of Cx2 (powdered compound).

When comparing the plots obtained for all the samples containing Cx2 (Figure 35a) with a diffractogram of pure supramolecular compound (Figure 36) one can easily observe that even in the case of the salt free membrane a complete amorphisation of the calix[4]arene derivative is observed. This observation proves that even a polyether of high molecular weight somehow interacts with the receptor. Additionally, a comparison of the plots obtained for the pristine samples (Figure 35b) and ones containing the additive (Figure 35a) shows clearly that the modified membranes exhibit a stronger amorphous bump around the PEO reflections. This phenomenon can be also attributed to the polymer-receptor interactions. The distortion effect is stronger for the Cx2 receptor which shows that the interactions of the Cxg derivative with the crystalline PEO phase (resulting in lowering ionic conductivity) are weaker. Finally, the crystallinity data are gathered in Table 20. The values obtained, identically to the case of samples containing C6P, were calculated by integration of the reflexes located near $2\theta = 19^{\circ}$ (characteristic for the crystalline phase of pure polymer). A $P(EO)_{20}$LiI sample was used as a reference with crystallinity degree equal to 70%.

The results show that the samples containing LiTf are generally less crystalline than the ones doped with LiI. Additionally, both compounds lead to the amorphisation of composites containing triflate while the crystallinity of iodide complexes remains almost unchanged.

Sample	Thickness μm	$2\Theta=19^{\circ}$ a.u.	$2\Theta=23^{\circ}$ a.u.	$2\Theta=19^{\circ}$ corrected	$2\Theta=23^{\circ}$ corrected	X_c
PEO-Cx2	135	3759	12552	27840	92750	0.79
PEO-LiI	117	2889	4274	24690	36530	0.70
PEO-LiTf	131	1750	9728	13318	74030	0.38
PEO-LiI-Cx2	73	1703	4794	23580	66390	0.67
PEO-LiTf-Cx2	149	623	2965	4158	19790	0.12
PEO-LiI-Cxg	63	1486	3506	23587	55650	0.67
PEO-LiTf-Cxg	55	630	3148	11454	57236	0.33

Table 20. XRD crystallinity data of the electrolytes studied.

In the first case the Cx2 compound reveals a stronger amorphisation activity in comparison with Cxg. The intensity of the second peak typical for the PEO crystalline phase was also analyzed. The study shows that for some samples the intensity of the peak is much larger than that predicted on the basis of the crystalline phase content. Additionally, the peak maximum is slightly shifted and/or the peak can be split. This phenomenon is related to the formation of the crystalline polymer salt complex characterized by a much higher specific reflexivity. The intensity of the signal is, thus, a combination of two unequal contributions and cannot be easily interpreted quantitatively.

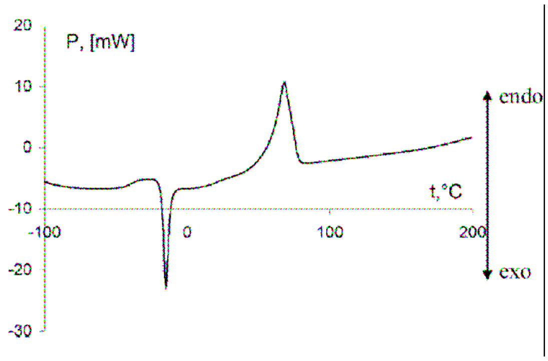

Figure 37. DSC trace for the PEO-LiTf-Cx2 system.

6.4.7 DSC results.

DSC traces in the case of membranes containing calixarene-based anion receptors are very similar to these of PEO-lithium salt-C6P systems. The main characteristic processes i.e. glass transition and melting of the PEO crystalline phase are at very similar temperature ranges in all the studied systems containing anion receptor. The DSC trace for PEO-LiTf-Cx2 systems which is typical for all samples containing calixarene-based anion receptor as an additive is depicted in Figure 37. A typical DSC trace for the PEO-lithium salt system [451, 453, 461] presents two signals: one (baseline shift) characteristic for the second order transition, which is observed between −40 and −10ºC, can be assigned to the glass transition, while the other (endothermic peak) is located between 60 and 75ºC and can be attributed to the melting of the PEO crystalline phase. In the case of samples containing Cx2 and Cxg, one can observe an additional exothermic peak between −15 and 10ºC which can be attributed to the crystallization of the PEO and salt–PEO complexes from the amorphous phase present in the sample.

Sample	Glass Transition		Sample	Glass Transition		Recrystalization	
	T [°C]	Δc_p [J mol^{-1} °C^{-1}]		T [°C]	Δc_p [J mol^{-1} °C^{-1}]	T [°C]	ΔH [J g^{-1}]
PEO	-48.8	0.035	PEO-LiTf-Cx2	-38.9	0.396	-8.6	24.2
PEO-LiTf	-46.0	0.058	PEO-LiI-Cx2	-38.9	0.343	-18.0	21.7
PEO-LiI	-12.5	0.210	PEO-LiTf-Cxg	-38.4	0.321	-17.1	14.8
			PEO-LiI-Cxg	-22.8	0.219	16.5	8.0

Table 21. Temperatures, specific heat of T_g and enthalpy of recrystallization in the composites.

Table 21 presents the temperature and enthalpy of recrystallization and glass transition temperature together with changes in specific heat capacity (c_p) for glass transition. Interestingly, in the case of receptor-free membranes no recrystallization process is observed. Moreover, changes of the c_p related to glass transition are one order of magnitude higher than in the case of receptor free membranes. This result proves that the receptor plays an important role in the stiffening of the polymeric chains. Table 22 gathers the temperature of the crystalline phase melting, specific enthalpy of melting as well as the calculated crystallinity degree. The normalized values are obtained on the basis of pure PEO mass fraction in the composition studied. A comparison of the values obtained for PEO and PEO-Cx2 samples shows that the addition of this supramolecular additive does not prevent the crystallization of the polymer. In the case of the samples containing the salt the presence of Cx2 even promotes matrix crystallization. Remarkably, an important observation can be made for the Cxg composites. Here the normalized crystallinity values are extremely and unreasonably high. This effect clearly shows that the excess heat effect observed must be related to the co-crystallization of oligo(oxyethylene) chains of the receptor with the PEO matrix. Therefore, the previously mentioned link between these two phases is observed confirming the better polymer-anion trap compatibility. The co-crystallization effect is stronger for samples containing LiTf.

Sample	T_m, °C	H_m, J g^{-1}	X_c, %	X_c^N, %	Sample	T_m, °C	H_m, J g^{-1}	X_c, %	X_c^N, %
PEO	80.1	183	85	85	PEO-LiI-Cx2	75.1	98	46	74
PEO-Cx2	74.2	121	57	83	PEO-LiTf-Cx2	78.8	99	47	76
PEO-LiI	75.5	114	52	61	PEO-LiI-Cxg	63.5	73	34	84
PEO-LiTf	72.2	110	51	61	PEO-LiTf-Cxg	75.5	83	39	98

Table 22. Melting points, enthalpies of melting and DSC-based calculated degrees of crystallinity.

6.5 The effect of C6P addition to the oligomeric analogs of PEO

6.5.1 Introduction

Poly(ethylene glycol) dimethyl ether (M_W between 350 to 1000) has a coordination (very similar Donor and Acceptor Numbers) and dielectric properties very similar to PEO (in fact, the dielectric constant ε in PEODME is slightly higher than in PEO). Thus, PEODME is often used as a solvent being a liquid model of the polymeric matrix as the ionic equilibriums should be similar in PEO and in the PEODME solution. One of the differences between high M_W PEO and PEODME is that salt solutions in the liquid solvent are homogeneous and, consequently, the diffusion of charged species in PEODME is identical in the whole volume of the electrolyte. Contrary to that, solid and polymeric matrix consists of several phases characterized by slightly different constitution and different physicochemical properties (such as e.g. crystallinity). Hence, ionic diffusion in the each phase of the heterogenic system depends on the phase.

Thus, it was interesting i) to study this model system and ii) to compare the changes related to the receptor addition in the liquid and solid (polymeric) systems. Even if studies on salt solutions in PEODME are of relatively weak practical meaning, it is easier to ascribe the changes in ion transport properties to particular charged specimen in the PEODME solution than in a PEO-based SPE in which the measured conductivity of the electrolyte depends on the ion transport properties of each phase present in the system as well as geometric arrangement of the phases. Liquid samples are also easier in preparation in comparison with casting PEO-based electrolytes.

In this subchapter, ionic transport properties such as conductivity and lithium transference number - measured by means of the Newman technique (being a combination of three experiments: diffusion coefficient determination, in-time DC polarization and voltage registration, and measurements of OCV of the concentration cell) are presented. These results will be used in further discussion of the changes which result from adding C6P to the system.

This subchapter is prepared on basis of the publications [448] and [462].

6.5.2 Effect of adding C6P on conductivity in LiI-PEODME systems.

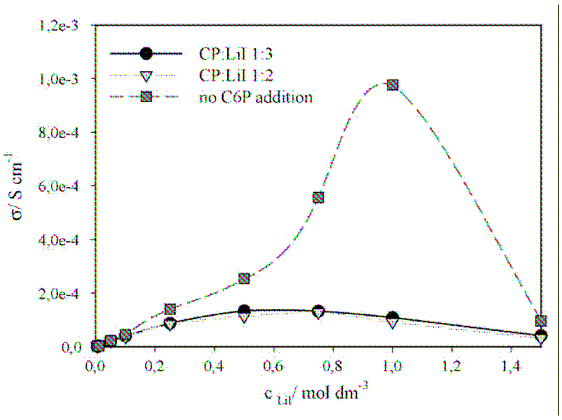

Figure 38. Conductivity of PEODME-LiI-C6P systems.

The conductivity values of PEODME-LiI-C6P composites are shown in Figure 38. An addition of calix[6]pyrrole derivative to a low M_W PEODME-LiI system leads to a decrease in overall conductivity of about one order of magnitude. Moreover, this decrease is observed only in samples of high salt concentration. In diluted samples the conductivity is almost the same for all the series. The maximum conductivity for the system with an additive can be found at lower salt concentrations (0.5–0.75 mol/kg) rather than in samples without additives (1.0 mol kg^{-1}). This can suggest that the decrease in conductivity is associated with complexation of an anion and higher transport suppression of negatively charged associates in samples with a supramolecular additive. The change of the additive content seems to have a negligible effect on conductivity.

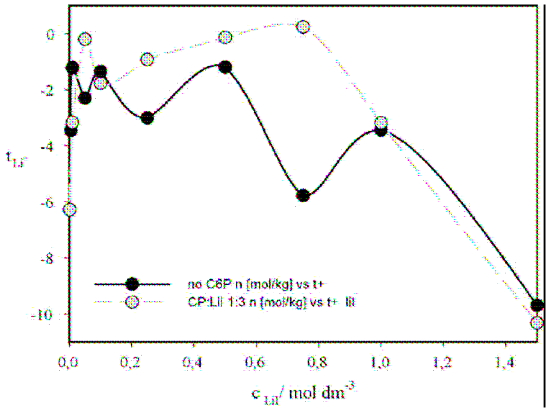

Figure 39. Li^+ cation transference numbers in PEO-LiI and PEO-LiI-C6P (LiI:C6P = 3:1).

6.5.3 The effect of adding C6P on t_{Li+} measured with the Newman technique in the LiI-PEODME system.

The estimated transference numbers (t^{Newman}_{Li+}) are presented in Figure 39. As one can easily notice they are generally higher in samples with a supramolecular additive. This is in agreement with the results presented in Chapter 6.1 for PEO-$LiBF_4$-C6P polymeric systems

[462]. This enhancement of t_{Li+} values is especially true for samples of highest conductivity. It seems that the main problem here is instability of the lithium–electrolyte interface in the presence of even a small electric field.

The growth of the passivation layer and change in overall resistance of the sample related to this effect are not the only phenomena to consider. The formation of the passivation layer is partially an electrochemical reaction and, thus, it decreases the current efficiency of the main process (lithium transport). Additionally, the charge carrier transport mechanisms within the layer are different in comparison with the bulk electrolyte. Finally, it can be assumed that the changes in the values measured come from both ion transport properties of the electrolyte and conducting properties of the SEI which change with the growth of the passivation layer.

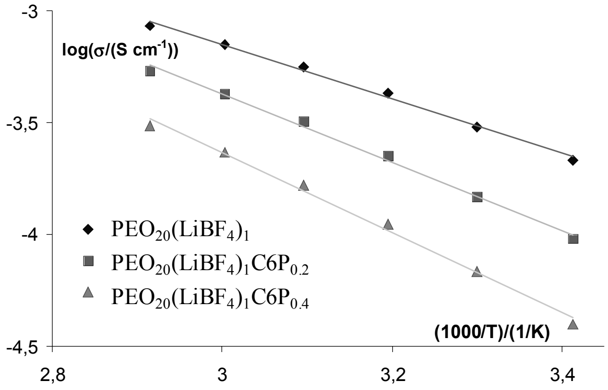

Figure 40. Arrhenius plots of ionic conductivity for PEODME-$LiBF_4$ electrolytes: Li:O=1:20.

The negative values of t_{Li+} can be explained by the assumption that there is significant contribution of charged aggregates, e.g. LiI_2^- triplets to ionic transport. In the case of this kind of charged species, the mass transport of lithium is connected with electric transport of the negative charge. Thus, the contribution of the negative charged triplet to the lithium transference number is equal to -1. Such a result suggests that most of ionic transport in the system studied is realized by negatively charged ionic agglomerates, such as LiI_2^- or $Li_2I_3^-$.

6.5.4 The effect of adding C6P on conductivity in $LiBF_4$-PEODME systems.

$PEODME_{100}(LiBF_4)_XC6P_Y$						
	X=0		X=1		X=2	
	E_{act} [kJ mol^{-1}]	σ_0 [S cm^{-1}]	E_{act} [kJ mol^{-1}]	σ_0 [S cm^{-1}]	E_{act} [kJ mol^{-1}]	σ_0 [S cm^{-1}]
X=1	16.3	0.0642	20.8	0.146	26.9	0.844
Y=5	23.3	3.18	29.1	15.8	34.3	54.6
Y=10	37.8	623	35.0	195	33.0	65.4

Table 23. Arrhenius parameters of conductivity in PEODME-$LiBF_4$-C6P systems. Amount of PEODME calculated for a single -CH_2CH_2O- unit.

Figure 40 presents Arrhenius plots of ionic conductivity for PEODME-$LiBF_4$ (Li: O= 1:20) electrolytes with and without C6P additives. In Table 23, Arrhenius parameters for

PEODME-$LiBF_4$-C6P systems are given. For both systems the addition of C6P is followed by a decrease in conductivity. This decrease is more manifested for composite electrolytes with high concentration of the supramolecular additive. Also it can be noticed that the observed decrease is more pronounced for more diluted electrolytes.

6.5.5 Discussion - different behavior of liquid and solid systems.

C6P, in general, significantly changes ion transport properties of solid, PEO-based electrolytes. In some cases, no decrease in conductivity and a four-time higher lithium transference number can be observed. This improvement in properties of the ionic transport is observed at temperatures slightly lower than the melting point of the PEO.

Unfortunately, the enhancement of lithium transference numbers after the addition of the anion receptor in PEODME-based systems is much smaller than in the case of solid PEO-based systems. It proves that the length of the polyether chain is important when the role of the anion receptor in the properties of ion transport is analyzed. This assumption is supported by DSC data collected by Błażejczyk [257] for PEODME-LiI-**121** and PEO-LiI-**121** systems. It is observed there that salt addition in both systems leads to a T_g increase caused by temporary cross-linking of the polymeric chains. Taking into consideration the impact of the supramolecular additive on T_g, one can distinguish between a liquid system (M_W=500 g mol^{-1}) where Cx2 causes further stiffening of the system as well as an increase of the glass transition temperature from 199 K to 211 K and a solid system (M_W=5·10^6 g mol^{-1}) where a decrease from 251 K to 238 K is observed. It can be assumed here that in the first case the supramolecular additive is partially linked to the polymer matrix chain causing its stiffening while in the second it interacts mainly with the salt blocking the formation of the temporary cross-links. Spectroscopic studies on this phenomenon will be presented in the next Chapter.

6.6. Spectroscopic studies on the phenomena of C6P and Cx2 receptor complexation with anions and neutral solvent species.

6.6.1 Introduction

The previously gathered results show that significant discrepancies between the solid PEO-based and liquid PEODME-based electrolytes can be observed in terms of their transport properties such as conductivity or lithium transference numbers. As a direct explanation cannot be delivered by general electrochemical, spectroscopic and morphological studies of ready-to-use electrolytes, a more basic spectroscopic research was proposed and conducted to gather information of polymer-salt (e.g. [463-465]), liquid low molecular equivalent-salt (e.g. [181, 466, 467]), ion-ion (e.g. [468]), anion-receptor (e.g. [469, 470]), as well as neutral

species (e.g. solvent-receptor and cation-receptor interactions). The data collected are believed to be valuable in evaluating the changes in transport properties of electrolytes.
In the studies presented, Raman, FTIR as well as ^{1}H and ^{19}F NMR spectroscopy was used.

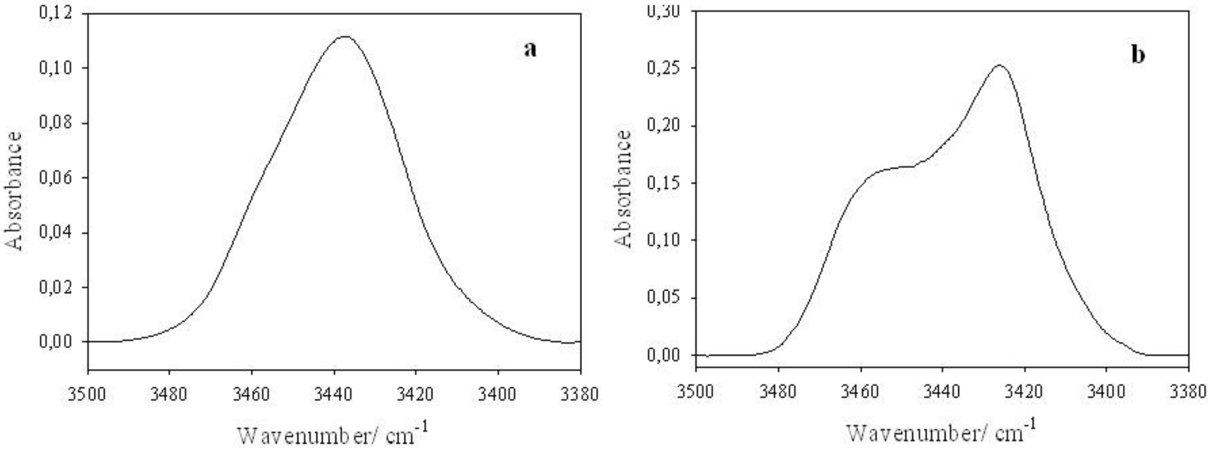

Figure 41ab. A comparison of FTIR spectra of the C6P solution in CCl_4 (a) and DME (b). Concentration of the C6P equal to 20 mmol/kg.

6.6.2 FTIR studies of C6P

FTIR spectroscopy is widely used to analyze the interactions mentioned above. In the studies on interactions of anion receptors interacting with anions by urea, pyrrole or amide groups, the NH stretching vibration spectral region is of main interest. The FTIR spectra of C6P in solvents of various polarity ($CHCl_3$ and DME) and also those of C6P-DME and C6P-LiTf-DME with the same C6P concentration (Figure 41ab) were compared. It can be clearly seen that the shape of the NH band depends on the solvent used. In the C6P/CCl_4 solution, a maximum of the peak was observed at 3443 cm^{-1} (Figure 41a) while in the C6P-DME solution this band is split into two distinct contributions, with maxima at 3426 and 3260 cm^{-1}. However, these bands are, in fact, more complex and their deconvolution reveals the presence of at least four peaks, with maxima at 3412, 3424, 3436 and 3459 cm^{-1}.
Additionally, in diglyme solution there are two weaker but broad bands, at 3315 and 3500 cm^{-1}, one corresponding to H-bounded NH group and the other to free NH groups. The same bands but far less intense (in particular that at 3315 cm^{-1}) were found in the spectrum of C6P/CCl_4 solutions. This indicates that non-bonded NH groups predominate in the CCl_4 solution, while in the DME solution a part of the NH groups can interact with the molecules of the solvent.

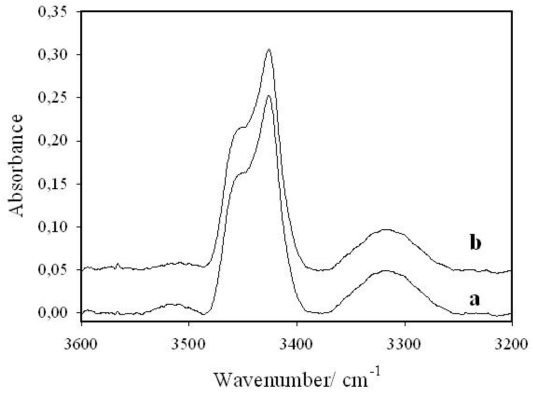

Figure 42. FTIR spectra of C6P-DME solution (5a) and C6P-DME-LiTf solution, C6P: salt molar ratio 1:3 (5b). C6P content was equal to 20 mmol kg^{-1}.

Figure 42 shows a comparison of the spectra of C6P-DME and C6P-LiTf-DME solutions of the same C6P concentration. As can be seen, the addition of the salt does not influence the shape of the NH band significantly. The only visible difference is slightly lower intensity of the band at 3515 cm^{-1} for the sample containing the salt. This can suggest that in the case of a DME-based diluted solution the preferred interaction is observed between the receptor and the solvent and not between the receptor and anion. This is so as even for a much lower receptor-solvent complex formation constant (in comparison with that of the receptor-salt complex) the concentration of the solvent is three orders of magnitude higher than that of the receptor.

Similar FTIR studies were performed for solutions of C6P in various solvents characterized by different affinity to C6P because of their various coordinating properties (Figure 43). In this case, the ν_{NH} vibration mode was the most sensitive for complexation. Thus, in the solution in $CHCl_3$, ($CHCl_3$ has rather poor coordinating properties and should not interact with C6P in terms of receptor-neutral molecule complex creation), the maximum of this peak was centered at 3446 cm^{-1}. The replacement of this solvent with DME (characterized by much stronger donor properties) involved splitting the peak into two constituents; in pure DME a doublet with maxima at 3454 and 3434 cm^{-1} and a broad shoulder at 3309 cm^{-1} can be observed. In the dioxane solution spectrum was similar to that in DME but the band at 3454 cm^{-1} was stronger than that at 3434 cm^{-1} and the intensity of the band of the associated NH group was lower. In the DMF-based solution, (DMF exhibits the strongest donor properties among the solvents studied) only a weak band 3460 cm^{-1} and a very strong shoulder with maximum at ~3300 cm^{-1} were observed.

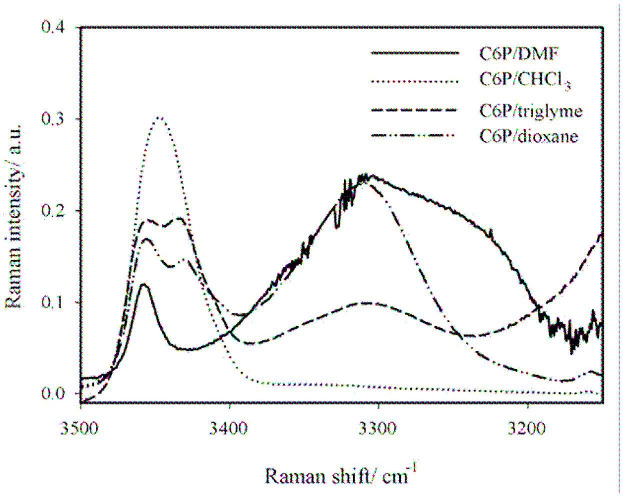

Figure 43. FTIR spectra for ν_{NH} spectral region of C6P-polar solvent solutions. C6P concentration equal to 10 mmol dm^{-3}.

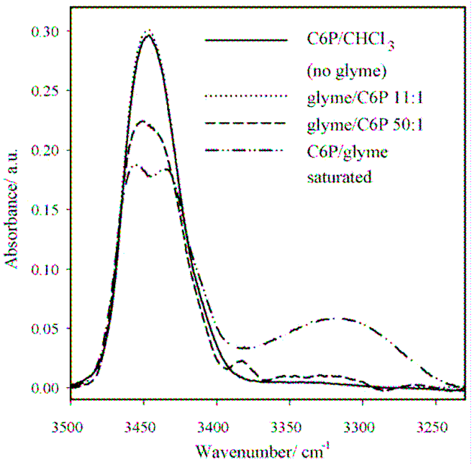

Figure 44. FTIR spectra for ν_{NH} spectral region of C6P-DME solutions in $CHCl_3$ with C6P concentration equal to 10 mmol/l. DME: C6P ratio equal to 0:1, 11:1 and 50:1. For comparison, a spectrum of saturated solution of C6P in triglyme is shown.

Figure 44 shows a comparison of FTIR spectra of C6P–$CHCl_3$–DME mixtures in the NH stretching vibration range. With C6P/DME molar ratio equal to 1:10, the shape of the band was the same as for the solution in pure $CHCl_3$. A slight broadening of this peak appeared at C6P/DME molar ratio equal to 1:100 and more distinct changes at molar ratio as high as 1:500. A shoulder at 3309 cm^{-1} ascribed to bonded NH groups can be found only in the spectra of samples with high excess of DME (C6P/DME molar ratio less than 1:500).

For C6P-$CHCl_3$-DMF (spectra not presented here) systems the shift of the maximum of ν_{NH} band from 3446 to 3457 cm^{-1} was observed as the C6P/DMF molar ratio decreased. In the spectrum of C6P in pure DMF the band attributed to the “free” NH group significantly decreased in intensity while the intensity of the band of bonded NH groups, with maximum at 3305 cm^{-1}, increased. This indicates that C6P forms a complex with DMF easier than with DME which can be explained by higher donor properties of the former.

6.6.3 Vibrational spectroscopy studies on Cx2.

The vibrational spectroscopy results obtained for C6P also encouraged the study of changes in the Cx2 molecule bearing in mind that the role of both C6P and Cx2 on ion transport properties of PEO-based SPEs was studied previously. Different changes in conductivity and lithium transference numbers after the addition of Cx2 and C6P can be ascribed to different interactions with the polymeric matrix and ionic species (See Chapter 6.3.7 and the last paragraphs of Chapter 6.1). Fortunately, in the case of both C6P and Cx2 receptors, the changes in the NH stretching vibration spectral region are of main interest. The formation of hydrogen bonds results in a decrease of the "free NH" stretching band intensity and the formation of an additional band. Other changes can be observed in the C=O stretching band in the amide I spectral region.

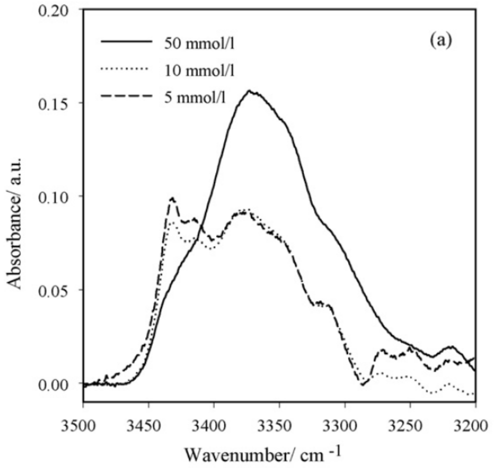

Figure 45. The Cx2 FTIR spectra - NH stretching band regions for different Cx2 concentrations.

Figure 45 shows a comparison of spectra of Cx2/$CHCl_3$ solution with various concentrations of Cx2. At the highest (50 mmol dm^{-3}) concentration of Cx2, the maximum of the ν_{NH} vibration is found at 3370 cm^{-1} which indicates strong association of Cx2. With a decrease in the content of Cx2, the intensity of this band decreases while the intensity of two bands with maxima at 3431 and 3418 cm^{-1}, attributed to "free" N-H stretching vibration of aryl and alkyl NH moieties, respectively, increases. However, for the systems studied, a band of the H-bonded N-H group is still present in the spectra with Cx2 concentration of 5mmol dm^{-3}. The deconvolution of the 3500-3200 cm^{-1} spectral region allows distinguishing at least 7 bands. Spectral contributions with maxima at 3377, 3341 and 3310 cm^{-1} correspond to various "bonded" aryl and alkyl NH groups. Weaker bands below 3300 cm^{-1} are most probably overtones.

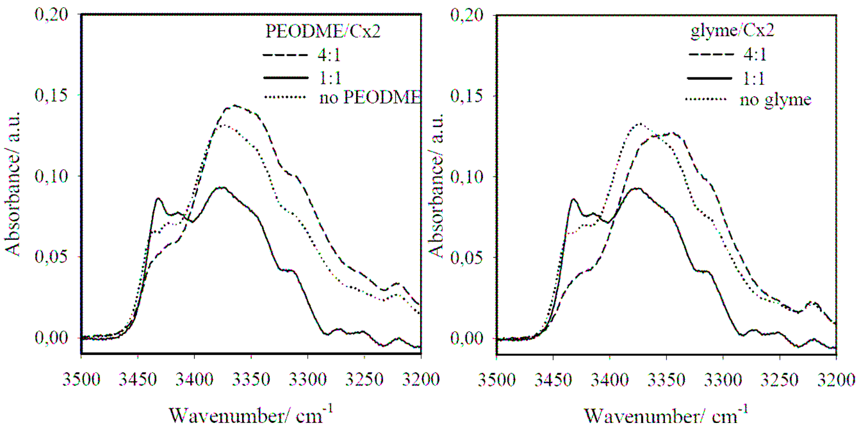

Figure 46. The FTIR (NH stretching band region) of Cx2-$CHCl_3$-PEODME (a) and Cx2-$CHCl_3$-DME (b) systems.

In solutions of Cx2-DME or Cx2-PEODME mixtures in $CHCl_3$ the bands attributed to the "free" NH groups decrease with the increase of the DME/PEODME: Cx2 molar ratio. Figures 46ab show a comparison of the spectral region corresponding to the NH stretching vibrations of Cx2. It is noteworthy here that for the lower "guest" solvent: Cx2 ratio the spectra of both systems are essentially the same. For the solutions of highest (4:1) "guest" solvent: Cx2 ratio, in the solution containing DME (46a) and PEODME (46b) the maxima of ν_{NH} band are found at 3340 cm^{-1} and 3364 cm^{-1}, respectively. This is the evidence that Cx2 molecules interact stronger with DME than with its oligomeric analogue PEODME.

Figure 47 presents the amide I spectral region of Cx2-$CHCl_3$ and Cx2-PEODME-$CHCl_3$ solutions. In all the spectra of Cx2 in $CHCl_3$ four spectral contributions can be distinguished, with maxima at 1743, 1711, 1682 and 1667 cm^{-1}. The band at 1743 cm^{-1} seems to be independent of the concentration of Cx2, while those at 1711 and 1682 cm^{-1} decrease in intensity and the one at 1667 cm^{-1} increases with the rise in Cx2 content in the studied concentration range of Cx2. Therefore, bands at 1711 and 1682 cm^{-1} can be ascribed to the "free" carbonyl groups and that at 1667 cm^{-1} to the hydrogen-bonded ones. In the spectra of mixture containing DME or PEODME one can observe an increase in relative intensity of the band at 1682 cm^{-1} and a decrease at 1667 cm^{-1}. This effect can be explained as a consequence of formation of hydrogen bonds mostly between the "guest" solvent and the Cx2 molecules and, therefore, an increase in the concentration of "free" carbonyl groups as the solvent/Cx2 ratio increases.

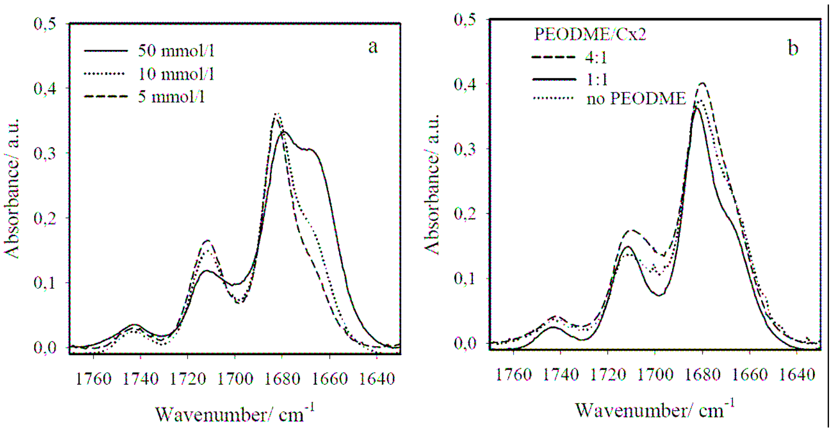

Figure 47. The FTIR (CO stretching band region) of Cx2-$CHCl_3$ (different concentration of Cx2) (a) and Cx2-$CHCl_3$-PEODME (b) systems.

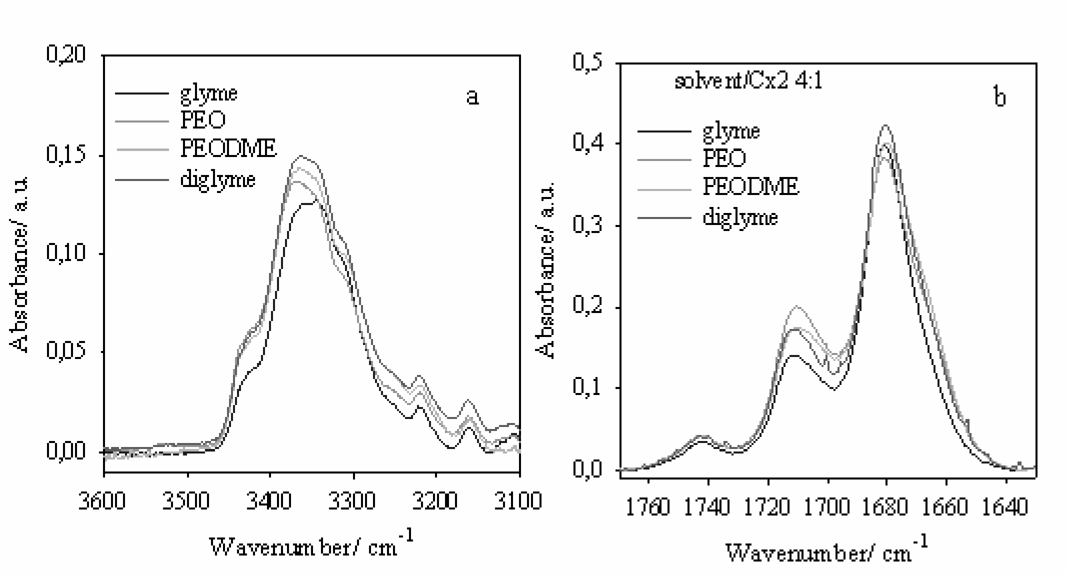

Figure 48. FTIR spectra of glyme, diglyme, PEODME and PEO– NH (a) and C=O (b) stretching band region.

The chain length strongly influences the ability of ether to form complexes in systems containing -OCH_2CH_2- units and characterized by different chain length is depicted in Figure 48. In solutions of the same ether/Cx2 molar ratio, the complexation effect is the strongest for DME and the weakest for PEO. In conclusion, in such systems a complex is preferably formed between the oxygen atoms of the OCH_3 groups of the ether and NH groups of the urea moieties.

To study the phenomenon of complex formation deeper, 2D-FTIR (correlation spectrum) experiments were performed. Figure 49 presents a synchronous correlation spectrum of 3200–3500 and 1630–1730 cm^{-1} spectral range for solutions of PEO and Cx2 in $CHCl_3$. The negative crosspeaks between bands of the “free” carbonyl groups (at 1711 and 1682 cm^{-1}) and the band of the bonded NH groups indicate that the hydrogen bonds linking Cx2 molecules disappear at the expense of the solvent–Cx2 hydrogen bonds as the PEO/Cx2 molar ratio increases.

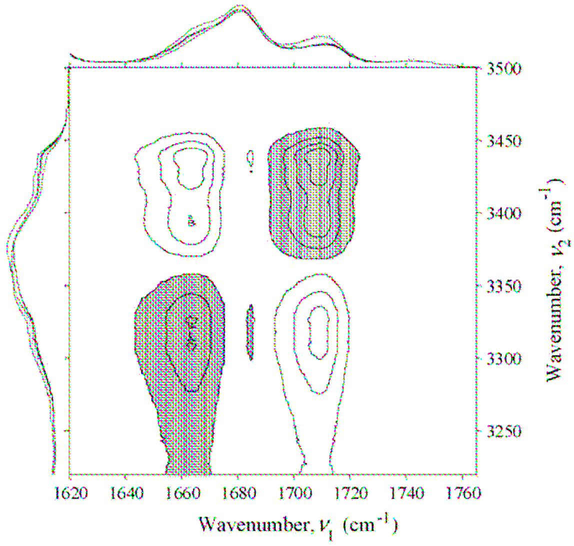

Figure 49. Synchronous 2D correlation spectrum of the ν_{NH} and $\nu_{C=O}$ spectral region. The FTIR spectra are for Cx2–PEO–$CHCl_3$ solutions. The Cx2 concentration is equal to 10 mmol dm^{-3} $CHCl_3$ and the PEO:Cx2 molar ratio was equal to 4, 2, 1, 0.5 and 0.

In order to compare the phenomena of ester- and ether-type neutral solvent-Cx2 complex formation also FTIR studies for dialkyl (or alkene) carbonate-Cx2 complex formation in $CHCl_3$ were performed. Figure 50 presents amide I spectral region of Cx2-EC solutions in $CHCl_3$. It is seen that at the same solvent-Cx2 molar ratio the share of the bonded C=O at 1667 cm^{-1} is slightly higher than for the samples containing ethers (see Figure 48b). The ratio of the area of the contributions at 1682 and 1667 cm^{-1} obtained from the deconvolution of this band is equal to 3.3:1 for DME and 2.9:1 for EC. The possible explanation is that the solvent of lower basicity i.e. EC interacts weaker with the receptor than with the ethers. This reasoning is also supported by the fact that even at the highest (4:1) EC-receptor molar ratio such a increase of intensity of the associated NH groups was not observed; the maximum of this peak was centered at 3372 cm^{-1} for all of the samples. The intensities of peaks with maxima at 3431 and 3418 cm^{-1}, attributed to the "free" NH groups decrease at a higher EC/Cx2 molar ratio but can be distinguished in the spectra of all the samples studied.

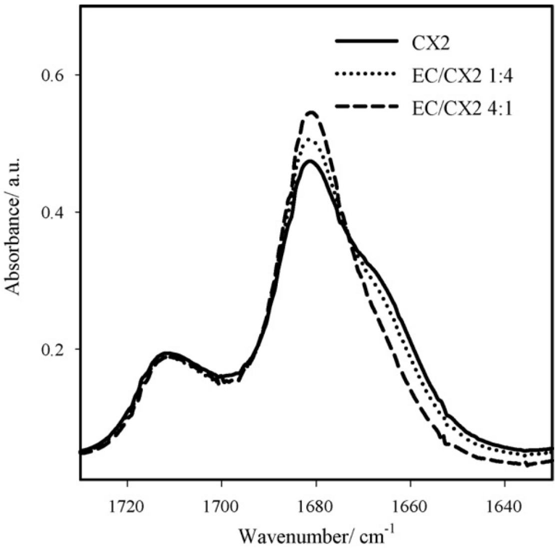

Figure 50. FTIR spectra for the $\nu_{C=O}$ spectral region of Cx2/EC solutions in $CHCl_3$. Cx2 concentration in EC/Cx2–$CHCl_3$ solutions was equal to 10 mmol dm^{-3}. EC/Cx2 ratio equal to 4:1, 1:1 and 0:1.

The most prominent change in the spectral pattern of the polar solvent is the shift and separation of two strong bands in the EC C=O stretching vibration range (Figure 50). In the spectrum of pure EC a doublet with maxima at 1795 and 1768 cm^{-1} can be seen; one attributed to $_{C=O}$ and the other to an overtone of the $_{7}$ vibration (ring breathing) of EC diluted in $CHCl_3$. Both these bands are shifted to higher frequencies, with maxima at 1810 and 1779 cm^{-1}, respectively. These values are close to those obtained by Fini et al. [471] for diluted EC-benzene solutions. Such an effect was ascribed to the destruction of the short-range order responsible for intermolecular vibrational coupling through transition dipoles. However, any effect of the EC/Cx2 molar ratio on the position of the peak maxima in the samples studied was not found. Unfortunately, the bands ascribed to the EC ring breathing and bending modes which are more sensitive to complex formation cannot be analyzed because of their low intensity or overlapping with the bands of chloroform.

Solvent	DN	AN
Ethylene carbonate[a]	16.4	-
Dimethyl carbonate[a]	15.1	-
Ethylene glycol dimethyl ether[b]	20	10.2
Diethylene glycol dimethyl ether[b]	24	10.2
Triethylene glycol dimethyl ether[c]	-	10.5
CH_3CN[b]	14.1	18.9
DMF[b]	26.6	16
1,4-Dioxane[b]	14.3	10.3
$CHCl_3$[b]	4	23.1

Table 24. Properties of the solvents. [a]- Data from Ref. [472].[b]- Data from Ref. [473].[c]- Data from Ref. [474].

In the spectra of DMC-$CHCl_3$ mixtures (not depicted here) only slight changes can be observed, both in the C=O and NH stretching vibration range, in systems of DMC/Cx2 molar ratios up to 4:1. It is somewhat surprising considering similar donor properties of this solvent (see Table 24).

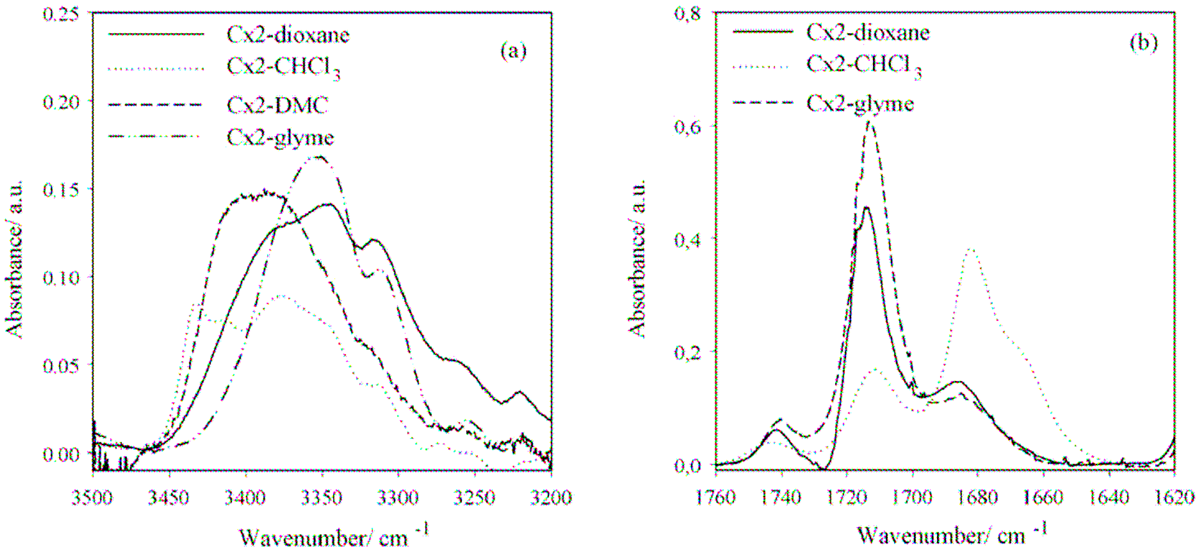

Figure 51. FTIR spectral range for ν_{NH} (a) and $\nu_{C=O}$ (b) of solutions of Cx2 solutions with Cx2 concentration equal to 10 mmol dm^{-3}.

Also the spectra of Cx2 solutions in polar solvents taken as guests during the studies of Cx2 complexation phenomena with neutral species were registered. This was done in order to compare two cases: i) concentration of the polar solvent at the same level as that of the anion receptor; ii) polar solvent concentration more than two orders of magnitude higher than the concentration of anion receptor.

When Cx2 was dissolved directly in DMC, the maximum of the ν_{NH} band appeared at 3410 cm^{-1}. As shown in Figure 51, for solutions of Cx2 in DME and dioxane, the maximum of this peak is much more shifted towards the lower wavenumber. The strongest effect was found for DME which is characterized by the highest DN (see Table 24). In the spectrum recorded for the solution in dioxane, a strong band with a maximum at 3340 cm^{-1}, originating from the associated NH groups and an almost equally strong shoulder with maximum at ~3380 cm^{-1}, can be observed. These results agree with the behavior expected on the basis of donor properties of the solvent (see Table 24), with the exception of DMC.

6.6.4 Discussion - a comparison between Cx2 and C6P

A comparison of FTIR data for C6P and Cx2 solutions in $CHCl_3$ shows a much higher capability of forming Cx2 complexes with solvents and of self-association. Our studies of the receptor-polar solvent interactions indicate that Cx2 forms complexes with a variety of polar solvents (glymes, alkyl carbonates, dioxane) at equimolar receptor-solvent ratio while for a system containing C6P a large 10- or 50-fold excess of polar solvent is required. It was also revealed that complex formation between the receptor and the solvent depends on the donor properties of the latter. In solvents characterized by stronger donor properties, such as DMF, NH groups of both receptors were almost completely associated.

An intermediate effect was observed in glymes and dioxane while in chloroform or CCl_4 either peaks of free NH groups (C6P) or bands or self-associated NH and C=O groups (Cx2) were found. Additionally, a detailed study of association of Cx2 in systems containing glymes and polyethers of various chain lengths showed that complex formation is affected by a steric effect. It is supposed that for the same reason a weaker hydrogen bond between DMC and Cx2 is observed.

Moreover, it was shown that the Cx2 compound can interact with neutral species (e.g. low M_w polyether analogues). This important phenomenon must also be taken into consideration when using DME-type solvents as model systems for PEO-based electrolytes. The chain length is important and the complexation of neutral species decreases with an increase of the molecular weight of the solvent used. This observation explains why the promising electrochemical properties obtained for high M_w solid systems (*vide* Chapters 6.1 and 6.5) cannot be explained by the data gathered in spectroscopic studies of the model liquid system.

6.6.5. The effect of adding C6P on the ^{19}F NMR chemical shift of the fluorine in the BF_4^- anion.

In several previously presented results vibrational spectroscopy data were used in order to study the phenomena of ionic agglomerate formation (ionic pairs and triplets). It seems that also NMR spectroscopy can be a useful tool in the studies of interactions between the receptor, the ions and electrically neutral solvent species. Firstly, it is possible to study diluted solutions of salts using NMR (down to 10^{-4}-10^{-5} mol dm^{-3}) when the studies through vibrational spectroscopy are limited to solutions of salt concentration not lower than 10^{-2} mol dm^{-3}. Secondly, the ratio between the half breadth of the NMR peak and the change of the chemical shift being a result of e.g. ionic pair formation is at least one order of magnitude higher than the respective ratio in IR spectroscopy. The main disadvantage of this technique is that all reactions such as $Li^+ + A^- \leftrightarrow LiA$, $Li^+ + LiA \leftrightarrow Li_2A^+$, $A^- + LiA \leftrightarrow LiA_2^-$ as well as other similar ionic reactions are much too fast (in the NMR timescale) to insulate peaks of ions, ionic pairs and other agglomerates. As a result, only one peak is observed. The chemical shift of this peak is the weighted average of chemical shifts of the ionic species present in the system with weights equal to that of the product of the molar fraction of the given specimen and the number of ions in the ionic agglomerate. For instance, when we assume that ions Li^+ and A^-, ionic pairs LiA and positively charged ionic triplets Li_2A^+ are present in the solution of the salt, the ^{7}Li NMR chemical shift observed for this sample δ can be given by the following equation: $\delta = \delta_{Li+}x_{Li+} + \delta_{LiA}x_{LiA} + 2\delta_{Li2A+}x_{Li2A+}$ where δ_x is the chemical shift of specimen x and x_x is its molar fraction. In the vibrational spectroscopy, each peak can be attributed to the particular specimen present in the system.

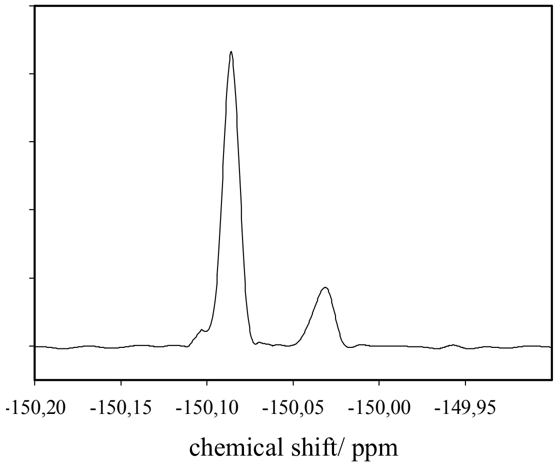

Figure 52. The ^{19}F NMR spectrum of $LiBF_4$ in CH_2Cl_2/ACN mixture.

Although a simple comparison of two NMR spectra gives no quantitative data on the complexation phenomena, the change in the chemical shift after the addition of the receptor can prove an interaction of the studied specimen with the receptor.

Solvent	δ, [ppm]			
	$LiBF_4$		$(C_2H_5)_4NBF_4$	
	No C6P	With C6P	No C6P	With C6P
CH_2Cl_2/ACN 1:9	-150.08	-149.99	-149.90	-149.91
CH_2Cl_2/ACN 5:5	-153.23	-152.83	-151.55	-151.56
CH_2Cl_2/ACN 9:1	-148.89	-150.66	-151.67	-151.69

Table 25. ^{19}F NMR chemical shifts (higher) of BF_4^- anion.

To omit the problem of deuterated solvents, it was decided to perform ^{19}F NMR measurements (instead of ^{1}H ones) for solutions of $(C_2H_5)_4BF_4$ and $LiBF_4$ in various solvents. The main aim was to determine if the presence of C6P (1 mole per 2 moles of salt) can result in a change of the chemical shift of the fluorine nuclei which, in turn, should prove the presence of the anion-receptor interaction. An attempt was also made to estimate the effect of Lewis acidity of the cation. A typical spectrum of ^{19}F NMR for sample containing $LiBF_4$ is shown in Figure 53. The presence of two peaks in the spectra should be attributed to different ^{19}F NMR shifts of anions containing two different boron isotopes: $^{10}BF_4^-$ and $^{11}BF_4^-$. All the values of the chemical shift of the maximum of the higher peak are shown in Table 25.

The highest change of the chemical shift, 1.77 ppm, is observed for the $LiBF_4$ solution in the least polar solvent mixture (CH_2Cl_2/ACN 9:1). As expected, the change of chemical shift is lower in solvent mixtures of higher dielectric constant and donor numbers which both have a significant influence on the salt dissociation and the equilibrium between the solvent-anion and receptor-anion interactions. Surprisingly, in the case of $(C_2H_5)_4NBF_4$, the changes in the chemical shift are not so significant (this result is in opposition to the changes in the ^1H NMR chemical shift in the of the C6P molecule dissolved in mixture of $CHCl_3$ and CH_3CN after addition $(C_2H_5)_4NBF_4$, observed by Eichen [406]). In this case the changes in the ^1H NMR shift were high enough to measure the anion-receptor complex formation constant using NMR titration). Thus, large changes in the ^{19}F NMR chemical shift in the case of systems containing $LiBF_4$ suggest that C6P addition to $LiBF_4$ solutions improves salt dissociation. In the case of $(C_2H_5)_4NBF_4$ there was no significant effect on ^{19}F NMR chemical shifts due to better salt dissociation. For samples of high dielectric constant, the complexation of the anions by the solvent particles (especially CH_3CN) can inhibit the anion-receptor interactions.

6.6.6 Results of NMR studies and titrations.

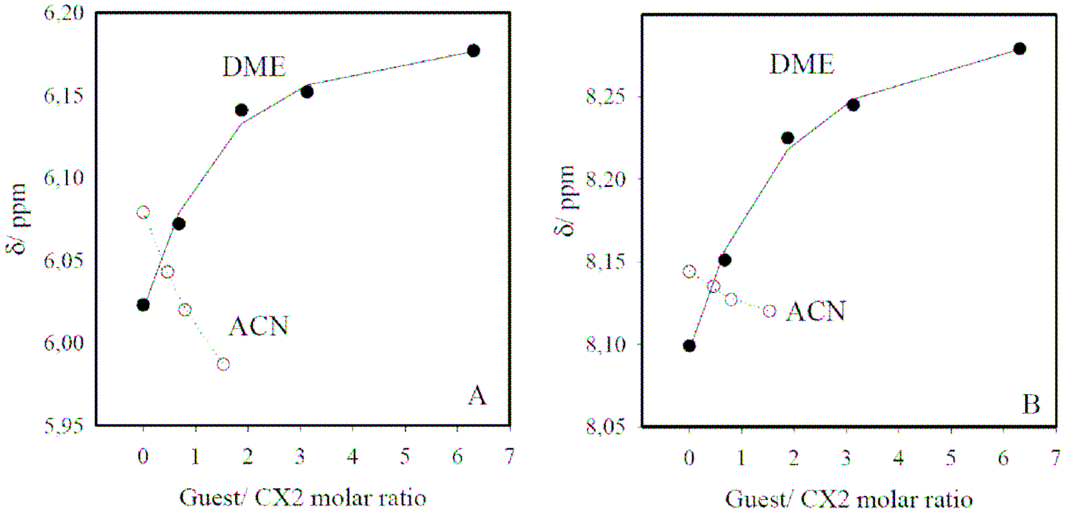

Figure 53. The ^1H NMR chemical shift of the Cx2 protons of NH connected with aliphatic chain (A) and with aromatic ring (B) after DME (filled) and CH_3CN (empty) addition.

In the previously presented studies, most of the results are qualitative or *semi*-quantitative and present tendencies (trends) and the strength of anion receptor-solvent (matrix)-salt interactions. For quantitative studies, i.e. estimations of complex formation constants, a technique taken from the chemistry of anion coordination, that is NMR titration was used. The details concerning the procedure estimating the formation constants used are presented in the Experimental section of this dissertation and in a review article [475] as well as in references cited there.

Using this technique, the studies of complexation phenomena were continued, starting also from the complexation of neutral solvent species (dioxane, DME and CH_3CN) by Cx2. The changes in the chemical shift of both NH groups were observed with increasing concentration of DME or CH_3CN. The curves obtained are shown in Figure 53. The estimated values of Cx2-CH_3CN and Cx2-DME complex formation were between 100 and 300 mol dm^{-3} (a more accurate estimation needs at least 12 measurements, i.e. 4 measurements for one estimated value). This result for DME in connection with the Cx2-I^- anion-receptor complex formation constant (about 10^3 mol^{-1} dm^3 in $CDCl_3$, see [476]) at least partially explains electrochemical behavior of PEO-LiI-Cx2 systems. In these systems the lithium cation transference number t_{Li+} remains the same for the low Cx2 concentration and the improvement is only for the high salt: PEO molar ratio (it should be higher than 1:20).

To confirm this result, it was decided to estimate the anion receptor complexation constant in the solution in which the solvent (mixture of 1,4-dioxane and acetonitrile) has the same dielectric constant as PEO ($\varepsilon=5.5$, dioxane:CH_3CN mass ratio 12:1) and its liquid oligomeric analogue PEODME ($\varepsilon=8$, dioxane:CH_3CN mass ratio 48:7). The choice of the solvent mixture was a compromise between the coordination properties (represented by the donor number DN related to the solvent-cation affinity and the acceptor number AN which is responsible for the anion-solvent interactions) and the solvent-receptor interactions inhibiting the anion complexation. As is shown later, the ideal mixture of DME and 1,4-dioxane (both solvents have DN and AN almost identical to the PEO matrix) must be replaced with a CH_3CN-dioxane mixture less ideal as regards physicochemical parameters but not complexing the supramolecular compound (the set of parameters for pure solvents was taken from [477] - dielectric constants and [474, 478] - AN and DN numbers; see also Table 24). To overcome the problem of the chemical shift change as the result of self-complexation of the receptor and forming of the ionic pairs, ^{19}F NMR titration of the anion was conducted. A set of solutions was obtained by the mixing the salt (LiTf) and the receptor solutions and the pure solvent in order to maintain both constant salt concentration and the appropriate host to guest ratio. It should be emphasized here that this procedure can be applied only for titration of the salts containing a fluorine atom. Thus, it was impossible to apply this procedure to the systems containing LiI.

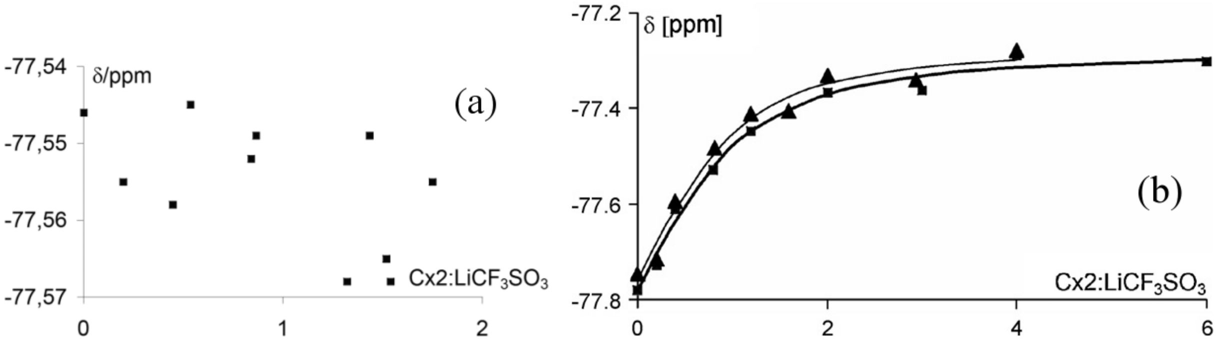

Figure 54. Figure a: ^{19}F NMR chemical shift of Tf as a function of Cx2:LiTf molar ratio in DME (c_{LiTf}=1.15 mmol (kg DME)$^{-1}$). Figure b: ^{19}F NMR chemical shift of Tf as a function of Cx2:LiTf molar ratio in dioxane-CH_3CN mixtures of σ=5.5 (squares, c_{LiTf}=5.34 mmol (kg of the solvent)$^{-1}$) and σ =8 (triangles, c_{LiTf}=5.76 mmol (kg of the solvent)$^{-1}$).

In order to use a solvent whose coordinating properties are similar to those of polymeric PEO, a mixture of DME and dioxane (dielectric constant equal to 5.67) was applied. Unfortunately, the registered dependency of the chemical shift on the salt: receptor ratio is not representative and cannot be used for estimation of the complexation constant (Figure 54a). This observation can be related to the phenomenon of complexation of a supramolecular additive with the solvent species previously studied by means of FTIR spectroscopy (see Chapters 6.6.2 and 6.6.3). Contrary to this, the ^{19}F NMR chemical shifts for the LiTf and Cx2 in dioxane: acetonitrile mixtures as a function of Cx2: LiTf molar ratios are depicted in Figure 54b. From these data the complexation constants equal to 650 mol (kg of solvent)$^{-1}$ for solvent having ε = 5.5 and 700 mol (kg of solvent)$^{-1}$ for solvent having ε = 8, respectively, were estimated.

6.6.7 Discussion

The quantitative data obtained give an insight into the interactions between the Cx2 receptor with anions and the electrically neutral solvent species. It was shown that even if DME is characterized by a dielectric constant lower than CH_3CN, the molecules of both electrically neutral solvent species have similar affinity to the receptor molecule, perhaps due to fact that DN of DME is higher. Another possible explanation is that Cx2 has a higher affinity to the $-OCH_3$ groups as suggested by FTIR studies. Moreover, it was proved that in a CH_3CN-dioxane system an interaction between the anion receptor is observed which is not the case of a DME-dioxane mixture. These results show that the addition of a particular receptor should be preceded by testing its coordinating properties in a particular solvent or solvent mixture. Moreover, the presented results show that the complexation process is more dependent on the coordinating properties of the given specimen than on the Coulombic interaction.

The results presented, due to both some discrepancies and the fact that the solid-state system differs from the liquid ones, do not fully prove the presence of the complexes in the PEO-based electrolyte. However, in opinion of the author of this dissertation, when we try to tailor the liquid system in order to model the interactions in a polymeric membrane, the dioxane-CH_3CN system is a better model than DME. It is due to fact that geometry of DME is different than that of PEO. Thus, the values of the anion-receptor complex formation constant should be similar in the case of dioxane-CH_3CN system and PEO.

Chapter 7

Discussion - Changes in the Electrolyte Properties After the Addition of the Receptor

7.1 The role of the salt in compatibility between the receptor and the polymeric matrix.

An interesting point of discussion here is the role of the salt in the prevention of receptor precipitation. As Peled and Golodnitsky published in their reports [479], the receptor precipitated from the PEO-$LiClO_4$-C6P system which was not the case with PEO-$LiAs_6$-C6P, PEO-$LiBF_4$-C6P, PEO-LiI-C6P and PEO-LiTf-C6P (Figure 55). Two possible explanations of this fact can be given. One is that in the case of system containing $LiClO_4$, the salt does not prevent receptor precipitation (e.g. due to fact that the $ClO4^-$-C6P complex is not formed) which is observed for the other system. However, if this assumption is valid, the precipitation of the receptor from the salt-free system should be observed. This is, however, not the case [450]. Thus, rather the hypothesis that the $LiClO_4$ catalyzes the process of the receptor precipitation is more probable. For instance, the compatibility between PEO and $Li[(ClO_4)_1C6P_X]$ may be, due to some reasons, lower than this between PEO and C6P.

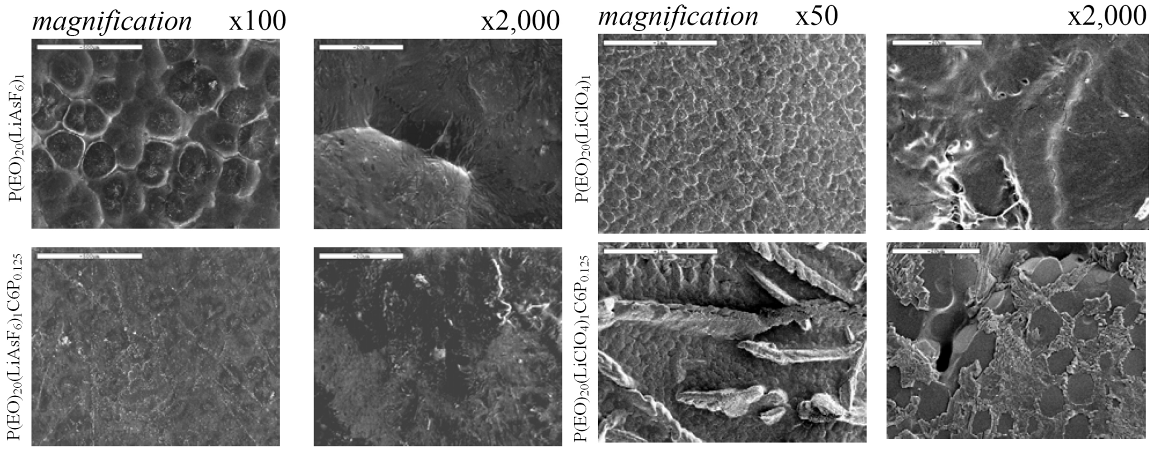

Figure 55. Comparison of the morphology of the PEO-$LiAsF_6$, PEO-$LiAsF_6$-C6P, PEO-$LiClO_4$ and PEO-$LiClO_4$-C6P membranes. After [480].

In the studies presented in this dissertation on PEO-LiTf-C6P systems of lower salt concentration, some agglomerates ("islands") of diameter over 10 μm were observed on the surface of the PEO-LiTf-C6P membranes with the receptor: polymer ratio equal to 1:100 or 1:200. In this case, contrary to the $P(EO)_{20}(LiTf)_1C6P_{0.25}$ system presented by Golodnitsky (in which the receptor: polymer ratio was equal to 1:80), the receptor: salt ratio is 1:2 or even 1:1. This fact proves the role of the salt in changing compatibility between C6P and PEO.

7.2 Changes in the phase structure of the electrolytes and their role in ion transport properties in the polymeric electrolyte.

A receptor-free polymer-salt electrolyte contains several phases, i.e. PEO crystalline phase, crystalline PEO-salt complexes and at least one amorphous phase. The addition of the receptor results in the generation of new phases, as well as changes in the constitution of the existing ones and their concentrations in the membrane.

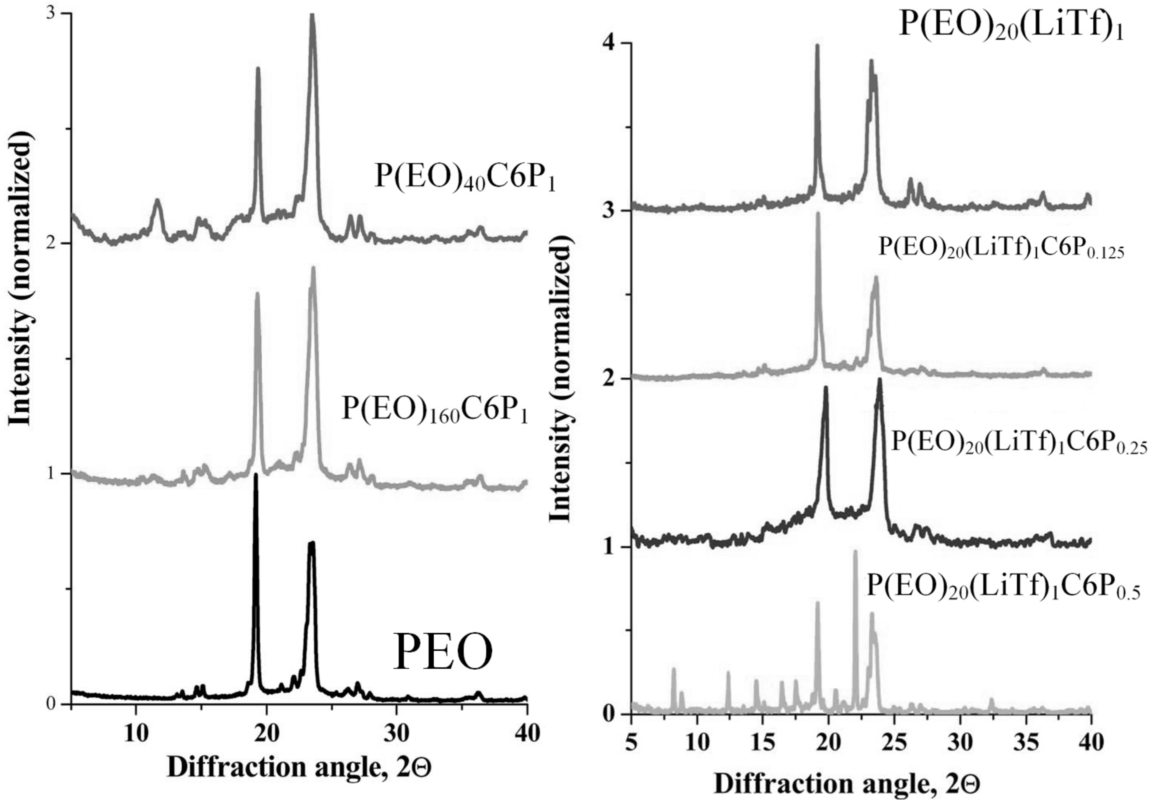

Figure 56. X-ray diffractograms of the salt-free PEO-C6P and PEO-LiTf-C6P systems. After [450]

In order to study the formation of new phases, several X-ray powder diffractograms were registered and analyzed (Figure 56). Particular attention was paid to changes in the shape of the peak near $2\theta=19^{\circ}$ after the addition of C6P [481]. In the studies presented in Chapter 6 of this dissertation, the analyzed peak looks symmetrical when samples of relatively high salt: receptor ratios (1:200 or 1:100) are taken into consideration. This effect is independent of salt concentration. A similar effect can be observed when the data obtained by Golodnitsky for $P(EO)_{20}(LiTf)_1C6P_X$ systems [450] are analyzed. For a receptor-free $P(EO)_{20}(LiTf)_1$ membrane, the peak is asymmetric: its left-hand side is narrow while the right-hand side is relatively broad. For $P(EO)_{20}(LiTf)_1C6P_{0.125}$ the peak is symmetrical. In the case of a $P(EO)_{20}(LiTf)_1C6P_{0.25}$ system, the left-hand side of the peak near 19° is broad while the right-hand side is relatively narrow. In these membranes the receptor: polymer ratio is equal to 0:1, 1:160 and 1:80, respectively. Hence, it can be assumed, taking both original and literature data into consideration, that addition of the receptor results in a change of the shape of the analyzed peak.

This analysis, however, is valid only for a system containing salt. In the cited article also salt-free PEO-C6P systems were studied using X-ray diffraction. Both in the membrane containing only the polymer and the salt-free polymer-receptor composite, the peak near 19° was symmetrical, independently of receptor concentration. This situation is opposite to the one observed in PEO-C6P-LiTf system when changes in the shape of this peak were observed. What must be stressed here, this peak cannot come from crystals of C6P which would eventually precipitate from the system as the main peaks observed in the C6P diffractogram, at 18 and 21...22° are not observed in the diffractograms of the samples with receptor concentration: salt concentration ratio equal to 0.125 and 0.25, respectively. No change in the shape of the peak also suggest that there is no significant change in the phase structure after receptor addition.

The assumption of formation of additional peaks (which would prove the formation of a new phase) can be supported by two additional phenomena also present in the cited work. Firstly (which was presented in the same article and confirmed in this dissertation), if it is assumed that the peak near 19° is a singlet, the addition of C6P to a salt-containing system results in peak broadening. Secondly, the diffractogram of the $P(EO)_{20}(LiTf)_1C6P_{0.5}$ membrane differs strongly from those of other samples. Indeed, in this diffractogram the peak at 19° cannot be observed while the peaks at 18 and 21° may be ascribed to the crystal of C6P precipitated from the system. The latter argument, however, has one significant weakness. In the $P(EO)_{20}(LiTf)_1C6P_{0.5}$ sample, the polymer: receptor ratio is 40:1 which is at least two times less than in any other sample presented here.

In fact, there are some additional arguments that $P(EO)_{20}(LiTf)_1C6P_{0.5}$ differs from other systems studied. DSC experiments conducted by Golodnistky revealed an additional endothermic peak at 249°C (the crystalline C6P melting point). Thus, it can be concluded that with so high receptor concentration the precipitation of C6P from the system can occur. On the other hand, the enthalpy of this peak normalized to the C6P content in the membrane was half of the enthalpy of melting of the crystalline C6P. Thus, it can be assumed that only half of the amount of the receptor was dispersed in the matrix and the other half exists in the form of precipitated crystals of C6P. This can be also supported by the fact that in the systems in which the polymer: receptor ratio was higher the peak at about 250°C was not observed.

Both elemental and Raman mapping experiments reveal that even if the receptor does not precipitate, it exhibits highly heterogeneous distribution while the other membrane constituents are distributed much more evenly. On the other hand, for PEO-salt-C6P neither evident additional reflexes in the X-ray diffractogram nor thermal effects in the DSC trace after changing the C6P concentration can be observed. This suggests that even if the new phases are created, their concentration is not high enough to be observed macroscopically through calorimetry or X-ray diffraction data. However, this argument does not negate the role of these areas in the change of ion transport properties of the electrolyte as they might exhibit much higher ionic conductivity. One can compare the lithium transference number and conductivity data for samples obtained through the casting technique (reported here and obtained by the Tel Aviv University and "La Sapienza" University research groups) and the hot-pressing technique (devised by the "La Sapienza" University research group [482]; both techniques of membrane synthesis were described in Chapters 5.2.3 and 5.2.4, respectively). The observed enhancement of lithium transference number for PEO-LiTf systems after the addition of C6P when the membrane was obtained using the casting technique was about 300% whereas in the case of the membranes of analogous constitution but obtained using the hot-pressing technique it was about 20...30% [483, 484]. If we take into account that in both cases the heterogeneity is at the level of a single μm, we can come to the conclusion that if the additional phases are formed they can be important in changing ion transport properties of the polymeric electrolyte. On the other hand, it is presented in Appendix A that even when the receptor: salt concentration ratio is as low as 1:16, it can influence the ion transport properties. Moreover, IR studies conducted by Golodnitsky revealed that even at as low receptor: salt concentration ratio as 1:8, the addition of the receptor results in a reduction of the fraction of ionic triplets and an increase in the fraction of "spectroscopically free" anions. This result was obtained when the deconvolution of the multiplet in the $\upsilon_{S(SO3)}$ spectral region was conducted for $P(EO)_{20}(LiTf)_1C6P_X$ membranes. Hence, the effect of change in the lithium transference number and conductivity values can result from the presence of receptor in the whole volume of the electrolyte even if the local concentration of C6P is very low. The previously presented influence of the method of membrane synthesis on the lithium transport number of the electrolyte can be explained as follows. During the hot-pressing process of the synthesis the receptor may not dissolve in the polymer. CH_2Cl_2 and CH_3CN used as solvents for the synthesis of membranes using the casting technique, even if they are not present in the polymeric electrolyte, can play the role of anion-receptor complex formation mediators (they can improve the velocity of the anion-receptor complex formation process) during the process of foil casting.

The addition of the receptor Cx2 resulted in an increase of the activation energy of conductivity and the addition of Cxg lowered this energy at temperatures lower than the melting point of the PEO crystalline phase. The data here should be compared with those obtained by Błażejczyk [257]. In this study, the addition of **114** (a receptor of chemical structure very similar to Cx2 but with C_6H_5 instead of $C_6H_4NO_2$ group linked to the urea group) resulted in lowering the activation energy of conductivity. This tendency can be explained by higher acidity of the Cx2 receptor urea groups in comparison with the ones present in **114** or other calix[4]arene derivatives which results in stronger cross-linking of the polymeric matrix via hydrogen bonds. In an alternative approach, higher acidity of the urea groups results in higher affinity of the receptors to the anions. Therefore, the formation of the anion receptor complexes leads to higher concentration of cations and positively charged triplets and, consequently, higher physical cross-linking of the polymeric membrane by these species. These data, when the roles of Cx2 and **114** are compared, can be confirmed by the analysis of changes of T_g. They are, for the system containing Cx2, much more significant than in the case of **114**. An even stronger effect on both the activation energy of conductivity and glass transition temperature can be observed when the addition of Cx2 to such systems is discussed. What is also worth stressing, not only systems containing Cx2 but also those containing C6P exhibit higher activation energy of conductivity. When also fact that the effect of anion receptor addition in the case of lithium transference number in case of Cx2 and C6P is more significant than in the case of other calix[4]arene derivatives, we can summarize that the Cx2 and C6P are much more effective in anion coordination than the other receptors studied previously. This summary has a strong support in the lithium transference number presented previously in Chapter 6.1 and works of Błażejczyk: C6P and Cx2 addition results in the increase of lithium transference number (measured by means of polarization technique) to values higher than 0.8 even when the receptor concentration in the membrane is some times lower than that of salt. For other calix[4]arene derivatives the increase in lithium transference number is observed for higher receptor concentration and the highest values of this parameter are below 0.7.

Another interesting tendency can be observed when the influence of receptor addition on the onset temperature of melting of the PEO crystalline phase is discussed. The addition of any calix[4]arene derivative results in the lowering of this temperature while in PEO-LiX-C6P systems the analyzed temperature is higher than in the case of PEO-LiX systems. This result also suggests better compatibility of the calixarene derivatives in comparison with C6P.

The Raman mapping experiments presented in this dissertation confirm a different influence of C6P and Cx2 on the changes of morphology of the PEO-based membrane. In the case of Cx2, the distributions of the receptor and the salt in the membranes studied are not ideally even; concentrations the receptor and the salt were slightly higher in the interspherulitic areas which are amorphous or at least less crystalline than the spherulites. This tendency of salt distribution can be also observed for the receptor-free systems [485]. This is, however, not the case when Raman mapping experiments of the membranes containing C6P are taken into consideration. It is due to fact that the chamges in the receptor concentration depending on the phase of PEO observed for membranes containing Cx2 are less pronounced than the effects of heterogeneous distribution of the receptor in systems containing C6P.

Similar conclusions for PEO-LiI-Cx2 and PEO-LiI-Cxg systems can be reached when their SEM images presented in this dissertation are compared with those for receptor-free and **114**-containing systems registered by Błażejczyk *et al.* [447]. In all the systems presented, the receptor addition does not significantly change the membrane morphology. The change can be observed only when the receptor concentration is very high, e.g. for the receptor: polymer ratio 1:20 (which corresponds to the system in the which the mass of the receptor added is about 150% of the mass of the polymeric matrix). This can be related to a strong change in the membrane constitution rather than the creation of new phases.

Summarizing these arguments, one can say that in systems containing Cx2 and Cxg, small concentration of the receptor does not change the phase structure and in concequecne the mechanism of ionic transport significantly. The changes observed in ionic transport properties in the systems these originate from lowering the diffusion velocity of anions after the receptor addition because of complex formation rather than from the changes in the phase structure of the membrane.

7.3 How the addition of anion receptors being the calix[4]arene and calix[6]pyrrole derivatives change electrolyte properties- a comparative study.

The observed effect of anion receptor addition on the membrane properties is dependent, in the simplest approach, on its coordination properties of the receptor and its compatibility with the matrix. On the other hand, also the tendency of the “free” ions to form ionic agglomerates should be taken into consideration. As shown in Appendix A, the addition of the anion receptor minimizes the amount of the non-agglomerated and non-complexed negatively charged species due to fact that anion-receptor complex is an additional negatively charged specimen (the whole system should be electrically neutral, thus, the number of positively charged species should equal that of the negatively charged ones). Moreover, the concentration of the anion receptor is far higher than that of the "free" anions, particularly when we analyze the system of the high concentrations of salt and the receptor. Thus, the lowering of the ionic pair fraction after the receptor addition can be also observed (see Appendix A).

The addition of **114** results in conductivity enhancement at relatively low (30ºC) temperatures [257]. This is in opposition to the results obtained when the addition of C6P was studied. In the case of C6P, the addition of the anion receptor resulted in increase in conductivity at temperatures slightly lower than the melting point of PEO [479]. This is in good agreement with the difference in the phase structures and thermal properties of the membranes containing C6P and those containing calixarene derivatives. In the region of the PEO melting point, the amount of the crystalline phase grows rapidly with the temperature increase [486]. Golodnitsky and Peled proved that the amount of the PEO crystalline phase in the electrolytes doped with calix[4]arene-based anion receptor is much lower than in the receptor-free system. Moreover, the onset temperature which can be ascribed to the PEO crystalline phase melting point in the system containing the receptor is lower than in the corresponding receptor-free one [487]. As it was shown previously in Chapter 6.3.4, the crystallinity values, when measured by means of DSC, of the PEO-C6P-LiTfSI are similar to that of the receptor-free system. Also in the PEO-C6P-LiTf the amount of the crystalline phase does not depend on receptor concentration[9]. Moreover, crystallinity values measured by means of XRD are higher for systems containing receptor than for receptor-free ones. Taking into consideration the values of crystallinity estimated by means of both XRD and DSC techniques, one can summarize that the increase of the amorphous phase concentration at temperatures slightly lower than the melting point of the PEO crystalline phase is more significant in the case of membranes containing C6P. This can explain the rapid conductivity increase of the systems containing C6P at these temperatures as the difussivity of the ions in the amorphous phases is about three orders of magnitude higher than in the crystalline ones [488].

The above-mentioned phenomena (beside the previously mentioned cross-linking) have a significant influence on the activation energy of conductivity. In the case of systems

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[9] The amount of the PEO crystalline phase in the studied systems is, naturally, dependent on the salt concentration.

containing C6P and Cx2, the addition of the receptor results in lowering conductivity at RT and its increase at elevated temperatures, thus, the slope of the $\ln(\sigma)=f_{(1/T)}$ dependency is increased. The addition of Cxg or **114** results in conductivity lowering at elevated temperatures, hence, the slope of the $\ln(\sigma)=f_{(1/T)}$ is in this case lower than for the receptor-free system.

The presented influence of these two receptors finds an additional confirmation in the studies of “binary” systems consisting of PEO, salt, anion receptor and ceramic filler. The change of conductivity in a binary system in comparison with filler-free PEO-salt-anion receptor one is very similar to receptor free PEO-salt-anion receptor one when compared to the PEO-salt one. This phenomenon was of very similar nature for systems containing both Cx2 and C6P [489, 490].

7.4 “Hydrogen bond” anion receptor versus “Lewis acid” anion receptors - the role of anion receptors in polymeric electrolytes dedicated to lithium batteries.

In Chapters 3 and 4, the problem of applicability of “hydrogen bond” anion receptors was critically discussed on the basis of the literature data regarding adding them as well as “Lewis acid type” anion receptors to the electrolyte. The conclusion was that an addition of “hydrogen bond” anion receptor, when the anion receptor molecules are stable against the electrodes, can improve the properties of ionic transport and, particularly, lithium transference number. The higher lithium transference number can enhance the stability of the battery during cycling. However, the problem of anion receptor stability discussed in these Chapters was not solved at the level of literature data analysis.

It was suggested in Chapter 4 that the addition of “hydrogen bond” anion receptor can result in a faster growth of SEI than in “Lewis acid type” receptors. Thus, the inner resistance of the battery can be higher and less stable after addition of the “hydrogen bond” anion receptor. On the other hand, the decomposition of the “hydrogen bond” receptor can, interestingly, even lower the resistance of SEI. The role of the anion receptor would hinge, when the mechanism is valid, on the introduction of nitrogen-containing moieties to this layer. A similar situation was described in Chapter 3, where the addition of the receptors containing boron atom or atoms resulted in the formation of SEI characterized by low resistance. This phenomenon was ascribed to the enriching of SEI in $LiBO_2$. As regards “hydrogen bond” receptors, SEI also can be enriched - in this case, with the nitrogen-containing, aromatic and other compounds being the products of anion receptor decomposition.

Another problem is related to thermal stability of the receptor. As the inner resistance of the battery with SPE is, for several applications, low enough only at temperatures over 50ºC, the membrane containing the anion receptor should exhibit stability not worse than the anion receptor-free system. This expectation is fulfilled in the case of both Cx2 and C6P (which are stable up to 300ºC [450]).

Summarizing this discussion, we can say that both "Lewis acid-type" and "hydrogen bond-type" anion receptors can be applied, at least in polymeric electrolytes. Considering the decision of application of the anion receptor, one should analyze the properties of the system and goals to be reached. The addition of the "Lewis acid-type" anion receptor brings more interesting results in systems in which SEI rich in LiF is formed (LiF comes from salt decomposition). In these systems, the addition of anion receptor results in enhancement of the SEI stability. Among other systems in which "Lewis acid-type" anion receptors are more interesting than the "hydrogen bond-type" there are electrolytes containing poorly soluble or poorly dissociating salt. In this case, "Lewis acid-type" anion receptor addition results in the formation of a complex characterized by higher solubility, lower Lewis basicity and lower affinity to the cations. "Hydrogen bond-type" receptors are more effective in electrolytes in which i) it is possible that matrix decomposition catalyzed by a Lewis acid can occur (e.g. in electrolytes working at elevated temperatures), ii) the immobilization of the anion by the "Lewis acid-type" receptor is impossible (e.g. in the case of LiTfSI-PEO electrolytes), iii) a very high lithium transference number without improvement in ionic conductivity is expected (e.g. in a polymeric electrolyte dedicated to 3D- or microbattery).

7.5 The addition of an anion receptor versus the addition of ceramic fillers - the role of anion receptors in polymeric electrolytes dedicated to lithium batteries.

In most cases analyzed in Chapters 2, 3, 6 and this Chapter, the addition of anion receptors resulted in changes in ionic equilibriums and, in some cases, in the plasticization of the membrane. The addition of the ceramic fillers resulted in lowering crystallinity [205, 491], formation of fast conducting paths [213, 492, 493] and enhancement of stability of the SEI, e.g. [85, 187, 494]. Considering the above-mentioned changes in properties of the composites containing the ceramic filler and the ones containing the anion receptor, one can conclude that a change in the properties of the polymeric electrolyte resulting from the anion receptor addition is independent of the presence of the ceramic filler in the electrolyte. It was proved by Golodnitsky [489] that the PEO-LiTf-C6P-SiO_2 "binary" system exhibits higher conductivity than ceramic filler-free PEO-LiTf-C6P and anion receptor-free PEO-LiTf-SiO_2 ones. Moreover, lithium transference numbers of the "binary" systems were higher than those in the anion receptor-free PEO-LiTf-SiO_2 electrolyte (Figure 57).

However, the previously presented argumentation is not valid when we take into consideration that in several cases the acidic groups on the surface of the ceramic filler interact with anions by means of acid-base interactions. In this case, the addition of the ceramic filler is responsible not only for changes in crystallinity and SEI stability but also for partial immobilization of anions by acidic groups on the surface of the filler. Thus, in this case the anion-receptor and anion-ceramic filler interactions can be competitive. On the other hand, acidic groups on the ceramic filler surface and anions interact by means of Lewis acid-Lewis base or Brönsted acid-Brönsted base interactions [495]. Thus, the mechanism of the anion-ceramic filler interactions is very similar to these between "Lewis acid-type" anion receptors and different from the case of "hydrogen bond" ones. In consequence, surface-modified ceramic fillers and "hydrogen bond" anion receptors are applied in order to fulfill different roles in the electrolyte.

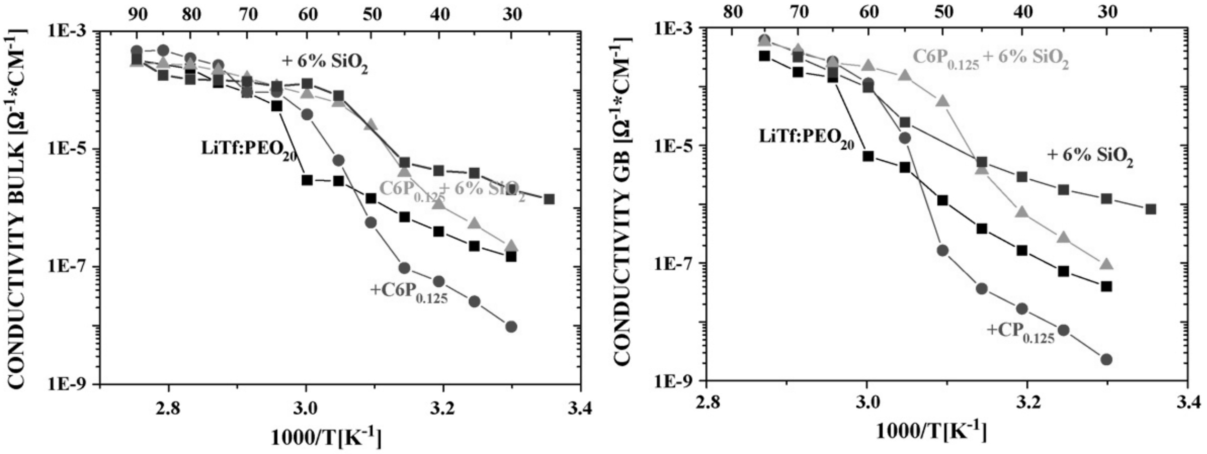

Figure 57. Arrhenius plots of ionic conductivity of $P(EO)_{20}(LiTf)_1$ polymer electrolytes with and without C6P and SiO_2 additives. After [489].

7.6 Application of the anion receptors in secondary lithium batteries.

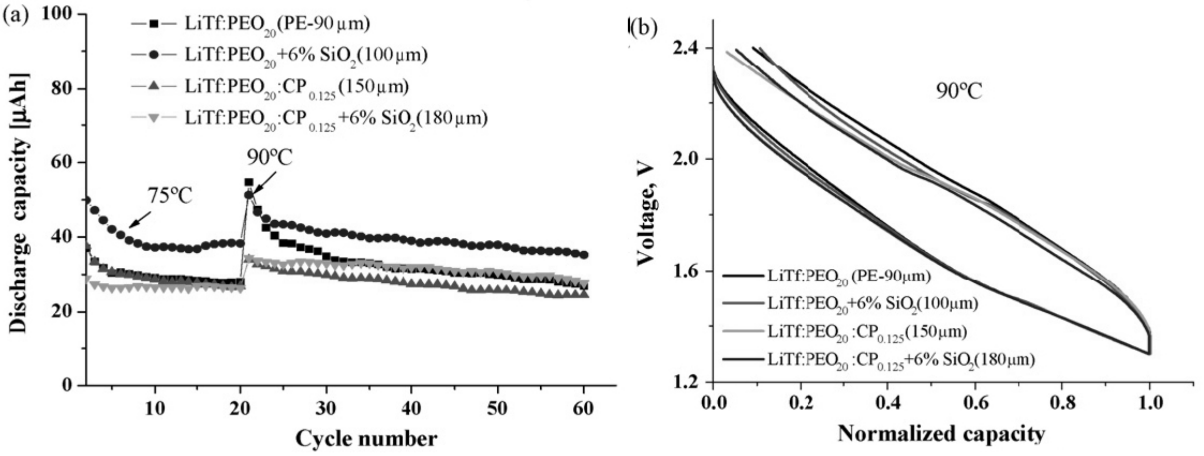

Figure 58. Cycle life (a) and normalized charge/discharge curves (b) of thin-film $Li|P(EO)_{20}(LiTf)_1C6P_N{:}SiO_2|MoO_XS_Y$ cells. After [489].

Studies on the charge-discharge cycling give the final argument for application of the polymeric electrolytes containing the anion receptor in the lithium secondary batteries. Golodnitsky studied the battery consisting of the “binary” composite electrolyte containing an anion receptor and ceramic filler, metal lithium anode and MoO_XS_Y cathode (Figure 58) [489]. The addition of the anion receptor to the ceramic filler-containing composite electrolyte resulted in the lowering of the discharge capacity but an enhancement in the stability of this parameter. Also ceramic filler-free PEO-$LiBF_4$-C6P systems, do not exhibit worse performance when compared with the PEO-$LiBF_4$ ones [480]. To sum up, we can conclude that “hydrogen bond” anion receptors can be successfully applied in the lithium batteries.

Chapter 8

Summary and conclusions

In this dissertation, elaborating of the electrolyte with increased cationic conductivity due to the addition of "hydrogen bond" anion receptors was presented. Three additives i.e. Cx2, Cxg and C6P, characterized by various affinities to anions and compatibility to polymeric matrix, were tested. The values of the lithium transference numbers measured by means of the polarization technique were higher for polymeric electrolytes containing anion receptors than for receptor-free ones. The same results were obtained when the lithium transference numbers were measured for PEO-$LiBF_4$ systems with and without anion receptors by means of PFG NMR. Moreover, the cationic conductivity of several systems containing the anion receptor was higher after the receptor addition. This very welcome result can have several explanations. The first one is that the receptor addition, due to forming of the complex with the anion, results in changes of the concentration of the ions and ionic agglomerates. The second is that the anion receptor can play the role of the plasticizer of the system (this was proved by the increase in the diffusion velocity of the polymeric chains after the receptor addition measured by means of PFG NMR).

In order to study the influence of the receptor on the properties of the membrane in the more detailed way, several experiments on the interactions between the anion receptor and electrically neutral molecules and anions were conducted. It was revealed that complex formation between the receptor and the solvent depends on the type of hydrogen bond donors present in the receptor, electron donor properties of the solvent as well as geometrical fitting between the host and guest. In general Cx2 (the calix[4]arene derivative with urea groups capable of interacting with anions in its structure) exhibited higher affinity to various solvent species and stronger tendency to self-association. On the other hand, it was possible to prove the presence of the anion-receptor complex and to estimate the formation of anion-receptor constant for system of coordinating properties very similar to PEO. For the C6P it was possible to show that addition of receptor result in changes of the spectrum of an anion (both by means of FTIR and NMR spectroscopy in the model system and by means of FTIR in PEO-LiTf-C6P SPE) and that the effect of the receptor addition depends on the cation used. Unfortunately, in opinion of the author, not all of the details of the mechanism of the changes in the properties of electrolyte after C6P addition, were not fully explained in this dissertation. As the PEO-based SPE is a heterogeneous system, the studies on the morphology of the electrolyte were performed. It was shown that the receptor distribution is different in each phase. Moreover, it can form additional phases due to precipitation from the electrolyte. It was demonstrated that the influence of the receptor is dependent not only on the receptor used but also on the salt present in the electrolyte.

Also a comparison between two receptors, characterized by identical coordination sphere (identical groups capable of interacting with anions and of identical geometric orientation) with and without oligo(oxyethylene) chains in their chemical structure was preformed. The receptor containing oligoether chains in its structure should be treated as the receptor of compatibility with the polymeric matrix better than previously studied ones rather than as a receptor "built" in the polymeric chain. It was due to the fact the mass of the calix[4]arene core and moieties in the narrow rim was comparable. The PEO-based SPE with the receptor containing oligoether chains exhibited conductivity significantly lower that a PEO-salt composite. It was also demonstrated that the properties of the electrolyte such as the activation energy of conductivity, microstructure (phase structure) and crystallinity are dependent on the compatibility between PEO matrix and the receptor.

The influence of the receptor on properties of electrolytes with a liquid oligoether matrix (PEODME) was tested in order to study the role of the state of matter of the matrix for systems containing an anion receptor. It was shown that in the liquid electrolyte the effects of the anion receptor addition are much weaker than in SPE. This can suggest that the simple models assuming full dissociation of the salt and the formation of the anion-receptor complexes, when applied to the polymeric system, are oversimplified not only because of the presence of the ionic agglomerates in the real system but also because of different mechanism of anion immobilization due to its complexation. The other explanation of this fact is that the receptor prefers to interact with the $-OCH_3$ end groups of the oligoether chains (which was confirmed for glymes and PEODME by means of FTIR). The concentration of such groups in PEODME is much higher than it is in the case of high M_W PEO.

Some scientists assumed that the "hydrogen bond-based" receptors cannot be applied in the electrolytes to the lithium batteries. This work demonstrates that adding of the "hydrogen bond-based" anion receptor in order to modify the ionic transport properties of SPEs dedicated for lithium batteries does not negatively influence the performance of the cell in which such electrolyte is tested. This conclusion comes both from polarization studies on lithium|electrolyte|lithium symmetrical cell as well as charge-discharge cycling of lithium|electrolyte|cathode battery. Also the CV tests of the solutions of receptors showed that they are resistant against oxidation or reduction.

Appendix A

The influence of Ionic Aggregates and Complex Formation Constants Values on Ionic Transport Properties of the Electrolyte

A.1 Introduction

The presence of the supramolecular additive results in changes of both concentrations of various charged species (i.e. “free” ions, ionic agglomerates and complexes containing receptor) and physicochemical properties of the electrolyte (ascribed, in the simplest approach, to the interactions between the receptor and the solvent as well as resulting from the above-mentioned changes in concentrations of various charged species)[10]. In this Appendix, the influence of the ionic agglomerate formation constant and anion receptor complex formation constant on conductivity and lithium transference number is presented. It was discussed in the main body of this work that the receptor addition results in an increase of the lithium transference number, and, in some cases, of conductivity. The exact evaluation of changes in the concentration of charged and electrically neutral species, when the values of complex and ionic agglomerates formation constants are given, was presented neither in this work nor in the literature [496]. It is mainly due to the fact that the changes of ion transport parameters are of complicated nature even if the system consists only of the salt and the matrix (liquid or polymeric). The addition of the anion receptor results in an increase in the number of the formation constants in the system and complicates the nature of the changes of conductivity and lithium transference number.

In a system containing anion receptor, the concentration of the particular specimen depends on:

- the formation of the complexes containing receptor as well as ionic agglomerates both in the sense of Law of Mass Action and Debye-Hückel limiting law,
- constitution (in the case of polymeric electrolyte local constitution) of the system.

The diffusion of the specimen in the liquid electrolyte depends (at least) on:

- interactions between the specimen and the solvent (coordination sphere formation).
- viscosity of the system.

In the Solid Polymer Electrolyte, the diffusion of the specimen in the particular phase depends (at least) on:

- strength of the interaction between the polymer and the specimen (both formation of the coordination sphere of the specimen and immobilization of the ion should be taken into consideration).
- dynamics of the polymeric chains segmental motions, depending mainly on

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[10] As in the main part of the dissertation a “material science” or “practical” approach was used and this part of the work describes mainly a “modeling” approach, it was decided to present this material as an Appendix to the main part of the disertation.

- local crystallinity of the system and local density of the defects in the crystallite, and
- the density of physical and chemical cross-linking between one or more polymeric chains.

When more complicated systems comprising not only the salt and the matrix but also other additives forming homogenous systems (e.g. plasticizers, anion receptors and others) are analyzed, the number of possible interactions between various species present in the system is huge. The case is similar or even more complicated when additives forming heterogenous systems, such as ceramic fillers, are researched. Hence, it is impossible to conduct a “total” analysis - parallel analysis of all the phenomena responsible for conductivity changes in the analyzed system.

Being aware of all limitations of this analysis (coming from all the previously mentioned facts), some simple simulations which entail the Law of Mass Action and omit other parameters responsible for conductivity changes were conducted. The simulations were conducted for arbitrary values of the conductivity of each specimen and arbitrary formation constants. An attempt was made to study the role of the anion receptor in the changes of lithium transport number and conductivity using these simple models. It is worth stressing that even in this simple case the equations applied in them are quite complicated.

A.2 The methods of calculation of the ionic transport parameters for given association constant values in receptor-free systems.

The method used is based on indirect calculations of the salt concentration, conductivity and lithium transference number. The following parameters should be given:

$$\lambda_{K^+}, \lambda_{A^-}, \lambda_{KA_2^-}, \lambda_{K_2A^+}, K_{KA}, K_{K_2A^+}, K_{KA_2^-}, [A^-]$$

The first four parameters are molar conductivity of cations, anions, negative and positive triplets, respectively. The next three are the formation constants of the ionic pair, positively charged ionic triplets and negatively charged ionic triplets, respectively. The last one is the concentration of “free” anions (when the concentration of “free” anion is taken instead of salt concentration, the equations are much simpler). The concentrations of ionic agglomerates can, in this case, be given in the following equations:

$$[K^+] = \frac{[A^-]^2 K_{KA} K_{KA_2^-} + \sqrt{(1-[A^-]^2 K_{KA} K_{KA_2^-})^2 + 4[A^-]^2 K_{KA} K_{K_2A^+}} - 1}{2[A^-] K_{KA} K_{K_2A^+}}$$

$$[KA] = K_{KA}[K^+][A^-], [K_2A^+] = K_{K_2A^+}[KA][K^+], [KA_2^-] = K_{KA_2^-}[KA][A^-]$$

With these values obtained, one can calculate salt concentration, conductivity of the lithium cation, and lithium transference number according to equations:

$$c_{salt} = [A^-] + [KA] + [K_2A^+] + 2[KA_2^-], \sigma_{Li} = \lambda_{K^+}[K^+] + \lambda_{K_2A^+}[K_2A^+],$$
$$\sigma = \sigma_{Li} + \lambda_{A^-}[A^-] + \lambda_{KA_2^-}[KA_2^-], t_{Li} = \sigma_{Li}\sigma^{-1}$$

A.3 The method of calculation of the ionic transport parameters for given association constant values in the systems containing receptor.

The presented system is more complicated than the one described previously. In general, the parameters mentioned below should be given:

$$\lambda_{K^+}, \lambda_{A^-}, \lambda_{KA_2^-}, \lambda_{K_2A^+}, \lambda_{[AR]^-}, K_{KA}, K_{K_2A^+}, K_{KA_2^-}, K_{[AR]^-}, K_{[KAR]}, [A^-], c_R$$

The additional parameters here (in comparison with receptor-free system) are: molar conductivity of the anion-receptor complex $\lambda_{[AR]-}$, anion-receptor formation constant $K_{[AR]-}$, ionic pair-receptor formation constant $K_{[KAR]}$ and receptor concentration c_R. As in this case 12 independent values should be given, it was decided to analyze only some particular but representative systems.

The equations from which conductivity and lithium transference numbers for given values of the association constant, salt and receptor concentrations can be calculated are presented in Table 26. When we analyze salt concentration-conductivity and salt concentration-lithium transference number dependencies, two main assumptions should be made. One is which species are present in the system whereas the other describes the dependency of salt concentration on receptor concentration.

This analysis began from the effect of parallel anion-receptor complex formation and cation-anion pairing. Then, the influence of the additional phenomenon such as formation of ionic triplets or receptor-ionic pair complexes were taken into consideration. It was also assumed that receptor concentration is either constant or is proportional to salt concentration.

Species present in the system	Additional assumptions	Equations valid
K^+, A^-, KA, $[AR]^-$	c_R=const.	$c_{salt} = [A^-](1+K_{KA}[A^-])(1+c_R K_{[AR]^-}/(1+[A^-]K_{[AR]^-})), [K^+] = c_{salt}/(1+K_{KA}[A^-]),$ $[KA] = K_{KA}[K^+][A^-], [R] = c_R/(1+K_{[AR]^-}[A^-]), [AR^-] = K_{[AR]^-}[R][A^-]$ $\sigma_{Li} = \lambda_{K^+}[K^+], \sigma = \sigma_{Li} + \lambda_{A^-}[A^-] + \lambda_{[AR]^-}[AR^-], t_{Li} = \sigma_{Li}\sigma^{-1}$
K^+, A^-, KA, $[AR]^-$	r=c_{salt}/c_R= =const.	$[R] = ((-[A^-]/r)(1+[A^-]K_{KA}))/(([A^-]K_{[AR]^-}/r)(1+[A^-]K_{KA}) - (1+[A^-]K_{[AR]^-})),$ $[AR^-] = K_{[AR]^-}[R][A^-], [K^+] = [AR^-] + [A^-], [KA] = K_{KA}[K^+][A^-]$ $c_{salt} = rc_R = [K^+] + [KA], \sigma_{Li} = \lambda_{K^+}[K^+], \sigma = \sigma_{Li} + \lambda_{A^-}[A^-] + \lambda_{[AR]^-}[AR^-], t_{Li} = \sigma_{Li}\sigma^{-1}$
K^+, A^-, [KAR],KA, $[AR]^-$	c_R=const.	$[R] = \frac{-([A^-]^2 K_{KA}K_{[KAR]} + K_{[AR]^-}[A^-]+1) + \sqrt{(([A^-]^2 K_{KA}K_{[KAR]} + K_{[AR]^-}[A^-]+1)^2 + 4[A^-]^2 K_{KA}K_{[AR]^-}K_{[KAR]}c_R}}{2K_{KA}K_{[AR]^-}K_{[KAR]}[A^-]^2},$ $[AR^-] = K_{[AR]^-}[R][A^-], [K^+] = [AR^-] + [A^-], [KA] = K_{KA}[A^-][K^+], [KAR] = K_{[KAR]}[KA][R]$ $c_{salt} = [K^+] + [KA] + [KAR], \sigma_{Li} = \lambda_{K^+}[K^+], \sigma = \sigma_{Li} + \lambda_{A^-}[A^-] + \lambda_{[AR]^-}[AR^-], t_{Li} = \sigma_{Li}\sigma^{-1}$
K^+, A^-, [KAR],KA, $[AR]^-$	$c_{salt}=c_R$	$[R] = -\frac{1+K_{[AR]^-}[A^-] - K_{[AR]^-}[A^-](1+K_{KA}[A^-])}{[A^-](1+K_{KA}[A^-])}$ $[AR^-] = K_{[AR]^-}[R][A^-], [K^+] = [AR^-] + [A^-], [KA] = K_{KA}[A^-][K^+], [KAR] = K_{[KAR]}[KA][R]$ $c_{salt} = [K^+] + [KA] + [KAR], \sigma_{Li} = \lambda_{K^+}[K^+], \sigma = \sigma_{Li} + \lambda_{A^-}[A^-] + \lambda_{[AR]^-}[AR^-], t_{Li} = \sigma_{Li}\sigma^{-1}$
K^+, A^-, [KAR],KA, $[AR]^-$	r=c_{salt}/c_R= =const. $r \neq 1$	$[R] = r\frac{1+K_{[AR]^-}[A^-] - rK_{[AR]^-}[A^-](1+K_{KA}[A^-]) - K_{KA}K_{[KAR]}[A^-]^2(1-r)/r - \sqrt{\Delta}}{2(1-r)K_{KA}K_{[AR]^-}K_{[KAR]}[A^-]^2},$ $\Delta = (1+K_{[AR]^-}[A^-] - rK_{[AR]^-}[A^-](1+K_{KA}[A^-]) - K_{KA}K_{[KAR]}[A^-]^2(1-r)/r)^2 +$ $+ 4(r-1)(1+[A^-]K_{KA})K_{KA}K_{[AR]^-}K_{[KAR]}[A^-]^3/r^2$ $[AR^-] = K_{[AR]^-}[R][A^-], [K^+] = [AR^-] + [A^-], [KA] = K_{KA}[A^-][K^+], [KAR] = K_{[KAR]}[KA][R]$ $c_{salt} = [K^+] + [KA] + [KAR], \sigma_{Li} = \lambda_{K^+}[K^+], \sigma = \sigma_{Li} + \lambda_{A^-}[A^-] + \lambda_{[AR]^-}[AR^-], t_{Li} = \sigma_{Li}\sigma^{-1}$
A^-, KA, K^+, KA_2^-, K_2A^+, $[AR]^-$	c_R=const.	$[K^+] = \frac{-1 - K_{KA_2^-}K_{KA}[A^-]^2 + \sqrt{(1+K_{KA_2^-}K_{KA}[A^-]^2)^2 + 4K_{K_2A^+}K_{KA}[A^-]^2(1+K_{[AR]^-}c_R/(1+K_{[AR]^-}[A^-]^2))}}{2K_{K_2A^+}K_{KA}[A^-]},$ $[KA] = K_{KA}[K^+][A^-], [KA_2^-] = K_{KA_2^-}[KA][A^-], [K_2A^+] = K_{K_2A^+}[KA][K^+],$ $[AR^-] = [K^+] + [K_2A^+] - [A^-] - [KA_2^-], [R] = [AR^-]/(K_{[AR]^-}[A^-])$ $c_{salt} = [K^+] + [KA] + 2[K_2A^+] + [KA_2^-], \sigma_{Li} = \lambda_{K^+}[K^+] + \lambda_{K_2A^+}[K_2A^+],$ $\sigma = \sigma_{Li} + \lambda_{A^-}[A^-] + \lambda_{KA_2^-}[KA_2^-] + \lambda_{[AR]^-}[AR^-], t_{Li} = \sigma_{Li}\sigma^{-1}$

Table 26. The equations needed to caluclate ionic conductivity and lithium transference number for the given ionic agglomerates formation constants, salt concentration and receptor concentration.

A^-, KA, K^+, KA_2^-, K_2A^+, $[AR]^-$	$r=c_{salt}/c_R=$ =const.	$[K^+]$ is positive solution of the equation $G[K^+]^2+H[K^+]+I=0$, where: $G=2\frac{K_{[AR]^-}K_{K_2A^+}K_{KA}[A^-]^2}{r(1+K_{[AR]^-}[A^-])}-K_{K_2A^+}K_{KA}[A^-]$, $H=\frac{K_{[AR]^-}[A^-]}{r(1+K_{[AR]^-}[A^-])}(1+K_{KA}[A^-]+K_{KA_2^-}K_{KA}[A^-]^2)+K_{KA_2^-}K_{KA}[A^-]^2-1, I=[A^-]$ $[KA]=K_{KA}[K^+][A^-],[KA_2^-]=K_{KA_2^-}[KA][A^-],[K_2A^+]=K_{K_2A^+}[KA][K^+]$, $[AR^-]=[K^+]+[K_2A^+]-[A^-]-[KA_2^-],[R]=[AR^-]/(K_{[AR]^-}[A^-])$ $c_{salt}=[K^+]+[KA]+2[K_2A^+]+[KA_2^-],\sigma_{Li}=\lambda_{K^+}[K^+]+\lambda_{K_2A^+}[K_2A^+]$, $\sigma=\sigma_{Li}+\lambda_{A^-}[A^-]+\lambda_{KA_2^-}[KA_2^-]+\lambda_{[AR]^-}[AR^-],t_{Li}=\sigma_{Li}\sigma^{-1}$

Table 26 (continued)

A.4 The role of ionic pairs and ionic triplet formation constant in the changes of ionic conductivity and lithium cation transport number.

In the first - simple and widely studied example, the assumption is that only “free” ions and ionic pairs are present in the system analyzed (Figure 59). For low values of the product of the salt concentration and ionic pairs association constant, the Kohlrausch equation is fulfilled. For the relatively high values of this product ($K_a c_{salt}$>400), conductivity is proportional to the square root of salt concentration. The lithium transference number does not, in this case, depend on both salt concentration and K_{KA} and is equal to the ratio between cationic and the sum of the anionic and cationic molar conductivities ($t_{Li+}=\lambda_{Li+}/(\lambda_{Li+}+\lambda_{A-})$).

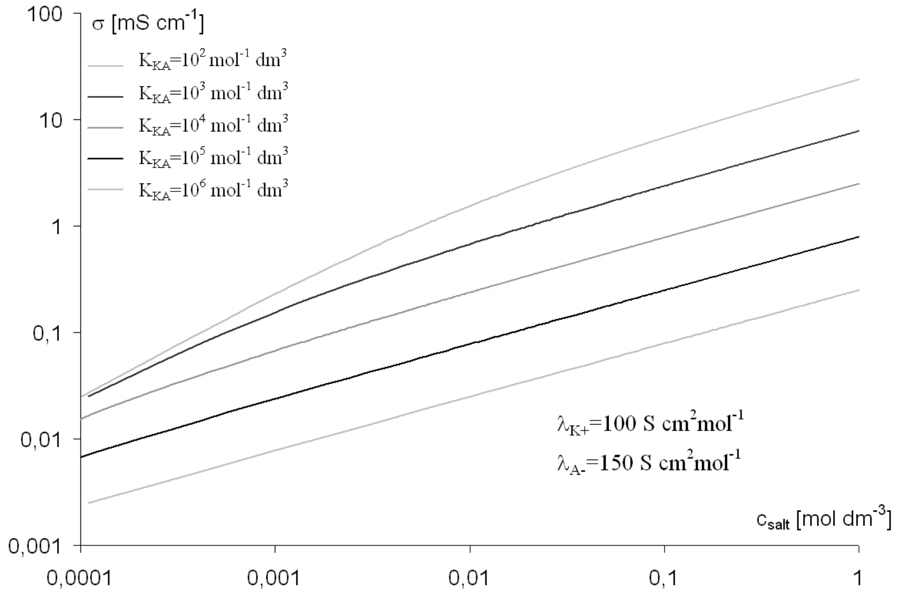

Figure 59. Dependency of salt concentration and ionic pair formation constant on ionic conductivity.

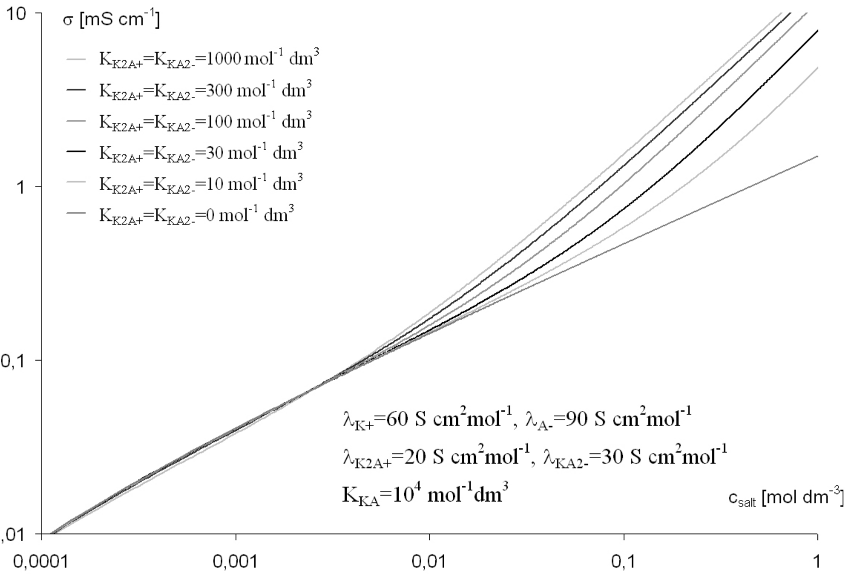

Figure 60. Dependency of salt concentration and ionic triplet formation constant on ionic conductivity. The ionic pairs formation constant equal 10^4 mol^{-1}dm^3.

The situation changes when not only ionic pairs but also ionic triplets are present in the system analyzed. Figure 60 presents such a situation. In this case, it was assumed that values of the formation constant of the positively and negatively charged ionic triplets are identical [497]. Hence, the lithium transport number does not depend on salt concentration but only on the ratio between molar conductivity of positively charged species to the sum of the molar conductivity of the salt ($t_{Li+}=\lambda_{Li+}/(\lambda_{Li+}+\lambda_{A-})$ for electrolytes with very low salt concentration, $t_{Li+}=\lambda_{Li2A+}/(\lambda_{Li2A+}+\lambda_{LiA2-})$ for electrolytes with high salt concentration)[11]. It is interesting that in salt concentrations higher than 0.01 mol dm^{-3} (in case of $K_{KA}=10^4$ mol^{-1}dm^3) the presence of the ionic triplets influences conductivity even in the case of low triplet formation constants. The next analysis is valid for a system in which the same ionic aggregates (“free” ions, ionic pairs and ionic triplets) are present. In this case, however, it was assumed that value of the KA_2^- and K_2A^+ formation constants are different. In such a system, changes both in conductivity and the lithium transference number can be observed. When the constant of the K_2A^+ formation is lower than that of KA_2^-, the lithium transference number is higher than the $\lambda_{Li+}/(\lambda_{Li+}+\lambda_{A-})$ and $\lambda_{Li2A+}/(\lambda_{Li2A+}+\lambda_{LiA2-})$ (Figure 61) and *vice versa*.

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[11] It is usually assumed that $\lambda_{Li+}/(\lambda_{Li+}+\lambda_{A-})=\lambda_{Li2A+}/(\lambda_{Li2A+}+\lambda_{LiA2-})$ as the estimation of the λ_{Li2A+} and λ_{LiA2-} from experimental data is practically impossible.

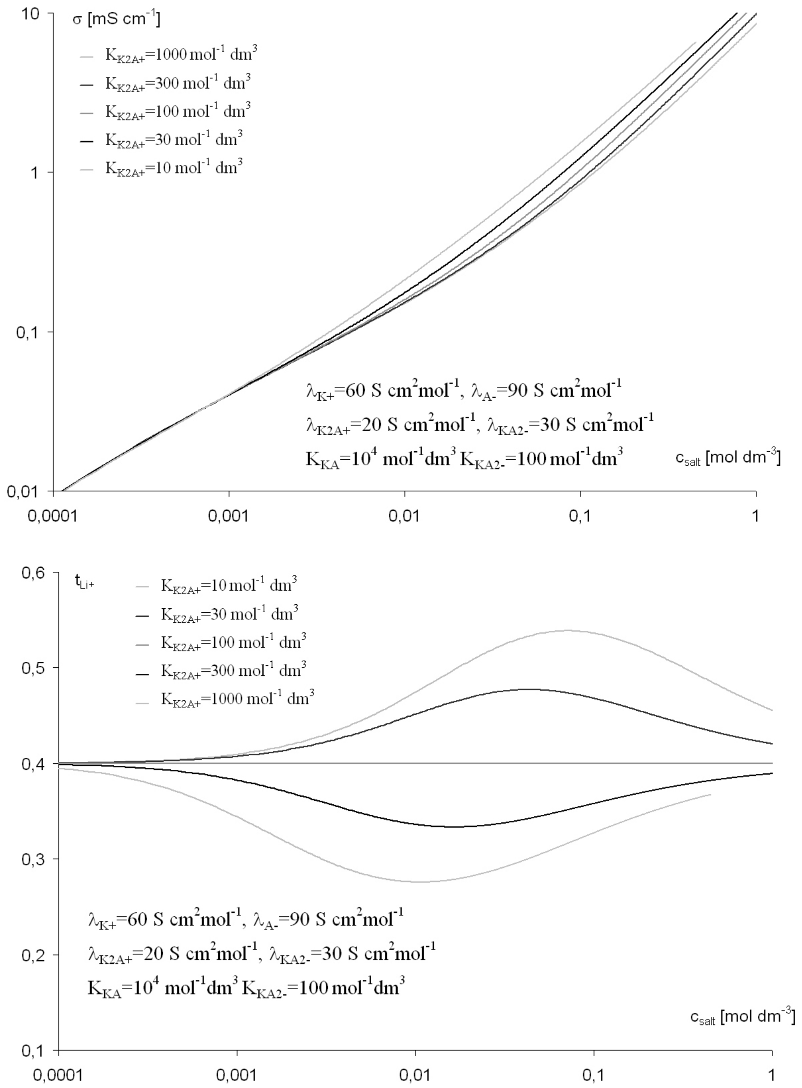

Figure 61. Dependency of the salt concentration and K_2A^+ triplets formation constant on the ionic conductivity and lithium transference number. The ionic pair formation constant 10^4 mol^{-1}dm^3, KA_2^- formation constant 10^2 mol^{-1}dm^3.

It is due to fact that $[K^+]+[K_2A^+]=[A^-]+[KA_2^-]$ and when $K_{K2A+}<K_{KA2-}$ the ratio between K^+ and KA_2^+ is higher than that between A^- and KA_2^-. Consequently, as it was assumed that $\lambda_{Li+}>\lambda_{Li2A+}$ and $\lambda_{A-}>\lambda_{LiA2-}$ t_{Li+} is higher than $\lambda_{Li+}/(\lambda_{Li+}+\lambda_{A-})$, the lithium transference number is higher when the ratio between constant of the K_2A^+ formation is lower than that of KA_2^-. The same way of reasoning can explain why the maximum exists. Indeed, when salt concentration is very low (in the analyzed case, below 0.001 mol dm^{-3}), practically only “free” ions and ionic pairs are present in the system, and, consequently, $t_{Li}\approx\lambda_{Li+}/(\lambda_{Li+}+\lambda_{A-})$. For highly concentrated salt solutions (salt concentration over 1 mol dm^{-3}), most of the charged species are ionic triplets and $t_{Li}\approx\lambda_{Li2A+}/(\lambda_{Li2A+}+\lambda_{LiA2-})$. In the moderate salt concentration, both “free” anions and ionic triplets have some influence on the ionic transport.

The same arguments are valid for the explanation of the $\sigma=f(c_{salt})$ dependency which is very similar to the system in which $K_{K2A+}=K_{KA2-}$.

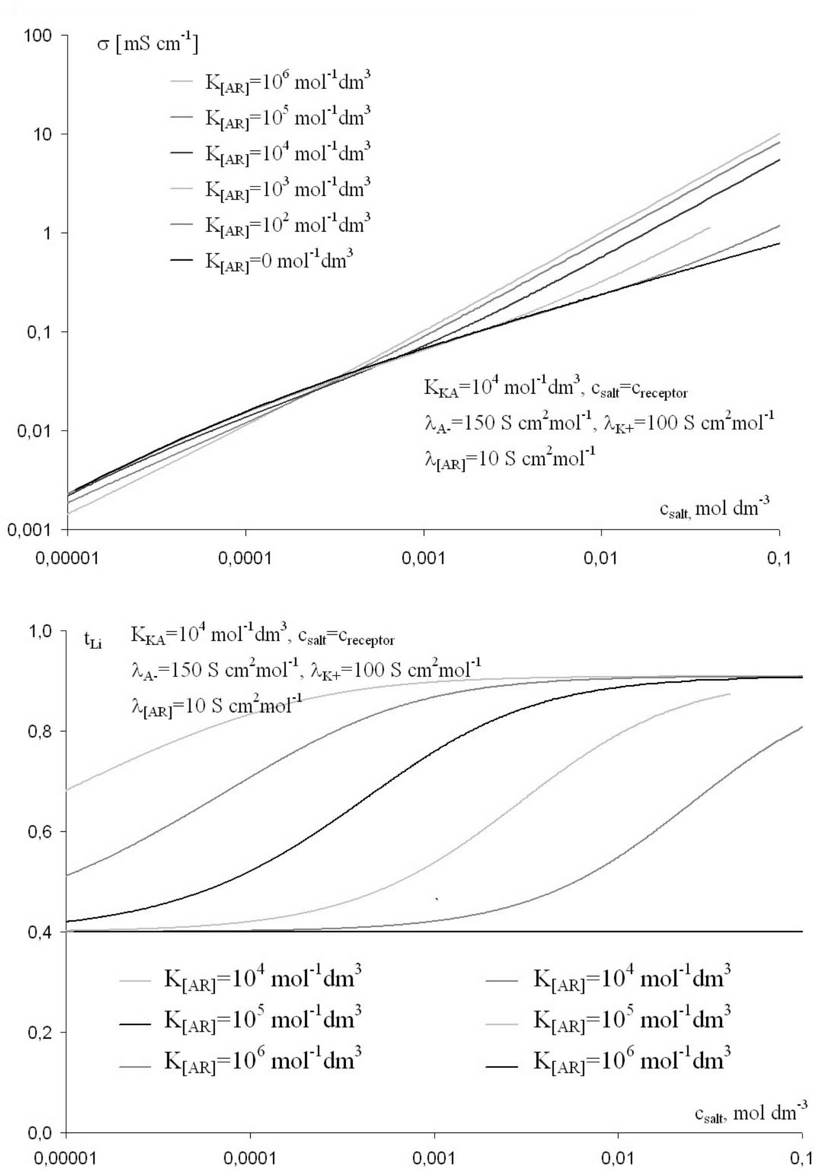

Figure 62. Dependency of the salt concentration and anion-receptor complex formation constant on the ionic conductivity and lithium transference number. The ionic pairs formation constant 10^4 mol^{-1}dm^3, $c_{salt}=c_{receptor}$.

A.5 How the addition of the anion receptor can change lithium transport number and ionic conductivity.

The relatively simple situation of a system in which the only ionic aggregates are ionic pairs can become complicated when a system consisting of matrix, salt and anion receptor is analyzed (in this case, an additional anion-receptor formation constant should be taken into consideration). As the formation of anion-receptor complexes reduces the concentration of the "free" anions due to the formation of the anion-receptor complex, it changes the values of the lithium transport number and ionic conductivity. Figure 62 presents how the addition of the anion receptor can change these parameters, when we assume that only “free” ions, “free” receptor molecules, ionic pairs and anion-receptor complexes are present in the system, and receptor and salt concentrations are equal.

Analyzing this case, one can observe some easy-to-predict tendencies. For high enough salt concentrations, the majority of ion containing species comprise “free” cations, anion-receptor complexes and ionic pairs (the conductivity of “free” anions can be neglected due to fact that $x_{A-} << x_{K+}$, thus $\sigma_{A-} << \sigma_{K+}$). Thus, the lithium transport number tends to the following ratio: $t_{Li+} = \lambda_{Li+}/(\lambda_{Li+} + \lambda_{[AR]-})$.

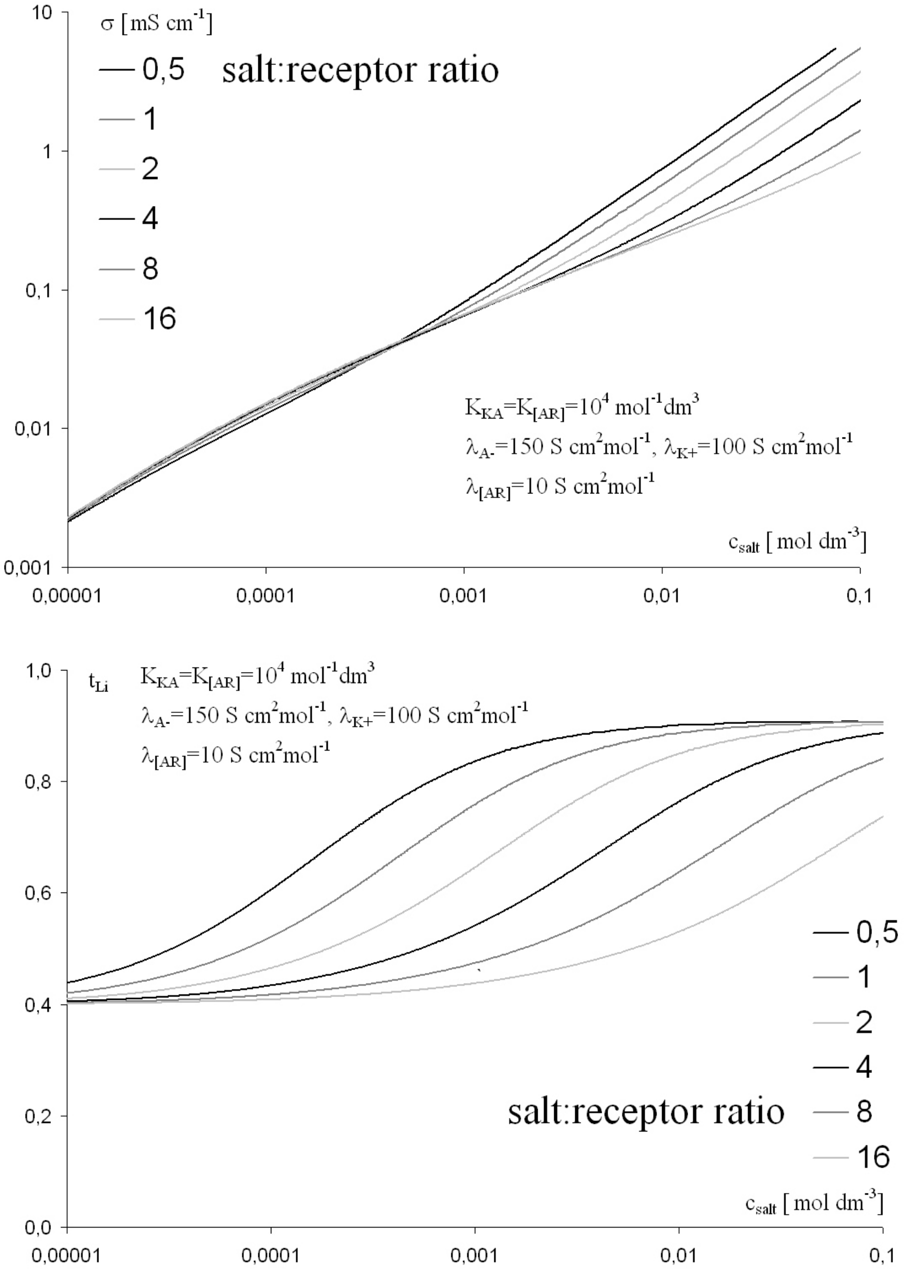

Figure 63. Dependency of salt concentration and the c_{salt}:$c_{receptor}$ ratio on ionic conductivity and the lithium transference number. The ionic pair formation and anion-receptor complex formation constants equal to 10^4 mol^{-1}dm^3.

In the systems in which association constants and salt concentration are low enough, the main species observed are "free" anions and "free" cations. Thus, the lithium transference number in this case is almost equal $t_{Li+}=\lambda_{Li+}/(\lambda_{Li+}+\lambda_{A-})$. The conductivity in this case is also linearly dependent on salt concentration as various agglomerates do not exist in the system.

Also in the case of highly concentrated systems is that conductivity is linearly dependent on the salt concentration. This can be also explained:

$$[KA]=K_{KA}[A^-][K^+]\approx K_{KA}[A^-][AR^-],[KA]/[AR^-]\approx K_{KA}[A^-]$$

The first of the equations comes from the Law of Mass Action. The second is the result of the previously mentioned assumption and its simple consequence: $[K^+]=[A^-]+[AR^-]\approx[AR^-]$. When the last equation is taken into account, it is, however, not obvious, that the right-hand side of the equation is constant when the salt concentration changes. The simplest explanation is that the concentration of the "free" anions is constant when salt concentration is high enough (the detailed receipt is quite complicated and cannot be presented here).

In the all cases presented here also systems of "intermediate" salt concentration area can be observed (the term "moderate" depends in this case on the values of the ionic pair and anion-receptor complex formation constants). In this case, one can observe that the lithium transference number in this area is between the values in the previously analyzed cases:

$$\lambda_{Li+}/(\lambda_{Li+}+\lambda_{KA})<t_{Li+}<\lambda_{Li+}/(\lambda_{Li+}+\lambda_{[AR]-})$$

The dependency of salt concentration on conductivity in this salt concentration range is strongly dependent on the ratio between the constant formation of the complex and the ionic pair. When this ratio is relatively low, the changes in the ion transport properties of the system resulting from the receptor addition can be observed only when the salt concentration in the system is relatively high.

The dependency of the ratio between salt and receptor concentration is presented in Figure 63. Even when the salt concentration: receptor concentration ratio is very high (e.g. 16:1), the effect of lithium transference number enhancement can be observed. This slightly confusing effect, observed for systems of high salt concentration, can be explained as follows. When this ratio is very high, $[KA]>>[A^-]$. Thus, the concentration of $[AR]^-$ can be higher than A^- even when the salt concentration is much higher than the receptor concentration[12].

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[12] In this and all previously analyzed systems, we assumed that i) no ion transport is conducted and ii) diffusion coefficients are independent of salt and receptor concentration (which is not the case in the real system due to physical cross-linking of the polymeric electrolyte or to a viscosity increase in the case of the liquid system).

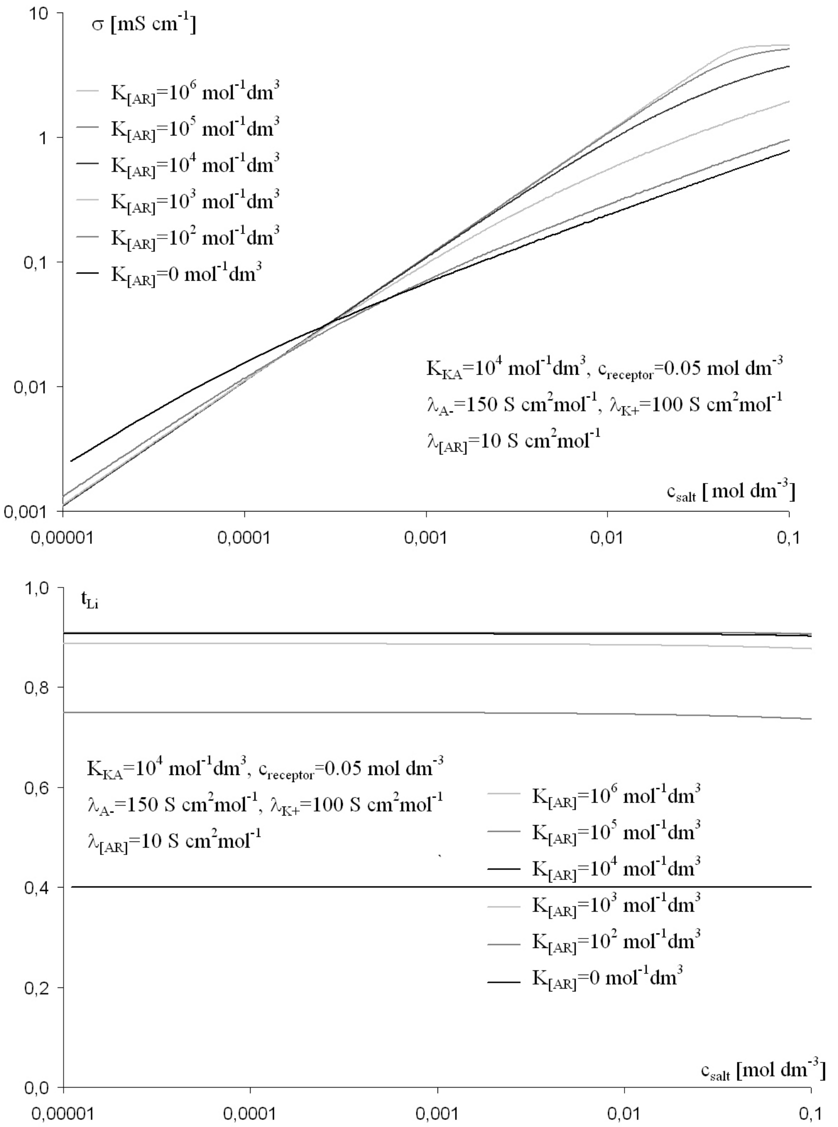

Figure 64. Dependency of the salt concentration and anion-receptor formation constant on the ionic conductivity and lithium transference number. The ionic pairs formation constant equal 10^4 mol^{-1}dm^3, salt concentration equal 0.05 mol dm^{-3}.

The last case analyzed with the same set of species is when the receptor concentration is fixed (Figure 64). As one can easily see, in this case the lithium transference number is practically independent of the salt concentration, at least for the given receptor concentration and in the salt concentration range analyzed. When salt concentration and complex formation constant are high enough, conductivity is also independent of salt concentration.

Next, a more complicated but also more similar to the real situation system will be studied. In the analyzed system we assume that not only “free” ions, ionic pairs, and anion-receptor complexes but also positively and negatively charged ionic triplets K_2A^+ and KA_2^- are present in the system[13].

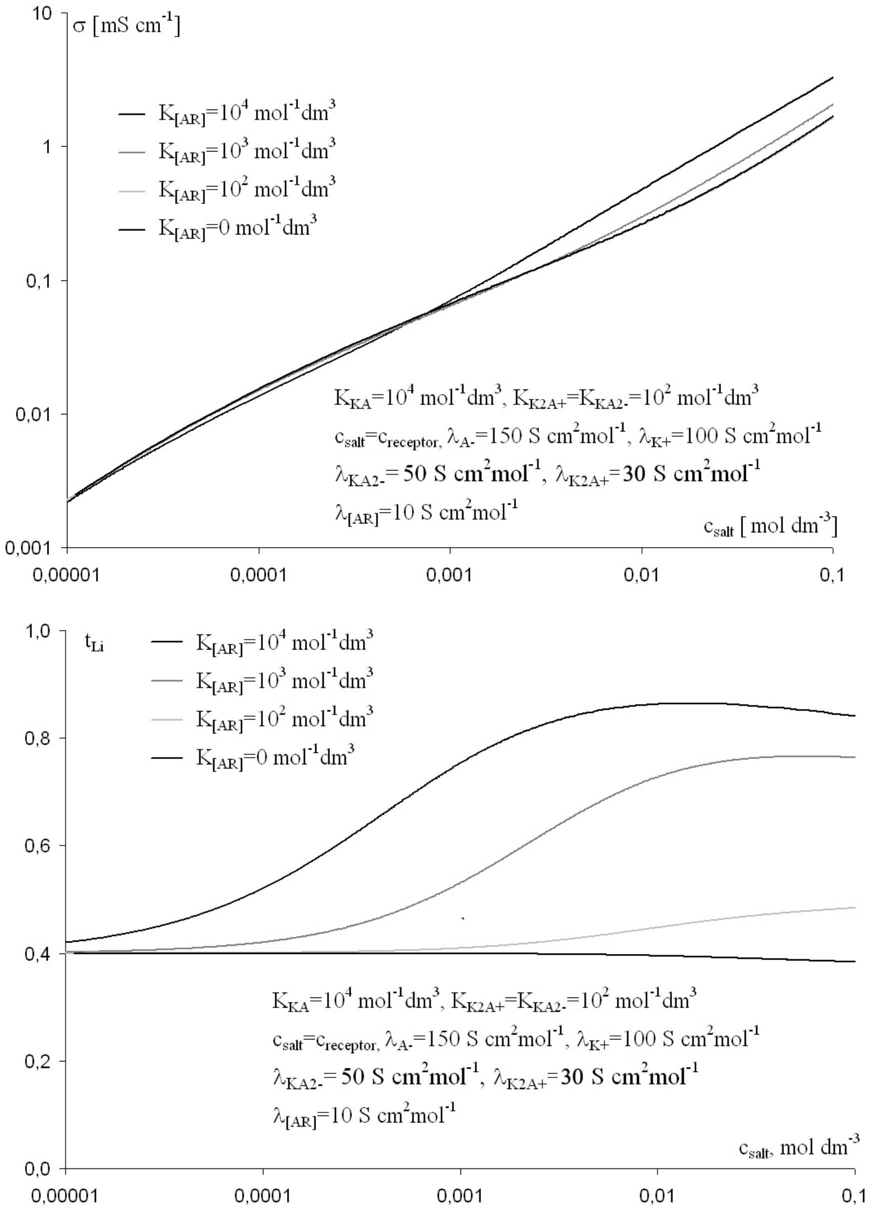

Figure 65. Dependency of salt concentration and the anion-receptor formation constant on ionic conductivity and lithium transference number. The ionic pairs formation constant equal to 10^4 mol^{-1}dm^3, salt concentration equal to 0.05 mol dm^{-3}.

When we consider a situation, in which salt and receptor concentrations are equal, the effect is, naturally, dependent on the ratio between the association constants (Figure 65). Contrary to

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[13] The lithium transference number tendencies described here, when no ion transport takes place, are also valid in the system in which ionic quadruplets K_2A_2 are also present. The only difference is that tendencies observed here are in the system in which quadruplets exist for higher salt concentrations. It is due to fact that electrically neutral species have no influence on the ratio between the „free” cations and the anions as well as on the ratios between positively and negatively charged species.

other previously studied systems containing receptor, the lithium transference number does not grow monotonically with the salt concentration increase. This can be easily explained by the fact that when the salt concentration is high enough, the majority of species present in the system are positively charged triplets and anion-receptor complexes. For the moderate salt concentrations, the effect of the anion receptor on lithium transference number is the strongest. It is due to fact that in this particular range of salt concentration all the charged species in the system i.e. “free” ions, ionic triplets and anion-receptor complexes have some impact on conductivity and the cation transference number. For high salt concentrations, when the anion-receptor formation constant is high enough, slight lowering of the lithium transference number is easy to explain. As it was assumed that the molar conductivity of ionic triplets is about three times lower than in the case of cations, the lithium transference number in systems with very high salt concentration tends to $\lambda_{Li2A+}/(\lambda_{Li2A+}+\lambda_{[AR]-})$ which is lower than $\lambda_{Li+}/(\lambda_{Li+}+\lambda_{[AR]-})$ - the value observed when the ionic triplets concentration is low enough to have no significant influence on conductivity.

Similarly to other previously analyzed systems, when the anion-receptor formation constant rises, the enhancement of ionic conductivity and lithium transference number is observed.

Figure 66 presents a system in which the same ion-containing species as in the former case are present. In this case, however, the anion-receptor complex formation constant was fixed and the influence of the ratio between salt concentration and receptor concentration on the equilibriums present in the system studied was analyzed. When the ratio is not lower than 4, anion the addition of the receptor results in a high lithium transference number enhancement. When this ratio is equal to 8 or 16, the lithium transference number increase is small. What is also worth noting, very similar results were obtained when the changes of conductivity resulting from the receptor addition were analyzed.

When we analyze the case in which the same species are present but the receptor concentration is constant (Figure 67), we can see that contrary to the situations previously described, conductivity does not increase monotonically with the growing salt concentration. It is due to fact that for the high salt concentration not only the fraction of the lithium cations but also the concentration of the lithium cations is lowered and the sum of concentrations of “free” cations and KA_2^+ agglomerates is nearly constant.

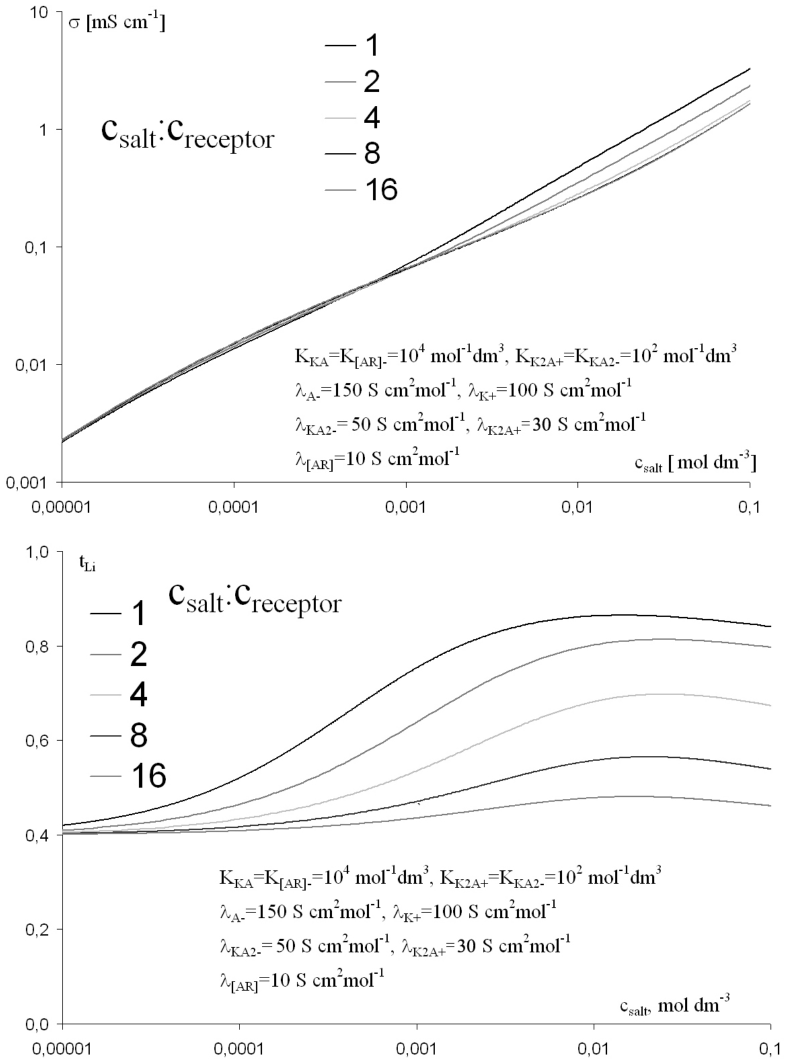

Figure 66. Dependency of salt concentration and the salt concentration: receptor concentration ratio on ionic conductivity and the lithium transference number. The ionic pair formation and anion-receptor complex formation constants equal to 10^4 mol^{-1}dm^3, ionic triplet formation constant equal to 10^2 mol^{-1}dm^3.

The tendencies observed for lithium transference number are rather easy to explain. The lithium transference number falls monotonically with the lowering of the anion-receptor formation constant and with raising salt concentration. The previously observed effect of the lithium transference number lowering with increase of the salt concentration in the system in which receptor concentration was constant and ionic triplets did not exist was in this case stronger due to fact that an additional effect related to the formation of the ionic triplets cationic triplets.

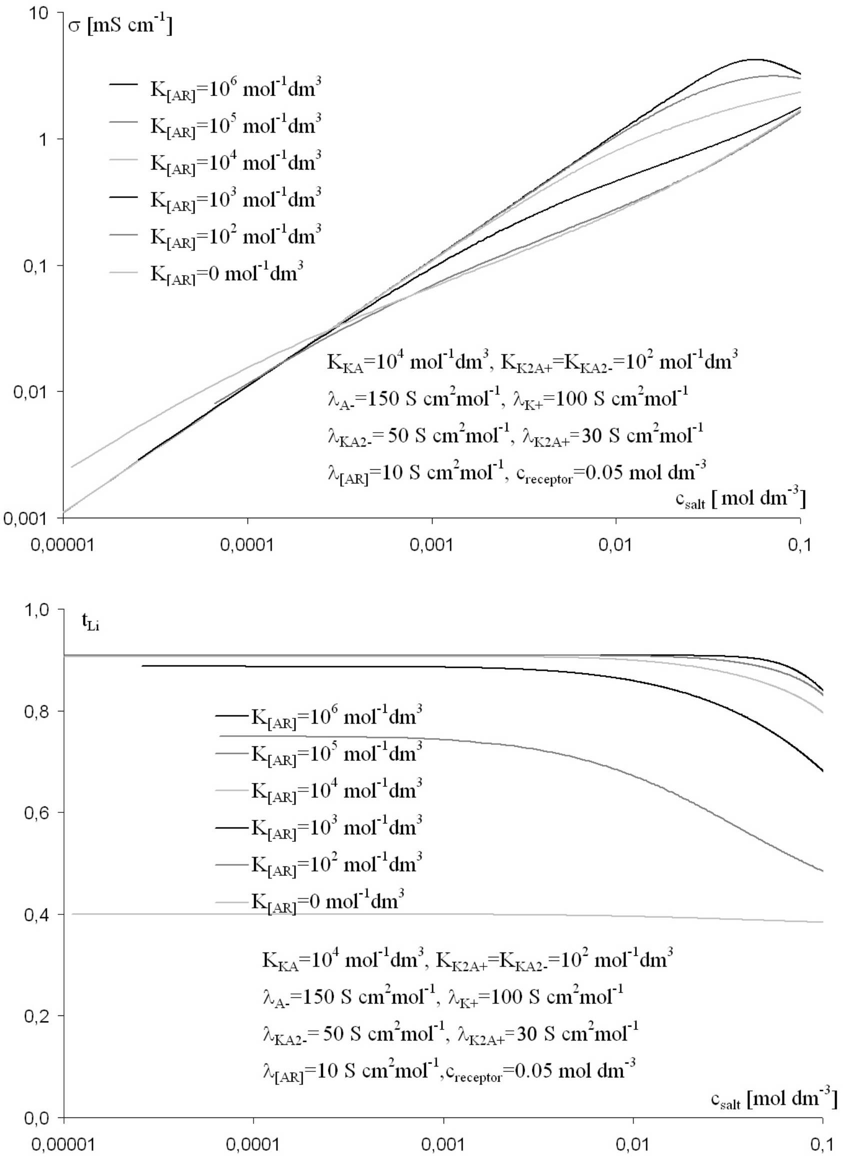

Figure 67. Dependency of salt concentration and the anion-receptor complex formation constant on ionic conductivity and the lithium transference number. The ionic pairs formation and anion-receptor complex formation constants equal to 10^4 mol^{-1}dm^3, ionic triplets formation constant equal to 10^2 mol^{-1}dm^3.

The last situation described in this part of the Appendix bases on the fact that the anion receptor is selective not only on anions but can also binds ionic pairs. To simplify such analysis, it was assumed that ionic triplets are not present in the system analyzed. In the first analyzed case, it was assumed that i) the salt and receptor concentrations are equal; ii) the ratio between the anion-receptor formation constant and ionic pair-receptor formation constant is 2:1 (this ratio is similar as measured in [498]). The results of this analysis are presented in Figure 68. In this case, the addition of the anion receptor results in lowering conductivity. It is mainly due to fact that the fraction of ionic pair-receptor complexes are some orders of magnitude higher than any other specimen present in the system. In consequence, the amount of charged species is lower than in the receptor-free system. The tendencies observed for the lithium transference numbers are very similar to those in the systems in which the receptor is not selective on ionic pairs. However, the processes observed when the receptor is selective on ionic pairs take place for higher salt concentrations than in situation in which the receptor is selective only on anions. This is due to the fact that the receptor-ionic pair complex does not transport any current and does not influence the proportion between positively and negatively charged species.

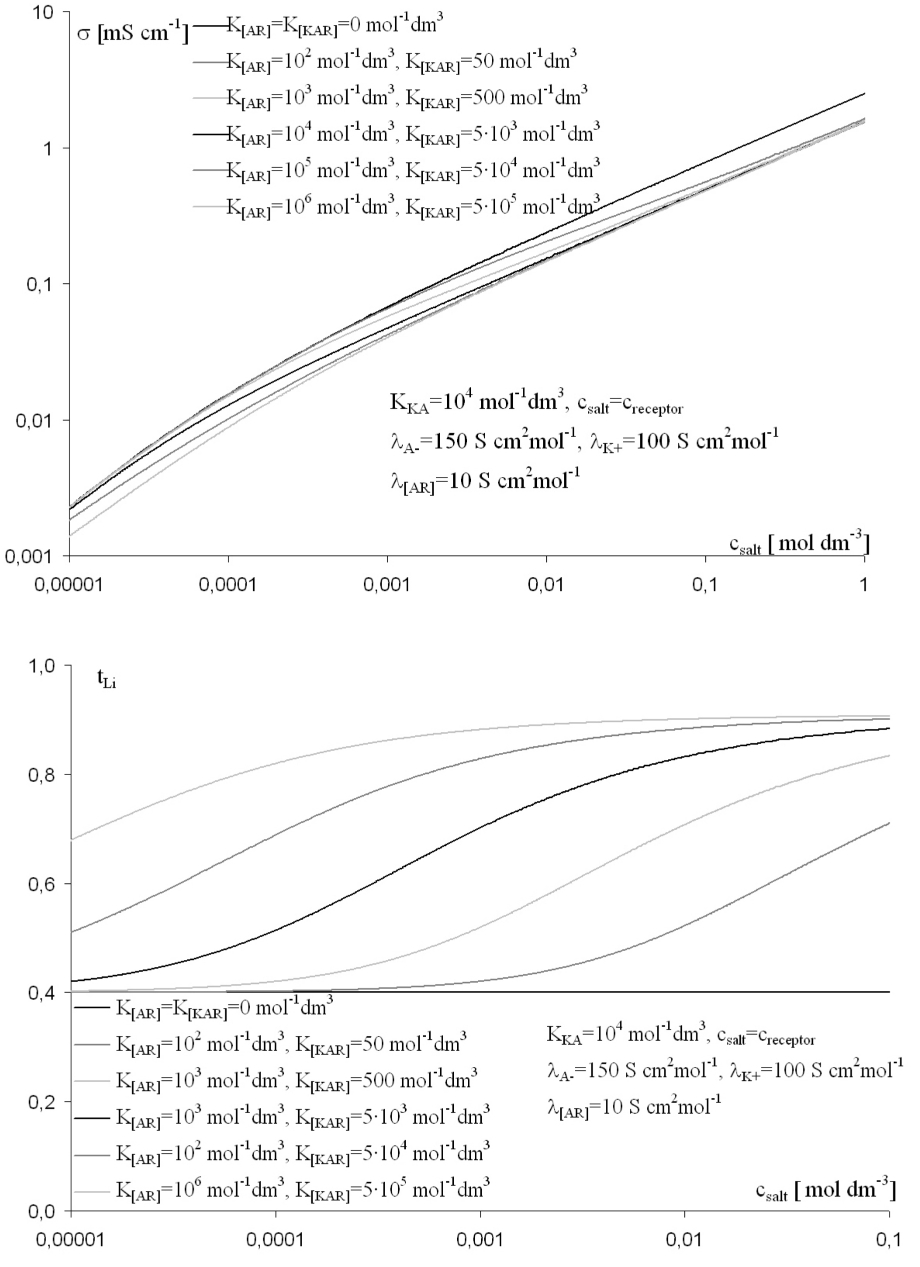

Figure 68. Dependency of salt concentration and anion-receptor complex formation constant on ionic conductivity and lithium transference number. The ionic pairs formation and anion-receptor complex formation constants equal to 10^4 mol^{-1}dm^3, ionic triplets formation constant equal to 10^2 mol^{-1}dm^3.

In the analyzed case, the receptor addition results in conductivity lowering. This tendency is opposite to that in case in which the receptor was selective on ionic pairs. This lowering is observed due to the fact that the ratio between anion-receptor complex concentration and receptor ionic concentration is equal to the ratio between anion and ionic pair concentrations. Thus, anion receptor addition in this case results mainly in the formation of non-charged species.

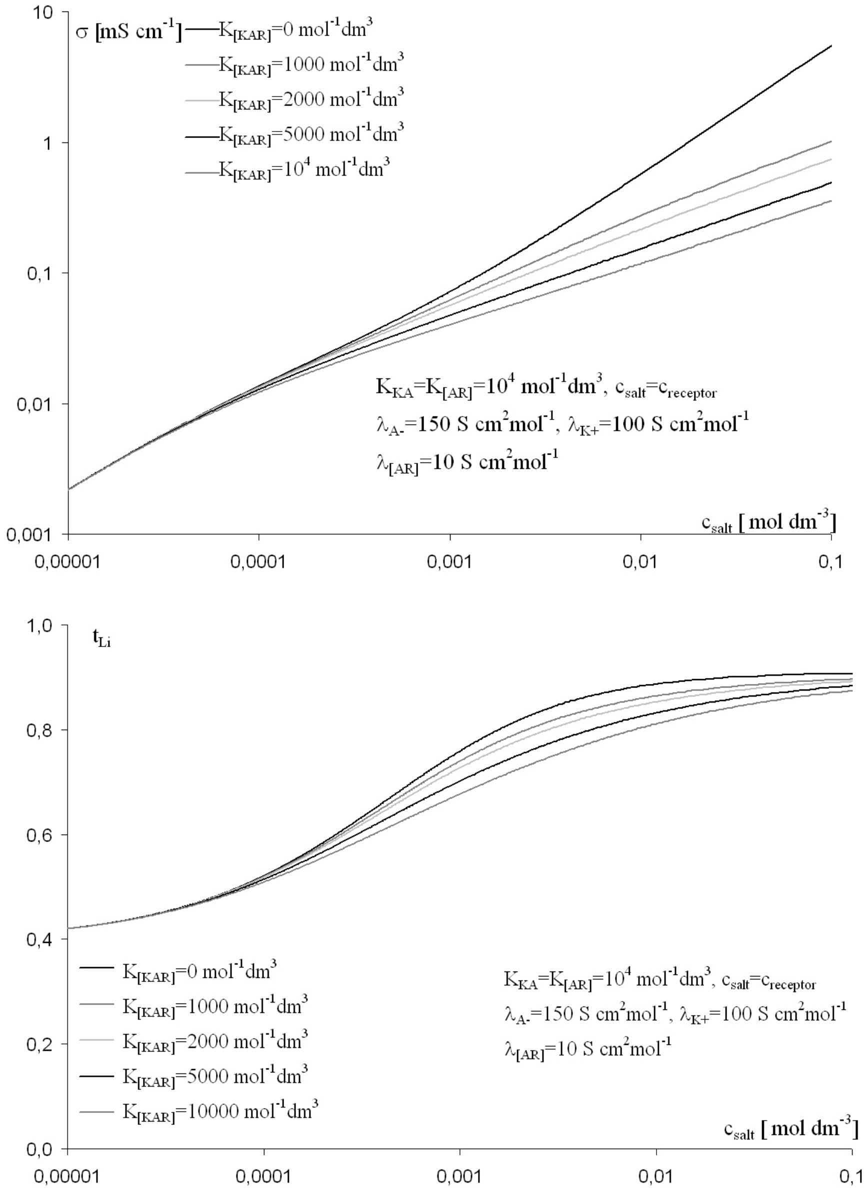

Figure 69. Dependency of salt concentration and the ionic pair-receptor complex formation constant on ionic conductivity and the lithium transference number. The ionic pairs formation and anion-receptor complex formation constants equal to 10^4 mol^{-1}dm^3.

In the next case, the system contains the same species but the anion-receptor complex formation constant is fixed and the ionic pair-receptor complex formation constant is varied (Figure 69). We can observe that the more significant is formation of the ionic pair-receptor complex, the lower is conductivity and the lithium transference number. The difference in conductivity between systems in which the anion receptor is selective only on anions and systems in which the receptor is selective on both anions and ionic pairs can be higher than one order of magnitude. This confirms the negative role of selectivity of the receptor on species other than the anion, particularly for systems in which salt concentration is high.

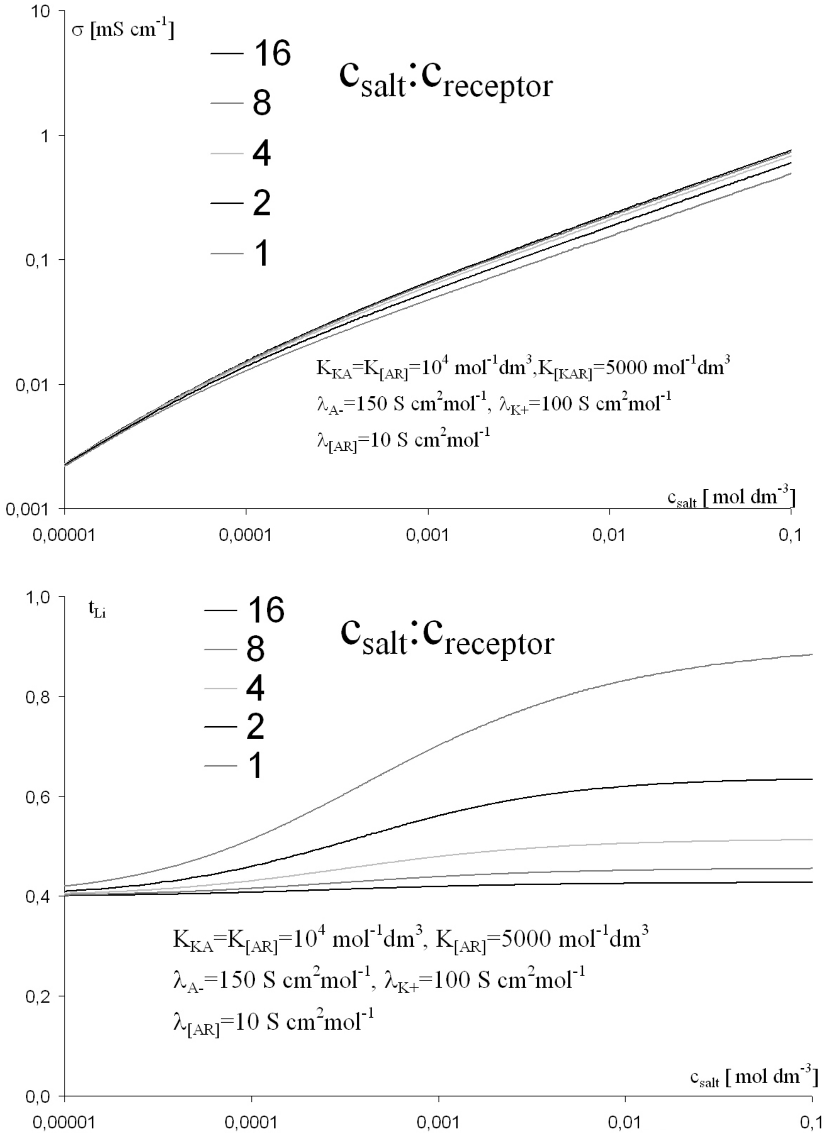

Figure 70. Dependency of salt concentration and salt concentration-receptor concentration ratio on ionic conductivity and the lithium transference number. The ionic pairs formation and anion-receptor complex formation constants equal to 10^4 mol^{-1}dm^3, ionic pair-receptor formation constant equal to $5\cdot10^2$ mol^{-1}dm^3.

The next figure (Figure 70) illustrates the case in which all the formation constants were fixed and the role of receptor concentration was analyzed. The observed tendency in lithium transference number (the increase in the lithium transference number with rising receptor concentration) is similar to that in the other systems, however, the changes are less significant than for other systems analyzed. It is due to fact that majority of the anion receptor molecules are engaged in the formation of the receptor-ionic pair complexes. Indeed, when the receptor concentration: salt concentration ratio is below 1:1, the concentration of ionic pairs is higher than the number of receptor molecules. Thus, the formation of ionic pairs-receptor complexes reduces the concentration of the "free" anion receptor molecules so much that they cannot influence the ion transport properties. This argumentation confirms also fact that the addition of the receptor has no significant influence on the ionic conductivity in the analyzed case.

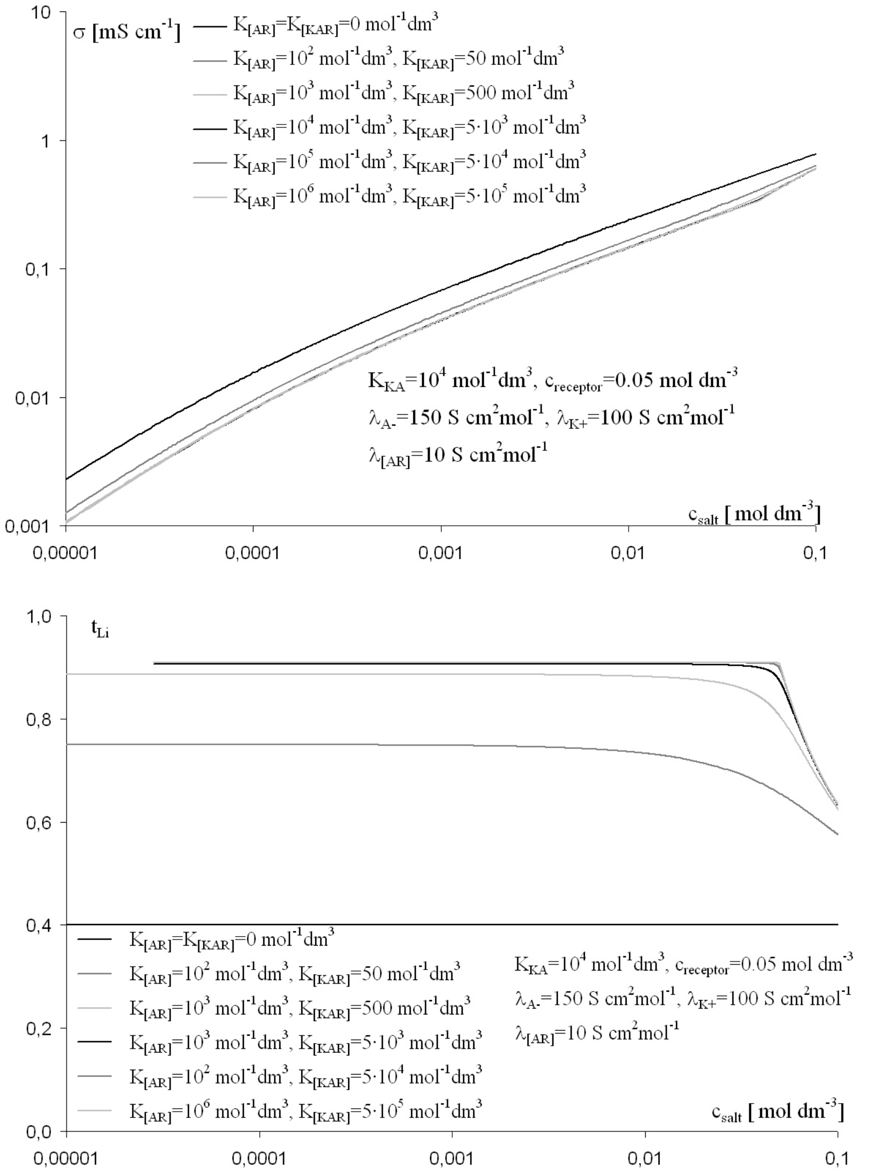

Figure 71. Dependency of salt concentration and salt concentration-receptor concentration ratio on ionic conductivity and the lithium transference number. The ionic pairs formation and anion-receptor complex formation constants equal to 10^4 mol^{-1}dm^3, ionic pair-receptor formation constant equal to 5•10^2 mol^{-1}dm^3.

In the last system analyzed in this part of the Appendix it was assumed that receptor concentration is constant (Figure 71). As we can see, the lithium transference number, when the salt concentration is low enough, depends only on the binding strength of the receptor. This is consistent with the analysis of other systems in which the receptor concentration was fixed. However, for higher salt concentrations the lithium transference numbers diminish faster than in the case of systems in which the receptor is selective on anions only.

In the analyzed case, the highest conductivity can be observed when the anions and ionic pairs do not interact with the anion receptor.

A.6 Conclusions: how receptor addition can improve ionic conductivity and the lithium transference number.

The aim of this part of the Appendix was to present for which ratios between complexes formation constants and ionic agglomerates formation constants an enhancement of the ionic transport in the electrolyte can be observed.

It was proved that the anion receptor improves the lithium transference number independently of its selectivity and of ionic agglomerate formation. The lithium transference number increase resulting from anion receptor addition takes place even if the anion-receptor complex formation constant is two orders of magnitude lower than that of ionic pair formation. This argumentation, however, is valid for systems in which no formation of ionic agglomerates higher than ionic pairs is observed. When we analyze a system in which also ionic triplets are taken into consideration, the effect of the anion receptor addition is observed when the anion-receptor complex formation constant is higher than the ionic triplet formation constants. It is due to fact, that in this case, not “free” ions but ionic triplets conduct the majority of ionic transport.

Another interesting conclusion is that the lithium transference number can be increased when anion receptor concentration is lower than salt concentration. It is, however, valid only when the anion receptor is not selective on ionic pairs. The fulfillment of this condition is possible only in very specific systems. It was presented by D’Aprano *et al.* [498] (see Chapter 3.1) that even aza-ethers are selective on both ionic pairs and “free” anions. This effect might explain why the addition of “hydrogen bond-type” anion receptors, in which the anion is well-shielded by the receptor molecule, is more effective than the addition of “Lewis acid type” receptors.

The analysis presented, however, does not take into consideration several parameters of the “real” electrolyte. In all typical liquid solvents such as organic carbonates, GBL or glymes, viscosity rises with the growing salt concentration in the system. Consequently, the velocity of ion diffusion (and molar conductivity of the particular ion) lowers with the raising salt concentration. As it was presented in Chapter 2 for “Lewis acid type” anion receptors, the viscosity of the system raises also when the anion receptor is introduced to the liquid salt-solvent system. The situation is similar in the polymeric systems. As it was discussed in Chapter 1, cations and positively charged triplets cross-link the PEO chains and, in consequence, the velocity of the PEO segmental motions is reduced. Thus, also in the case of the polymeric ion-conducting membrane, the velocity of ion diffusion lowers with rising salt concentration. The anion receptor can cross-link the PEO chains by the formation of pyrrole NH-ether oxygen hydrogen bonds. Thus, like in the liquid system, the addition of the anion receptor can lower the ion diffusion velocity.

The anion receptor can also play several other roles in polymeric system. It can e.g. lower the melting point of the electrolyte by forming an eutectic mixture with PEO or be a plasticizer- the anion receptor addition can lower the crystallinity of the membrane. When it precipitates, it can play the role of a filler. This Appendix presents the relatively simple model which can describe how the concentrations of various species in the system change when an additional compound is added to the system. An attempt at the change in the ion transport properties was presented in Chapter 7. The author direct the reader to this part of the dissertation.

Appendix B

Application of Anion Receptors in Well Dissociated, Gelled and Liquid Systems

B.1 Introduction[14]

As it was demonstrated in Chapters 2 and 3, also in the liquid systems the addition of the anion receptor to the system can change the properties of the electrolyte. The addition of the anion receptor can play both positive (enhancement of the lithium transference number) and negative (lowering of electrolyte conductivity and a faster growth of the SEI resistance) roles. As the liquid electrolytes are used in nearly all available lithium or lithium-ion batteries, it was interesting to determine if it is possible to apply anion receptors of hydrogen-bond type also in the liquid systems. To discuss the role of the anion receptor, two receptors being calixpyrrole derivatives i.e. C6P, widely researched in other systems presented in this work, and C4A, were tested. The latter one should exhibit a higher affinity to the anions due to fact that its molecule contains several amide groups (having strong affinity to the anion) in its chemical structure.

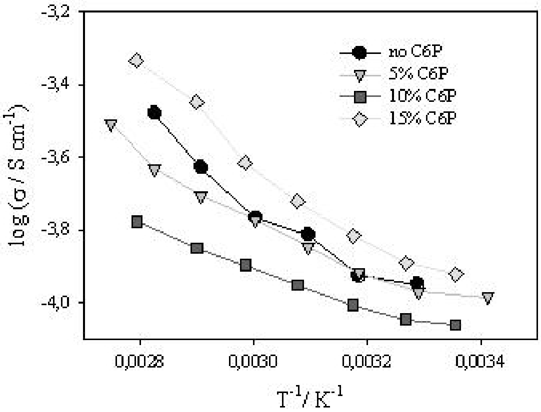

Figure 72. Conductivity of PVdF-based gels (PVdF-PC-LiTf-C6P)

B.2 Results - conductivity of PVdF-C6P-PC-LiTf gels

The gels prepared by both methods exhibited similar values of ionic conductivity with Arrhenius-type temperature dependence. The activation energy of conduction equals to 10-20 kJ mol^{-1}. This range of activation energy values was typical for liquid organic electrolytes. The addition of C6P did not influence the conduction parameters significantly. Figure 72 presents conductivity changes for gel containing LiTf obtained in a two-step synthesis.

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[14] The electrochemical data presented here were registered by Regina Borkowska, Ph.D., Filip Chyliński, MSc., Wojciech Adamiak, MSc. and Lech Niedzicki, MSc. The C6P and C4A receptors were critically chosen and synthesized by author of this dissertation.

B.3 Results - the impedance of Li-gel interface

The impedance spectra matched the overall equivalent circuit of serial connection of parallel resonators corresponding to conduction phenomena (HF), interfacial layer (MF) and charge transfer (LF), as revealed in idealized impedance spectra shown in Figure 73 (upper part).

Two phenomena are influenced by the C6P addition – the passive layer resistance R(MF) is significantly lower during a prolonged test (up to 350 h) in 5% and 19% gels containing C6P and the charge transfer resistance R(LF) reacts in the opposite way. All impedance results are very irregular - the reason might be structural difference between two sides of the gel separator, as proved by analysis of SEM images. The additive is not completely dissolved in the electrolyte and tends to sedimentate during 3-4 hours of curing and hardening of the gel. It is, however, possible that in suspensions complexes can be formed on the surface of C6P grains.

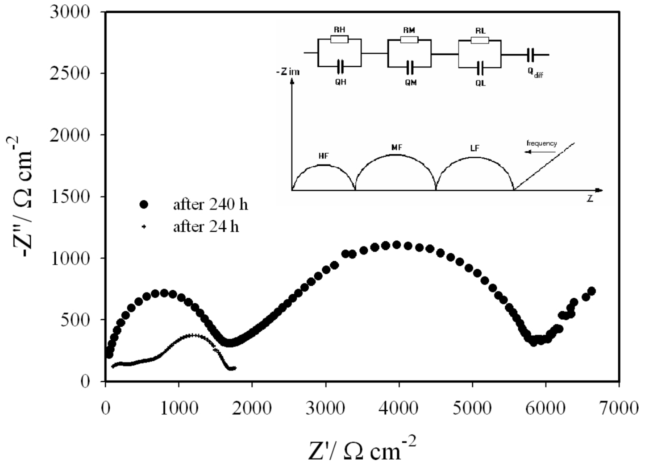

Figure 73. Idealized impedance spectrum and corresponding equivalent circuit for Li/gel/Li samples vs. real EIS spectra for the PVdF-PC-LiTf-C6P system.

B.4 Results - electrochemical behavior of C6P

In the presence of C6P an anodic peak appeared at ca. 0.7V/NHE in the gel electrolyte (Figure 74). Further CV-grams were registered in PC solutions (Figures 75-76). The peak, as shown in Figure 76, forms only in solutions of lithium salts with the anion complexed by the C6P macrocyclic ring - LiBF$_4$ and LiTf. Sodium salts, as NaBF$_4$, as well as (C$_2$H$_5$)$_4$NBF$_4$ and LiClO$_4$ do not exhibit anodic waves at these potentials. Because of poor solubility of C6P in PC and other polar solvents more concentrated solutions could not be studied.

The anodic peaks tend to disappear in time (Figure 76), which suggest that the equilibrium state of complex formation is reached slowly and does not exhibit further electrochemical activity.

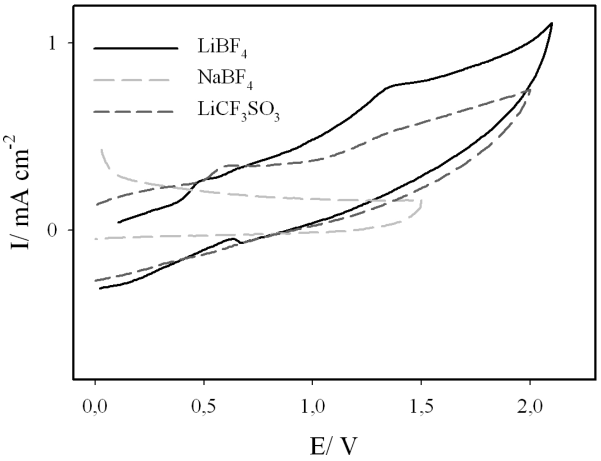

Figure 74. Anodic activity in PC solutions of various salts. Scan rate 50 mV/s, potential given vs. NHE.

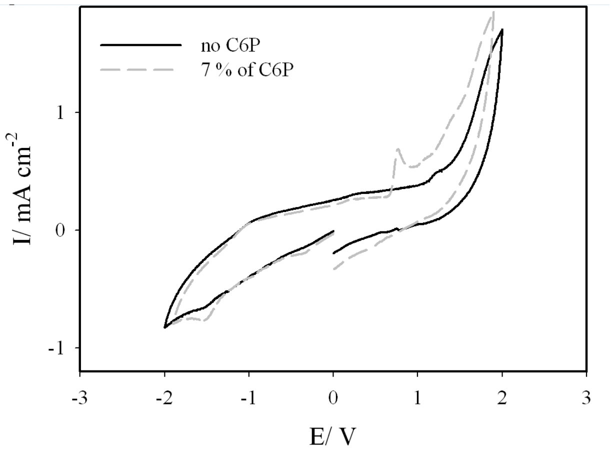

Figure 75. Comparison of CV characteristics of PVdF-PC-LiTf gel electrolytes. Scan rate 50 mV/s, potential given versus NHE.

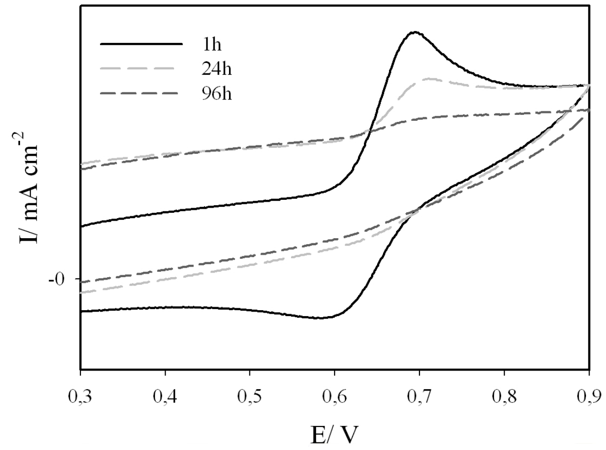

Figure 76. Anodic oxidation peak dependence on time in the LiTf-PC electrolyte. Scan rate 50 mV/s, potential given vs. NHE.

B.5 Results of measurements of the transference number of the $LiClO_4$-PC-C4A system

The results of polarization experiments for the $LiClO_4$-PC systems ($LiClO_4$ concentration equal to 0.1 mol dm^{-3}) are depicted in Figure 77. The lithium transference number for receptor-free system is equal to 0.58 while for the one containing the receptor it is 0.65. For the same system but with salt concentration equal to 1 mol dm^{-3}, the lithium transference numbers are equal to 0.48 (receptor free) and 0.66 (containing the receptor), respectively. Taking these results into consideration, one must state that the addition of the receptor slightly enhances the lithium transference number. The main problem observed is that the growth of the passive layer is faster in the case of the system containing C4A. For both salt concentrations, the electrode-electrolyte interface resistance is about 50% higher after the polarization experiment than the initial one while for the receptor-free one the increase observed is in the range of 25%.

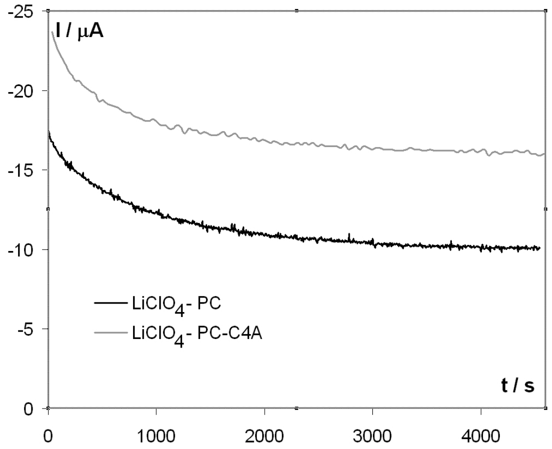

Figure 77. Polarization of the Li| electrolyte| Li cell. Salt concentration 0.1 mol dm^{-3}, receptor content 1% m/m. Polarization equal to 20 mV s^{-1}.

B.6 The electrochemical stability of C4A studied by means of CV

A comparison of the cyclic voltammograms of the PC-$LiClO_4$ systems with and without C4A additive is depicted in Figure 78. The peaks at about -3 V are characteristic for $Li^{+}+e^{-}\leftrightarrow Li$ reaction. Additional peaks which suggest decomposition of the receptor on the electrode are not observed.

Unfortunately, the CV of the next cycles reveals the formation of a poorly conducting and electrochemically active layer (Figure 79). One can observe the first reduction peak at about -1.5 V. Additionally, at -3 V, the oxidation peak is lower by about two orders of magnitude in comparison with the first cycle. The former suggests reduction of the amide group and the latter suggests the covering of the electrode with a poorly conducting layer. This assumption is supported by very similar electrochemical behavior of other amides such as acetamide or acetanilide (Figures 80-81).

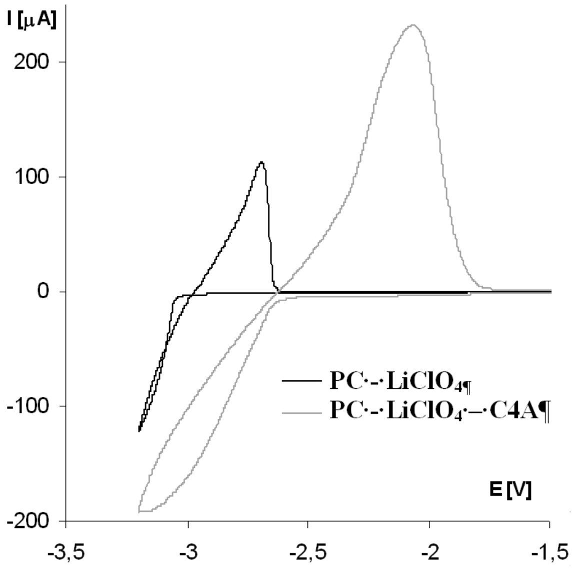

Figure 78. Cyclic voltammogram (1^{st} scan) of the PC- 1 M $LiClO_4$ systems with and without C4A additive. Scan rate 20 mV s^{-1}. C4A concentration about 1%.

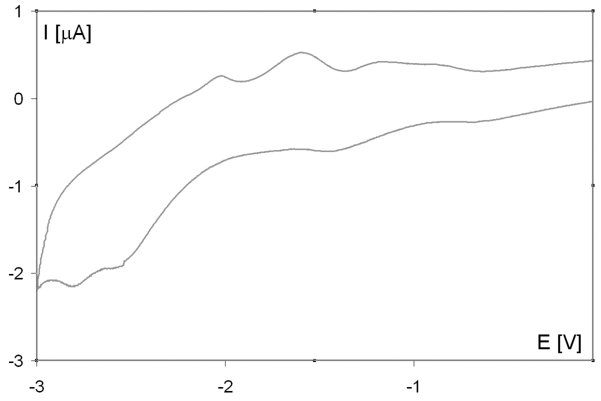

Figure 79. 2^{nd} cycle of CV for 1 M $LiClO_4$-PC-C4A system. Scan rate 20 mV s^{-1}. C4A concentration about 1%.

B.7 Discussion and conclusions

In the case of non-compatible and, thus, poorly soluble receptor (C6P), after its addition no significant changes in conductivity can be observed. It is due to fact that the receptor crystals can neither coordinate the anion nor be active as the filler. Naturally, the diameter of the C6P crystals is some orders of magnitude too large to be active as the filler. However, even when the concentration of the anion receptor is so low, we can observe an additional oxidation peak. Moreover, the electrochemical behavior of the receptor during CV tests depends of the salt used. It might be due to the interactions between the salt and the receptor.

In the case of the receptor which is more compatible with the solvents (C4A), it has a significant influence on the conductivity and the lithium transference number. Unfortunately, the amide groups present in its structure can be easily reduced on the platinum electrode. This, however, does not influence the rapid growth of resistance of the lithium|electrolyte|lithium symmetrical cell in which the electrolyte contains a receptor. Thus, the addition of the anion receptor to the electrolyte may not have as important influence on the stability of the electrode-electrolyte interface as the CV studies suggest.

In further studies, one should design a receptor which has a better compatibility with the (in this case) polar solvents, and, thus, higher solubility. It is worth stressing here that all the expectations concerning the anionic receptor such as stability versus electrodes, high selectivity on the anion, weak interactions with the cation, low cost of the reagents as well as easiness of the synthesis should be also fulfilled.

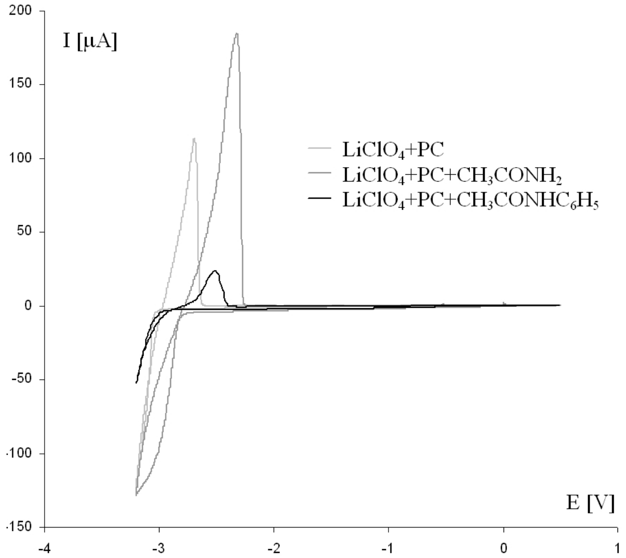

Figure 80. Cyclic voltammogram (1st scan) of the PC-1 M $LiClO_4$ systems with and without addition of amides (acetamide and acetanilide). Scan rate 20 mV s^{-1}. Amide concentration equal 0.1 M.

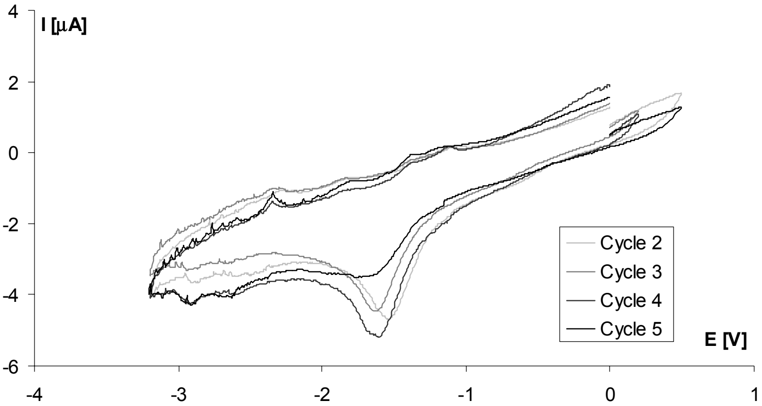

Figure 81. Cyclic voltammogram (2nd-5th scan) of the PC - 1 M $LiClO_4$ systems with and without addition of acetanilide. Scan rate 20 mV s^{-1}. Amide concentration equal 0.1 M.

Appendix C

List of publications

1. Articles.

N°	Authors	Title	Journal	IF 2007	Times cited
1	M. Kalita, M. Bukat, M. Ciosek, M. Siekierski, S. H. Chung, T. Rodríguez, S. G. Greenbaum, R.Kovarsky, D. Golodnitsky, E. Peled, D. Zane, B. Scrosati, W. Wieczorek	Effect of calixpyrrole in PEO-$LiBF_4$ polymer electrolytes	Electrochimica Acta 50 (2005) 3942.	2.955	21
2	A. Plewa, F. Chyliński, M. Kalita, M. Bukat, P. Parzuchowski, R. Borkowska, M. Siekierski, G. Z. Żukowska, W. Wieczorek	Influence of macromolecular additives on transport properties of lithium organic electrolytes	Journal of Power Sources 159 (2006) 431.	3.521	5
3	M. Pawłowska, G. Z. Żukowska, M. Kalita, A. Sołgała, P. Parzuchowski, M. Siekierski	The effect of receptor-polymer matrix compatibility on properties of PEO-based polymer electrolytes containing supramolecular additive. Part 1. Studies on phenomenon of compatibility	Journal of Power Sources 173 (2007) 755.	3.521	1
4	M. Kalita, A. Sołgała, M. Siekierski, M. Pawłowska, G. Rokicki, W. Wieczorek	The effect of receptor-polymer matrix compatibility on properties of PEO-based polymer electrolytes containing supramolecular additive. Part 2. Ionic transport study	Journal of Power Sources 173 (2007) 765.	3.521	0
5	P. Moszczyński, M. Kalita, P. Parzuchowski, M. Siekierski, W. Wieczorek	Interpenetrating Ionomer-Polymer Networks Obtained by The in-Situ Polymerization in Pores of PVdF Sponges as Potential Membranes in PEMFC Applications	Journal of Power Sources 173 (2007) 648.	3.521	0
6	D. Golodnitsky, R. Kovarsky, H. Mazor, Yu. Rozenberg, I. Lapides, E. Peled, W. Wieczorek, A. Plewa, M. Siekierski, M. Kalita, L. Settimi, B. Scrosati, L. G. Scanlon	Host-guest interactions in single-lithium-ion polymer conductor	Journal of the Electrochemical Society 154 (2007) A547.	2.387	0
7	A. Plewa, M. Kalita, M. Siekierski	Estimation of Ion Pair Formation Constants of Lithium Salts in Mixtures of Glymes and 1,4-dioxane	Electrochimica Acta 53 (2007) 1527.	2.955	0
8	A. Sołgała, M. Kalita, G. Z. Żukowska	Study of neutral species coordination by macrocyclic anion receptors using FTIR spectroscopy	Electrochimica Acta 53 (2007) 1541.	2.955	0
9	A. Hekselman, M. Kalita, A. Plewa-Marczewska, G. Z. Żukowska, E. Sasim, W. Wieczorek, M. Siekierski	Effect of calix[6]pyrrole addition on properties of PEO-based solid polymer electrolytes doped with plasticizing salts	Submitted to Journal of Power Sources.	3.521	-

N^o	Authors	Title	Journal	IF 2007	Times cited
10	A. Plewa-Marczewska, M. Kalita, M. Marczewski, M. Siekierski	NMR studies of equlibriums in electrolytes. Ionic pairing in glymes.	Submitted to Electrochimica Acta.	2.955	-
11	A. Hekselman, M. Kalita, A. Plewa- Marczewska, G. Z. Żukowska, E. Sasim, W. Wieczorek, M. Siekierski	Effect of calix[6]pyrrole addition on properties of PEO-based solid polymer electrolytes doped with plasticizing salts.	Electrochimica Acta (accepted)	2.955	-

11 articles (8 released, 3 submitted), 27 citations (October 2007), IF$_{(2006)}$ equal 34.768 (25.336 for articles released).

2. Publications in the conference materials.

N^o	Authors	Title	Journal
1	A. Plewa, M. Kalita, G. Z. Żukowska, A. Sołgała, M. Siekierski	Competitive Complexing of Supramolecular Additives with Anions and Neutral Solvent Species Verified by Spectroscopic Techniques	ECS Transactions, 3/12 (2006) 59.
2	A. Plewa, M. Kalita, A. Sołgała, M. Siekierski	Estimation of Ion Pairs Formation Constants of Lithium Salts in 1,2-dimethoxyethane and 1,4-dioxane Mixtures	ECS Transactions, 2/27 (2007) 117.
3	P. Moszczyński, M. Kalita, K. Nadara, M. Siekierski	Wybrane aspekty badań nad rozwojem ogniw litowych	Wiadomości Elektrotechniczne 8 (2006) 10.

3. Presentations and posters on the conferences.

N^{o}	Authors	Title	Conference
1	M. Bukat, M. Ciosek, M. Kalita, M. Siekierski, A. Plewa, G. Rokicki, W. Wieczorek	Kaliks[6]pirole jako receptory na aniony w zastosowaniach do elektrolitów polimerowych	Ogniwa i akumulatory. Chemiczne źródła prądu w nauce i technice. Poznań, 26-27.05.2004
2	M. Kalita, M. Siekierski, W. Wieczorek	Anion receptors as additives in PEO-based polymer electrolytes	Microseminar on polymeric electrolytes, 2.6.2005, Goeteborg, Sweden
3	A. Plewa, M. Bukat, M. Kalita, M. Siekierski, W. Wieczorek	Transference numbers determination in polymer electrolytes with supramolecular additive	Alistore Summer School on Synthesis of Nanostructured Materials for Polymer Batteries, 22-25.06.2005, Augustów
4	M. Siekierski, M. Kalita, A. Plewa	Estimation of ion pairing, anionic triplet forming and anion complexation with neutral species in PEODME- based electrolytes using ^{19}F NMR spectroscopy	209th Meeting of the Electrochemical Society, 05.2006, Denver, USA
5	D. Golodnitsky, R. Kovarsky, H. Mazor, E. Peled, W. Wieczorek, A. Plewa, M. Siekierski, M. Kalita, L. Settimi, B. Scrosati	Single-Ion Conductor for Lithium Batteries	7th Israel Conference on Corrosion and Electrochemistry, 10-11.05.2006
6	A. Plewa, A. Sołgała, M. Kalita, M. Siekierski	Electrochemical and ^{19}F NMR Studies of Ionic Associations in Low Molecular Weight Analogs of PEO-based Polymeric Electrolytes	10th Conference „Fast Ion conductors", 13-17.09. 2006, Augustów
7	P. Moszczyński, M. Kalita, W. Wieczorek, M. Siekierski	Interpenetrating Ionomer-Polymer Networks Obtained by the In-situ Polymerization in Pores of PVdF Sponges as Potential Memebranes in PEMFC Applications	10th Conference „Fast Ion conductors", 13-17.09. 2006, Augustów
8	A. Plewa, M. Kalita, G. Z. Żukowska, A. Sołgała, M. Siekierski	Anion-Receptor Interactions, Spectroscopic Study of the Competitive Complexing of Supramolecular Additives with Anions and Neutral Solvent Species	10th Conference „Fast Ion conductors", 13-17.09. 2006, Augustów
9	A. Plewa, M. Kalita, G. Z. Żukowska, A. Sołgała, M. Siekierski	Anion-Receptor Interactions, Spectroscopic Study of the Competitive Complexing of Supramolecular Additives with Anions and Neutral Solvent Species	10th Conference „Fast Ion conductors", 13-17.09. 2006, Augustów
10	R. Kovarsky, H. Mazor, Yu. Rosenberg, D. Golodnitsky, E. Peled, W. Wieczorek, A. Plewa, M. Siekierski, M. Kalita, L.Settimi, B.Scrosati	Host-guest Interactions in Single-lithium-ion Polymer Conductor	10th International Symposium on Polymeric Electrolytes, 15-19.10. 2006, Foz do Iguacu, Brasil
11	M. Kalita, A. Sołgała, G. Z. Żukowska, M. Siekierski	Competitive Complexing of Supramolecular Additives with Anions and Neutral Species Verified by Spectroscopic Techniques	10th International Symposium on Polymeric Electrolytes, 15-19.10. 2006, Foz do Iguacu, Brasil

N^o	Authors	Title	Conference
12	A. Plewa, A. Sołgała, M. Siekierski	Electrochemical and ^{19}F NMR Studies of Ionic Associations in Low Molecular Weight Analogs of PEO-based Polymeric Electrolytes	10th International Symposium on Polymeric Electrolytes, 15-19.10. 2006, Foz do Iguacu, Brasil
13	M. Siekierski, A. Plewa, M. Kalita, A. Sołgała	Electrochemical and ^{19}F NMR studies of ionic associations in low molecular weight analogs of PEO-based polymeric electrolytes	210th Meeting of the Electrochemical Society, 10.2006, Cancun, Mexico
14	M. Siekierski, M. Kalita, A. Plewa, Z. Żukowska, A. Sołgała	Competitive complexing of supramolecular additives with anions and neutral solvent species verified by spectrosopic techniques	210th Meeting of the Electrochemical Society, 10.2006, Cancun, Mexico
15	A. Hekselman, M. Kalita, M. Siekierski	The effect of calixpyrrole addition in PEO-LiTf and PEO-LiTfSI systems	211th Meeting of the Electrochemical Society, 05.2007, Chicago, USA
16	A. Sołgała, M. Kalita, M. Siekierski	The Anion Receptor Complexation Dependency on Solvent Properties and its Relation to the Anion Complexation Phenomena in Solid Polymer Electrolytes	212th Meeting of the Electrochemical Society, 10.2007, Washington, USA
17	P. Moszczyński, M. Kalita, M. Siekierski	Interpenetrating Ionomer-Polymer Networks Obtained by The In-Situ Polymerization in Pores of PVdF Sponges as Potential Membranes in PEMFC Applications	212th Meeting of the Electrochemical Society, 10.2007, Washington, USA
18	M. Siekierski, M. Kalita, A. Plewa, A. Piśniak	Competitive complexing of supramolecular additives with neutral solvent species verified by spectrosopic techniques	11th International Symposium on Polymeric Electrolytes, 09.2008, Ofir, Portugal
19	M. Siekierski, K. Pindelska, A. Plewa-Marczewska, M. Kalita, W. Wieczorek, D. Golodnitsky	Novel ceramic supramolecular two additive composite polymeric electrolytes	11th International Symposium on Polymeric Electrolytes, 09.2008, Ofir, Portugal
20	A. Hekselman, M. Kalita, M. Siekierski	The effect of calixpyrrole addition in PEO-LiTf and PEO-LiTfSI systems	11th International Symposium on Polymeric Electrolytes, 09.2008, Ofir, Portugal
21	D. Pourjafarinokande, H. S. Emami Meibody, S. Ketabi, W. Adamiak, L. Niedzicki, M. Kalita, A. Plewa-Marczewska, R. Borkowska, M. Siekierski, W. Wieczorek	The effect of anion receptor addition in highly dissociated liquid and gelled systems	11th Conference „Fast Ion conductors", 14-17.09. 2008, Grybów
22	M. Siekierski, K. Pindelska, A. Plewa-Marczewska, M. Kalita, W. Wieczorek, D Golodnitsky	PEO based binary composites based on inorganic filler and the supramolecular additive	11th Conference „Fast Ion conductors", 14-17.09. 2008, Grybów
23	A. Hekselman, A. Plewa-Marczewska, M. Kalita, M. Siekierski	The effect of calixpyrrole addition in PEO-LiTf and PEO-LiTfSI systems	11th Conference „Fast Ion conductors", 14-17.09. 2008, Grybów
24	M. Siekierski, A. Plewa-Marczewska, K. Pindelska, M. Kalita, D. Golodnitsky	Novel ceramic supramolecular binary composite polymeric electrolytes	214th Meeting of the Electrochemical Society, 10.2008, Honolulu, USA

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[1] Estimated using data from D. Linden, T. B. Reddy, (Eds.) Handbook of Batteries (3rd Edition) and report "World Batteries" published by The Freedonia Group.

[2] D. Linden, T. B. Reddy, (Eds.) Handbook of Batteries (3rd Edition), chapter 14, 2002 McGraw-Hill**.**

[3] The market for Li-ion batteries is estimated at 2.5 billions units and the sales revenue equalled $7 billion in 2006 (Global Li-ion Battery Market Report 2007, Market Avenue & Partners, 2007; http://www.marketavenue.cn/upload/REPORTS_330.htm). Market sales revenue in lithium primary batteries is significantly higher than $1 billion (World Primary Lithium Battery Market, Frost & Sullivan's. after: Advanced Battery Technology, July 2004).

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Table of contents