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Advanced lithium energy storage system

Polymers vs. liquids, gels and ionic liquid electrolytes.

Any winners?

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General ideas

In spite of over 200 years history of the voltaic cell technology the real milestone was the introduction of nonaqueous electrolytes, characterised by broader electrochemical stability window (in standard conditions at pH=0, water gets oxidized at ~1.2V vs. SHE and reduced at 0.000 vs. SHE). Conceptually, the electrolyte should not undergo any net chemical changes in a voltaic cell and do not contribute to the Faradaic processes that are expected to take place within/at the electrodes and not alter the electrolyte composition. Since the energy density of a battery is a linear function of its voltage, and the power increases with its square, search for new electrode materials offering higher and higher cell voltages goes on. One should keep in mind, that the electrolyte remains in contact with both negative and positive electrode and increasing the cell voltage we increase the possibility of destroying the electrolyte by reduction/oxidation at either of the electrodes.

These processes can be avoided either due to safe potentials of the electrodes, or kinetic restrictions. On example of a cell working out of equilibrium is a well-known lead-acid battery. Its usual potential of 2.02V exceeds the stability window of water (1.2V), however the cell works fine for years due to very slow kinetics of water reduction at the lead electrode and oxidation at lead dioxide.

In the pursuit for high performance batteries, alkali metals have been recognised as good candidates for electrode materials owing to their low standard potentials and densities. Among them, lithium was the most attractive. It has the lowest standard potential among all metals, the lightest metal in the periodic table and its cation is very small giving it a chance to diffuse quickly in solids. Alkali metals are reactive with water, giving the metal hydroxide and hydrogen gas.. Therefore as early as in the 1950s electrochemistry of lithium in nonaqueous solvents was established. Its stability in certain liquids was attributed to the formation of protective passive films that is also responsible for stability of stainless steel or aluminium in oxidising conditions. In no time at all, the first primary lithium cells appeared on the market where they keep their well-established position until the present days. But still there was a lot of effort made to develop lithium technology as to introduce secondary lithium cells. The problem was the plating of lithium during the recharge. Highly inhomogeneous nature of the lithium-electrolyte interface provoked growth of lithium dendrites. Their erratic shape caused their dissolution and disattachment from the electrode on discharge, leading to capacity losses (that could be overcome by putting excess lithium in a new cell). Even worse was the presence of finely divided metallic lithium inside the electrolyte, that combined with this dendritic growth could lead to short-circuits and thermal runaway. For years different electrolyte compositions were examined in the hope of finding one that could lead to uniform lithium deposition. An ether-based electrolyte was introduced into the market in 1980s, which operated satisfactorily for over 300 deep cycles, however these batteries were still not perfect and several spectacular cells failures in 1989 finished the commercial viability of lithium metal/liquid non aqueous electrolyte secondary cells.

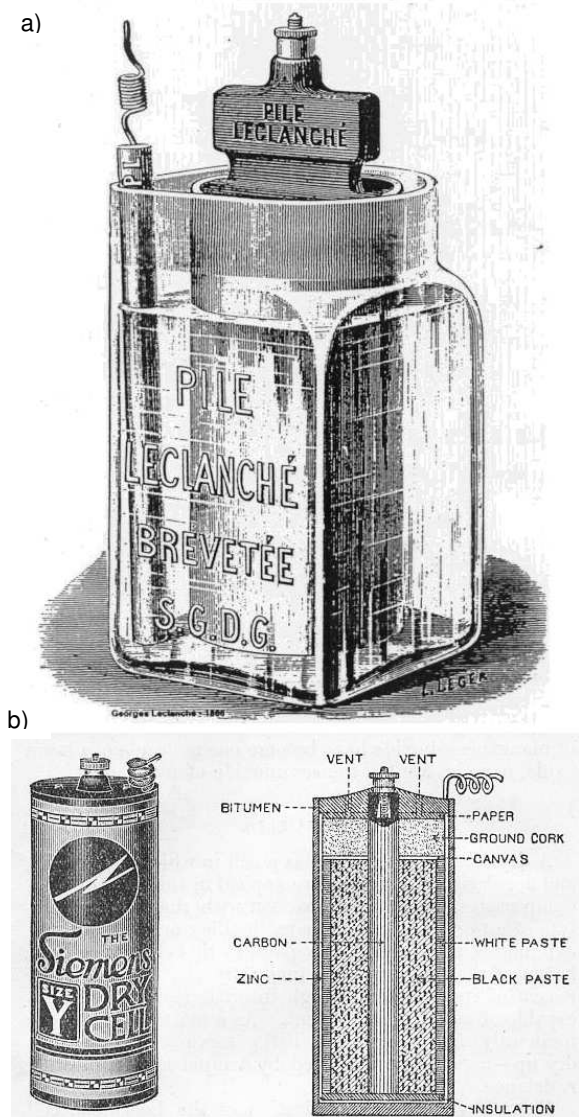


Fig.1
Evolution of the cell design oriented towards
optimisation of power and energy density

Safety issues related to the lithium metal electrode stimulated researchers to look for new negative electrodes for lithium technology. Looking at the lithium cell one can see, that the positive electrode chemistry is of the guest-host type, i.e. lithium cations are introduced into/removed from the stable structure of the host. At the same time electrons are injected into/removed from the highest energy bands of the material. All that happens at a certain potential. This class of materials (TiS_2 , LiMn_2O_4 , LiCoO_2) were introduced by Whittingham and Goodenough back in the 1970's [1,2]. These materials were cycled vs. metallic lithium electrode where it is plated/stripped. Extending the approach to the positive electrode into the negative one would lead to something called a "rocking-chair", shuttle-cock" or "swing" battery in which lithium exists only in ionic state. The battery operation results from transfer of lithium between two materials of different Fermi levels combined with corresponding transfer of electrons. First materials tested were lithiated oxides: $\text{Li}_6\text{Fe}_2\text{O}_3$, LiWO_2 that were cycled vs. WO_3 ,

TiS_2 and V_2O_5 . Such cells, despite being very safe and offering long cycle life were not able to enter the market because of low energy and power density as compared with other technologies. It was only at the beginning of the 1990's when Li-ion cells were marketed thanks to the application of petroleum coke as the negative electrode material. Cokes and graphitic materials offer relatively high gravimetric capacities, operating potential very close to the one of lithium metal and most of all, low price.

It took over 10 years before non-carbonaceous materials were introduced into the negative electrode of lithium ion cells. These were tin-based composites in which lithium creates an alloy with tin on charging the cell. However being quite satisfied with well-performing carbon electrodes more effort was devoted to positive electrodes in the search of cheaper and more available (Co is expensive and limited in supply) materials,

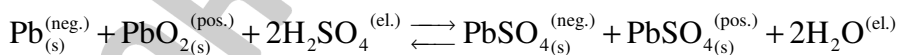
characterised by higher capacity ($140\text{mAh}\cdot\text{g}^{-1}$ of LiCoO_2 is quite low compared with LiC_6 's $372\text{mAh}\cdot\text{g}^{-1}$) and possibly by higher operating potential (however this is still under debate if very high potential positive electrodes are really a good solution to enhance the performance of the cell as a whole). The most explored materials are LiNiO_2 (and its intermediates with LiCoO_2 and LiMnO_2), LiMn_2O_4 and LiFePO_4 [3].

The general trends observed recently is the search for new electrode materials are ruled by the demand for safe, cheap and well-performing cells for automotive industry. Use of rare and expensive elements is expected to be minimized in order to lower the price and allow large-scale production; operating potentials of the electrodes should lay within the stability domain of the electrolyte in order to minimize the safety hazards that in case of large cells/battery packs are an important issue; also the cycle life should be long enough to guarantee up to 10 years operation. Of course these cells should offer as good capacities and power capabilities as possible, however these cannot be traded for the safety or unreasonably high price. Also the ability of large charge and discharge rates is not an issue since the power demand of a car is limited and peak power can be increased with supercapacitors. Furthermore in order to charge the car's battery pack in seconds a high power grid connection would be necessary and the heat generated within the pack would be difficult to dissipate (safety hazard).

Apart from optimisation of electrodes materials, that are not to be discussed here, a lot of effort was devoted to the development of electrolytes, tailored to the specific electrochemical system.

The role of electrolyte is two, or sometimes threefold:

- It should provide ionic contact between electrodes allowing to close the circuit when the cell is operational
- It should assure electronic and spatial separation of the positive and negative electrode in order to avoid short-circuit and as a result – self discharge of the cell, which in some cases can be very spectacular (as those of failed high power Li-ion cells)
- In case of electrochemical systems where electrode components are not the only reactants appearing in the overall cell reaction, the electrolyte is the source (storage) of the remaining ones:



In most cases the 3rd function of the electrolyte is not required (or very limited), therefore from the point of view of the cell mass balance, electrolyte is considered as a dead mass which should be cut down to the indispensable minimum. Taking into account simple Zn-MnO_2 cells, the change that took place between the first and commercial design is more than clear when looking at the geometry evolution which allowed to decrease drastically the amount of the electrolyte (Fig. 1 a and b [4]).

In general the electronic and spatial separation can be obtained easily with application of dielectric solids. On the other hand solutions of proper electrolyte (acid, base or salt) in a suitable liquid solvent can provide good ionic conductivity needed for operating the

cell. For many years these two functions have been separated and provided by different phases i.e. liquid electrolytes soaked into a porous separator.

The same approach (liquid electrolyte and a porous separator) was applied for both primary and secondary lithium cells (the development of the liquid electrolytes for lithium cells was described exhaustively in the great review published a couple of years ago [5]. For completeness of the work just a brief summary is given here). It's just the choice of solvents and solutes that had to be made correctly to make the system work. Not everybody knows that most of the lithium cells work out of equilibrium and as such are subject to runaway once the kinetic restrictions is lost for any reason.

In lithium-ion technology generally three groups of electrolytes are considered for ambient and moderate temperature application. These are: liquid systems (solutions of lithium salt in aprotic solvents), polymeric electrolytes (solid or gel systems) and solutions of lithium salts in ionic liquids. The present report deals with positives and drawbacks of each group of electrolytes mentioned above.

The present work is not intended to be a general overview of the electrolytes studied for lithium and lithium-ion battery technologies. For these purposes there are recent excellent reviews available dealing with liquid [5], polymer [6] and ionic liquids [7] systems. Readers are welcome to use them for further extension of their knowledge regarding each group of electrolytes used. In the present paper an authoritative report based on opinion of the group of experts working in the field of electrolytes for battery application are presented. In the following sections first each group of the material will be introduced and the recent ideas how to improve their performance in lithium and (or) lithium-ion battery technology will be discussed. This will be followed by the presentation of ideas which in our opinion open new fields of research possibly leading to an improvement of the battery performance in the future.

Liquid Electrolytes

As was stated above the liquid electrolyte is a solution of an appropriate lithium salt in a polar organic (aprotic solvent) The list of solvents currently used, or tried) in lithium - ion batteries are included in Tables 1 and 2 [5]. Table 1 lists carbonates and esters used as solvents and Table 2 ethers.

Generally an ideal electrolyte solvent should meet the following criteria:

- be able to dissolve lithium salts to sufficient concentration
- its viscosity should be low so fast ion transport can occur within electrolyte
- be inert to all cell components especially anode and cathode materials
- it should remain liquid in a wide temperature range (low melting and high boiling temperature are desirable)

The choice of solvent for electrolyte dedicated for practical lithium cell (consisting of very low potential negative and very high potential positive electrode) is rather limited. Electrolyte should be characterised by high dielectric constant and ability to complex at least one of the ions coming from the dissociation of the electrolyte salt. In aprotic solvents (because protic ones are unstable at low potentials) we lose the ability to complex anions first of all. Then – in order to get a high dielectric constant only a limited number of polar groups to choose from remain (many of them can be easily oxidized/reduced at the electrodes) i.e. carbonyl, nitrile, sulfonyl, ester and ether groups. Some heterocyclic compounds can be considered as well as long as they lack acidic protons and are stable against oxidation and reduction. Compounds that offer high dielectric constant and form low energy complexes with lithium cations were found to be cyclic organic carbonates. Many lithium salts can be dissolved in ethylene and/or propylene carbonates. The problem is that these solvents are characterised by high viscosity and often high melting point therefore they are solid at room temperature. In order to decrease the viscosity (and in this way increase the conductivity) and melting point – simple (linear) alkyl carbonates are usually mixed with the cyclic ones. These acyclic carbonates offer low viscosities, however their dielectric constant is also low. Furthermore their boiling and flash points are also low thus limiting the safety margin of the practical cell. Mixtures of organic carbonates are the solvents of choice for the commercial cells anyway. Figure 2 clearly describes the concept of the application of mixture of solvents instead of using a single one due to the opposite dielectric constant and viscosity trends.

Coming into solutes, properties of the salt used for battery applications are as follows:

- it should be able to completely dissolve in the applied solvent at desired concentration and ions should be able to transfer through the solution
- anion should be stable towards oxidative decomposition at the cathode
- anion should be inert to electrolyte solvent
- both anion and cation should be inert towards other cell components
- anion should be nontoxic and remains thermally stable at the battery working conditions

As one can see, the choice of an appropriate electrolyte salt is not easy. First of all, the cation is fixed i.e. we need lithium cation as the electroactive species in the electrolyte. Then the choice of anion is restrained by several factors. Firstly, the dissociation free enthalpy of its lithium salt should be as low as possible so that the dissociation constant is high and so is the maximum concentration of lithium cations. Secondly, the anion should be stable at low and high potentials, therefore not all the polar groups can be used to make up the anion (for the anodic stability of anions and solvents see Tables 4 and 5 in [5]). It should also be non-reactive towards carbonate solvents. Small and simple anions such as O^{2-} or F^- cannot be used because their small ionic radius induces low dissociation constants. Use of softer anions like S^{2-} or I^- is prohibited because of their low oxidation potentials. In order to get an anion with well-distributed charge, simple fluorine or chlorine anions were combined with strong Lewis acids such as PF_5 , AsF_5 , BF_3 or $AlCl_3$ in order to get PF_6^- , AsF_6^- , BF_4^- and $AlCl_4^-$, respectively, which are stable at low and high potentials and are highly soluble even in low dielectric media.

Table 1. Organic Carbonates and Esters as Electrolyte Solvents


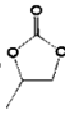




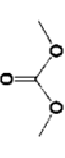
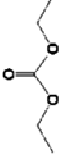
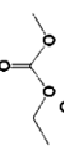
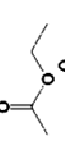
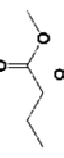
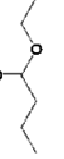
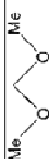







Solvent	Structure	M. Wt	T _m /°C	T _b /°C	η/cP 25 °C	ε 25 °C	Dipole Moment/debye	T _f /°C	d/gcm ⁻³ , 25 °C
EC		88	36.4	248	1.90, (40 °C)	89.78	4.61	160	1.321
PC		102	-48.8	242	2.53	64.92	4.81	132	1.200
BC		116	-53	240	3.2	53			
γBL		86	-43.5	204	1.73	39	4.23	97	1.199
γVL		100	-31	208	2.0	34	4.29	81	1.057
NMO		101	15	270	2.5	78	4.52	110	1.17
DMC		90	4.6	91	0.59 (20 °C)	3.107	0.76	18	1.063
DEC		118	-74.3 ^a	126	0.75	2.805	0.96	31	0.969
EMC		104	-53	110	0.65	2.958	0.89		1.006
EA		88	-84	77	0.45	6.02		-3	0.902
MB		102	-84	102	0.6			11	0.898
EB		116	-93	120	0.71			19	0.878

Table 2. Organic Ethers as Electrolyte Solvents

Solvent	Structure	M. Wt	T _m /°C	T _b /°C	η/cP 25 °C	ε 25 °C	Dipole Moment/debye	T _f /°C	d/gcm ⁻³ , 25 °C
DMM		76	-105	41	0.33	2.7	2.41	-17	0.86
DME		90	-58	84	0.46	7.2	1.15	0	0.86
DEE		118	-74	121				20	0.84
THF		72	-109	66	0.46	7.4	1.7	-17	0.88
2-Me-THF		86	-137	80	0.47	6.2	1.6	-11	0.85
1,3-DL		74	-95	78	0.59	7.1	1.25	1	1.06
4-Me-1,3-DL		88	-125	85	0.60	6.8	1.43	-2	0.983
2-Me-1,3-DL		88			0.54	4.39			

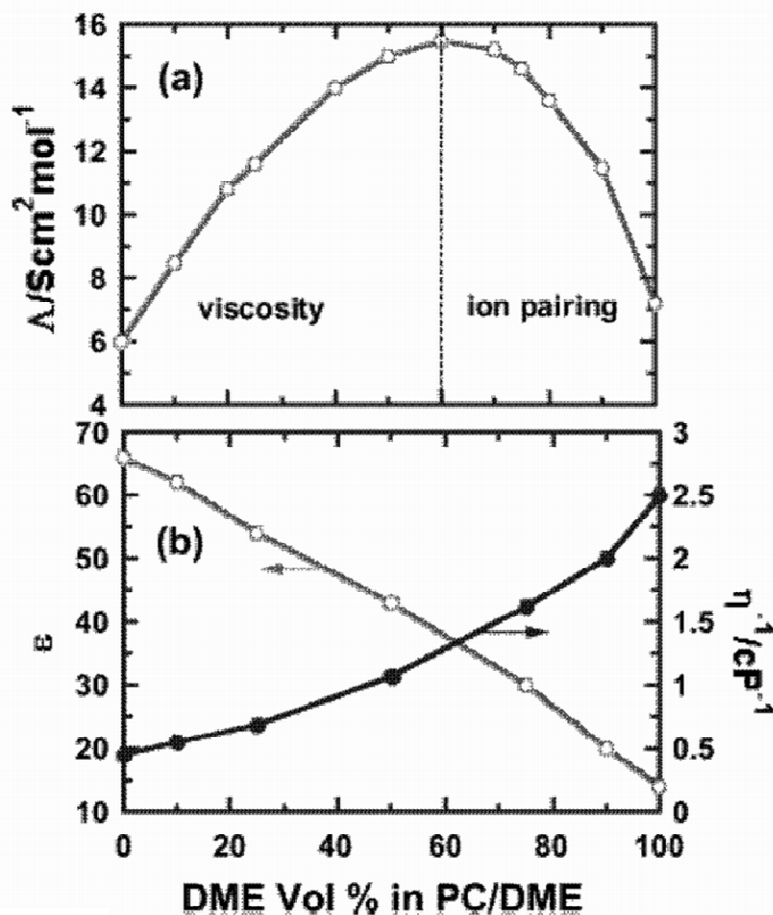


Figure 2 a) Optimization of ion conductivity in mixed solvents: 1.0 M LiClO_4 in PC/DME. (b) Dependence of dielectric constant (ϵ) and fluidity (η^{-1}) on solvent composition.

Since these acids are so strong, their complexation with weak bases like fluoride or chloride does not neutralize their activity and they can react with cell components like electrolyte solvent, current collectors and electrode active materials. Depending on the anion the structure and properties of electrode-electrolyte interfaces differ (it's not only the electrolyte solvent that determines the interfacial properties).

Another class of anions is the one based on the Pearson's theory of soft and hard acids/bases. According to it, soft acids are likely to form stable salts with soft bases, as well as hard acids with hard bases. LiF is a combination of hard acid (Li^+) with a hard base (F^-). Therefore its solubility is low in low dielectric solvents. If we combine hard acid with a soft base (formal charge localized at soft centre) in which charge is well-delocalized (strong electron withdrawing groups attached to the centre by covalent bonds) a well-soluble salt of high dissociation constant should be obtained. After a new acid based on imide with 2 electron withdrawing groups (trifluoromethanesulfonyl) had been reported in 1984, in 1989 Armand proposed using it in its lithiated form as an

electrolyte. Despite excellent intrinsic properties of electrolytes based on LiTFSI and its analogues they have never been applied in commercial cells because of corrosion problems. The aluminium current collectors are stable at high potentials because of passive layer protecting the metal against corrosion. Many fluorinated anions like TFSI or Tf provoke aluminium corrosion and inhibit their application.

Lithium conductive salt is the most important element of the electrolyte and one of key elements of whole lithium-ion cell. Surprisingly, while there is a numerous list of publications on the new lithium-ion cell electrode materials (or additions to those), with also big amount of those on electrolytes additives, there have been very little stress given to new salts used in lithium electrolytes themselves. Even though there have been some previous achievements in the field since the introduction of LiPF₆ in 1990's, in fact, no other salts made it through for mass production of commercial rechargeable lithium-ion battery cells. Below the summary of the preparation of commercially used as well as laboratory developed salts are presented. Emphasize is put on the ease of the salt preparation, cost of production, way of handling and positives as well as drawbacks when applied in lithium or lithium ion cells.

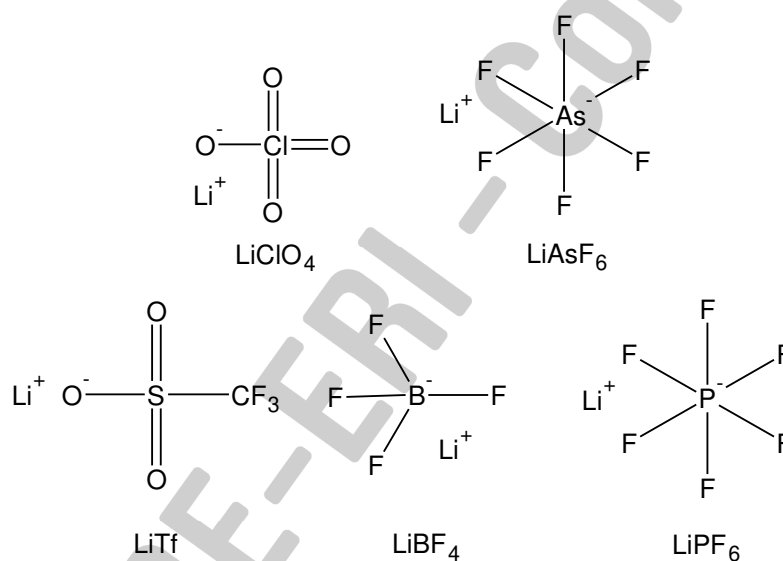


Figure 3. Lithium salts known before the introduction of lithium-ion batteries onto market.

LiClO₄ - lithium perchlorate; LiAsF₆ - lithium hexafluoroarsenate;

LiTf - LiSO₃CF₃ - lithium triflate - lithium trifluoromethanesulfonate;

LiBF₄ - lithium tetrafluoroborate; LiPF₆ - lithium hexafluorophosphate.

Before introduction of lithium-ion battery technology onto the market, many lithium salts were known and used in experimental cells (Figure 3). So it was already known for years that LiClO₄ (lithium perchlorate) is explosive [8] when used with electrodes built from transition metal compounds, LiAsF₆ (lithium hexafluoroarsenate) is very toxic and LiBF₄ (lithium tetrafluoroborate) has inferior solid electrolyte interface (SEI), which

results in an instability of cell's conductivity and current density when cycled. LiTf (LiCF₃SO₃ - lithium triflate) was known to have low conductivity. On the other hand, LiPF₆, still the most popular salt nowadays, is spontaneously decomposing to LiF and PF₅, which blocks lithium cations movement through the SEI (LiF layer on electrodes), reacts with solvent (PF₅) and forms HF (as a result of PF₅ hydrolysis) that destroys transition metal oxide cathode structure. LiPF₆ has also been recognized as unstable above 50°C.

LiPF₆, which was the best salt in terms of conductivity from salts known before the introduction of lithium-ion cells, has the ionic conductivity in organic carbonate solvents (optimized mixtures) not exceeding 11·10⁻³ S·cm⁻¹ and in plain PC of about 6·10⁻³ S·cm⁻¹ at 25°C (maximum at 1 mol·dm⁻³ concentration).

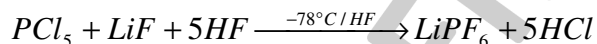
Big vulnerability of LiPF₆ to moisture is not only a problem in batteries, but also in the salt synthesis. Wider application of LiPF₆ started after pure salt, not decomposed with moisture or not containing HF, was possible to obtain. Problematic preparation is one of the big disadvantages of this salt. Special methods were designed for obtaining LiPF₆ without any decomposition before battery application. These all methods need special conditions, like glovebox filled with dry clean inert gas and special anhydrous substrates, which are sometimes difficult to handle. One of the methods is the following synthesis:



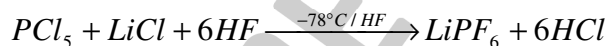
(Where DME is dimethoxyethane).

Special apparatus for reaction is necessary, given lithium hydride is used and gaseous hydrogen evolves, while whole reaction have to be secured against any moisture.

Another method can be made in two ways:

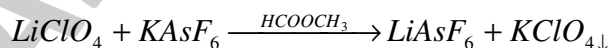


Alternatively, it can be made with LiF produced in situ, thus potentially less contaminated:



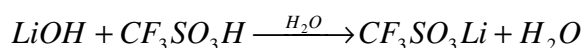
The most important problem of this method is HF handling, which is present in large quantities, being not only a substrate, but also a solvent. This requires special reactor, just like very low reaction temperatures need special treatment to keep it that low, increasing cost in industry-scale production. Finally, the product is mixed with HCl and HF, which keep with the salt in at least trace quantities into the battery. All this makes LiPF₆ synthesis more expensive, problematic and difficult, meanwhile not omitting all problems with the salts (residue HF, the biggest fraction of hydrogen fluoride residue among inorganic salts).

The analogue of LiPF₆, the LiAsF₆ salt, surprisingly is not so difficult to obtain and is not so vulnerable to moisture, like the hexafluorophosphate:

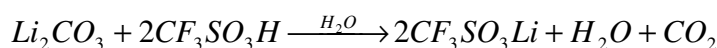


Which is quite easy-to-make reaction and KClO_4 precipitates from the mixture, making separation easier. This time, the main problem is not the reaction, but the toxicity of LiAsF_6 , which disqualifies the salt from application.

Another salt known for quite a long time among lithium salts used or considered for lithium-ion cells is lithium triflate. Its synthesis is as follows:



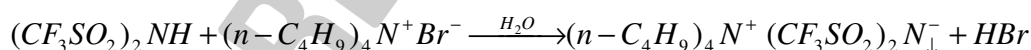
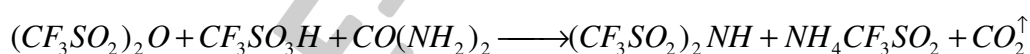
Where the lithium compound can be altered:



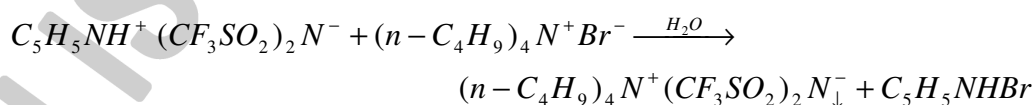
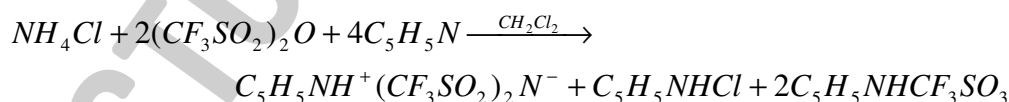
Both reactions are quite easy, taking place in water, in fact being rather a titration, so not demanding any type of heating, also, unlike LiPF_6 , not demanding in terms of dryness. Few cycles of vacuum drying of ready product are needed, though. Low conductivity of this salt was the cause for lack of application in battery industry.

Apart from salts known before 1990 (LiClO_4 , LiAsF_6 , LiPF_6 , LiBF_4 or LiCF_3SO_3), so far there were very few promising introductions of new anions for lithium salts. Examples include LiTFSI ($\text{LiN}(\text{SO}_2\text{CF}_3)_2$), then methide ones, $\text{LiC}(\text{SO}_2\text{CF}_3)_3$, $\text{LiC}(\text{SO}_2\text{CF}_3)_2(\text{RCO})$ and $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ (LiBETI). Unfortunately, all of them, including LiTFSI , LiBETI (Figure 4) and methide anion salts had the crippling drawback of being unable to form a passivation layer on Al current collectors when applied to a cell. $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ and $\text{LiC}(\text{SO}_2\text{CF}_3)_3$ were also claimed to be too expensive for commercial application. Meanwhile, a whole class of sulfone-imide and methide-imide salts was designed and synthesized with no bigger success claimed since their introduction.

The most important and successful of the imide salts class were LiTFSI (ionic conductivity of about $4.25 \cdot 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ in PC at 30°C at $0.6 \text{ mol} \cdot \text{dm}^{-3}$) and LiBETI . Apart from other mentioned problems, their failure to be predominant on the batteries market was due to their synthesis. Two methods of LiTFSI were proposed. In the first one the product is made from trifluoromethanesulfonic (triflic) acid and its anhydride, where both are quite toxic and expensive, especially pure triflic acid:

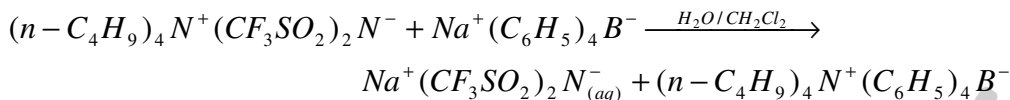


Another method involves pyridine and triflic anhydride:

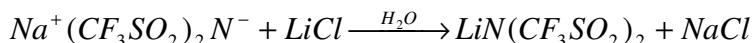


This method avoids using two expensive substrates, but it also gives a lot of by-products, which waste half of triflic groups from anhydride. To obtain the final

product, for both methods ionic exchange has to take place with phase change due to hydrophilic nature of newly created ion pair:

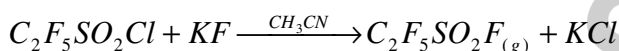
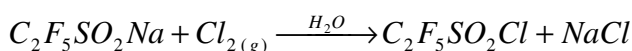
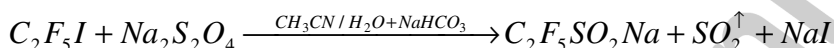


And the synthesis for both methods ends with ionic exchange to lithium salt:

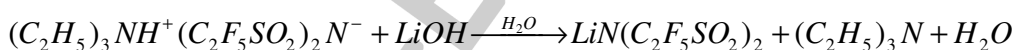


As it can be seen in the above, the synthesis is multi-step and complicated, due to changes of solvents and many intermediate steps related to stripping.

The LiBETI salt also has complicated synthetic procedure, because it involves very low temperatures, expensive reagents and gaseous moieties. Whole procedure is multi-step. First part yields the main substrate for salt production:



Although the substrates for this reaction are quite cheap, the necessity of handling gaseous chlorine, sulphur dioxide or product as well as not very high yield (64 % for whole preparation), make it quite problematic. Then, the substrate (pentafluoroethanesulfonyl fluoride) is used in gaseous form to obtain lithium salt (so the starting temperature is -78°C, increasing while stirred):



Final product is obtained with very high yield (92 %), but due to the first part of the preparation, total yield is lower than 60 %. Several changes of the solvent and frequent cooling to low temperatures (lower than 0°C) for long periods (several hours), handling gaseous reagents and products as well as the need of using very dry reagents makes the whole synthesis quite expensive (due to high energy costs and substrates of required purity prices) and complicated.

A whole new class of orthoborate chelate-type anions (chelatorborates) was introduced by Barthel et al. [9-13] (Figure 4), e.g. lithium bis[1,2-benzenediolato(2-)-O,O']borate (LBBB). Then Xu et al. brought-in borates of lithium bis(oxalato)borate (LiBOB) type and other chelate ones [14-20]. While chelate salts based systems suffered from high viscosity (because of bulkiness of the anion) and as a result, poor conductivity, LiBOB and similar salts electrolyte systems were found to form poorly conducting solid electrolyte interface, which led to low power battery capability. These salts exhibit also poor solubility in commercial-type solvents and, thus, the electrolytes obtained exhibited weaker conductivity. Also, syntheses of croconatoborate class took place, e.g. LiBCB (lithium bis(croconato)borate). Other asymmetrical anion was found in search for the

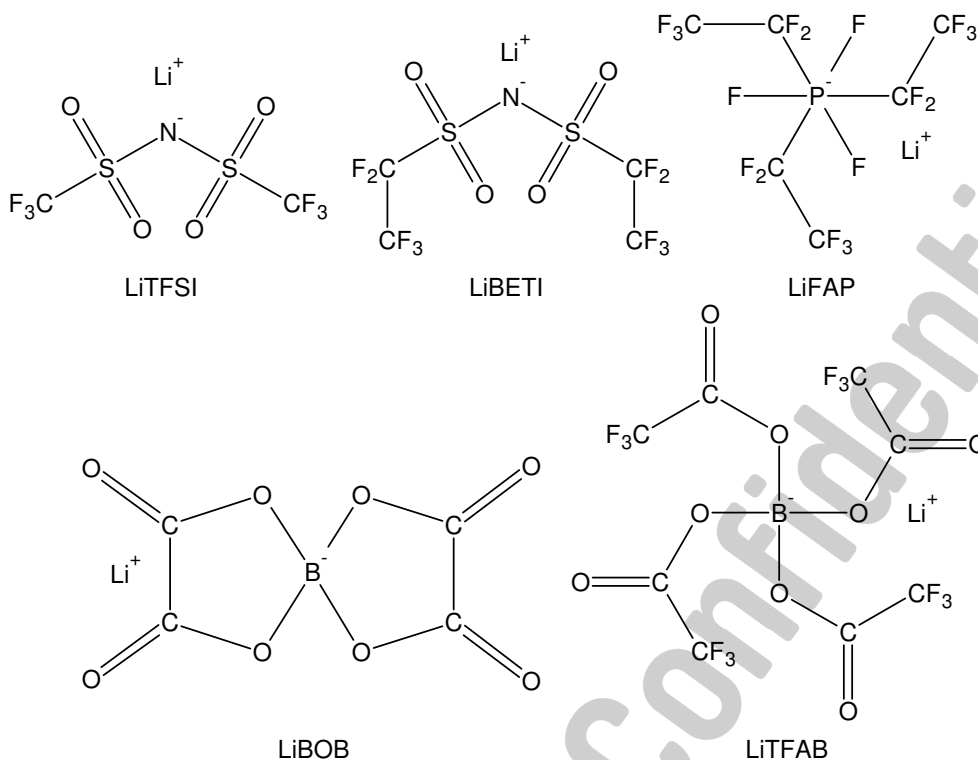


Figure 4. New lithium conductive salts created for application in lithium-ion batteries.

LiTFSI - $\text{Li}[\text{N}(\text{SO}_2\text{CF}_3)_2]$ - lithium bis(trifluoromethane sulfone)imide;

LiBETI - $\text{Li}[\text{N}(\text{SO}_2\text{CF}_2\text{CF}_3)_2]$ - lithium bis(pentafluoroethane sulfone)imide;

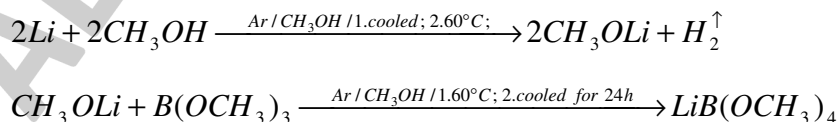
LiFAP - $\text{Li}[\text{PF}_3(\text{CF}_2\text{CF}_3)_3]$ - lithium fluoroalkylphosphate;

LiBOB - $\text{Li}[\text{B}(\text{C}_2\text{O}_4)_2]$ - lithium bis(oxalato)borate;

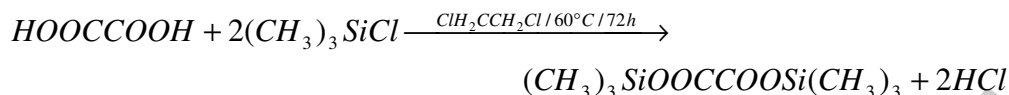
LiTFAB - $\text{Li}[\text{B}(\text{OCOCF}_3)_4]$ - lithium tetrakis(trifluoroacetoxy)borate.

synergy of LiBF_4 and LiBOB advantages – LiDFOB (lithium difluoro(oxalato)borate), which has unfortunately very poor conductivity (order of magnitude lower than LiPF_6). The best of this class was lithium tetrakis(haloacyloxy)borates family (LiTFAB) introduced by Yamaguchi et al. [21], also suffering from low conductivity in the liquid electrolytes (much lower than LiTFSI or LiPF_6). LiBOB, most successful (in commercial terms) from borate-class lithium conducting salts family, has an ionic conductivity of $3 \cdot 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ in PC at 20°C (maximum at $0.5 \text{ mol} \cdot \text{dm}^{-3}$ concentration).

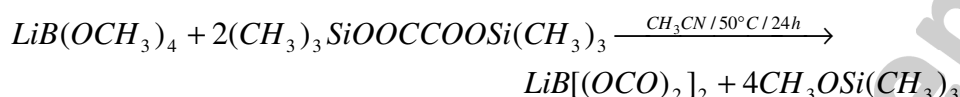
LiBOB salt is the next one, which requires sophisticated substrates that have to be synthesized especially for salt preparation. Hence, the synthesis has two parts. First part is the synthesis of these special substrates, lithium tetramethanolatoborate and di(trimethylsilyl)oxalate (DTMSO). Synthesis of lithium tetramethanolatoborate is as follows:



After 24 hours of crystallization and drying the first substrate is ready. Synthesis of DTMSO is even longer:

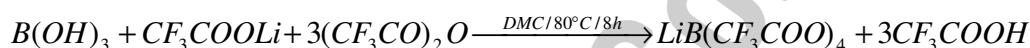


After three days of reaction and further stripping and distillation the second substrate is ready. Then it is possible to obtain the final product, LiBOB:



Thus, the LiBOB is produced, but similarly to previously described synthesis, it is quite long, energy-costly and involves special requirements such as high purity argon atmosphere and very dry (anhydrous) solvents. That makes the LiBOB synthesis quite expensive.

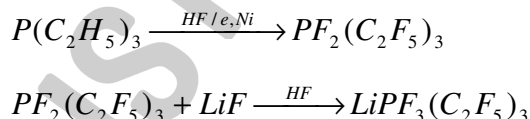
LiTFAB, a second popular borate-class lithium salt has much easier and less expensive preparation way:



The lithium tetrakis(trifluoroacetoxy)borate(LiTFAB) and its class are faster and with less energy-costly to obtain than most of previously described lithium salts. It is also very short, while it is only one-step process. Unfortunately, it is still quite expensive due to pure trifluoropropionic anhydride cost, especially that it is used in 3 to 1 ratio in regard to product yield.

Another approach to lithium conducting salts was to introduce phosphate salts, e.g. $\text{LiPF}_3(\text{CF}_2\text{CF}_3)_3$ (LiFAP) (Figure 4) and chelatophosphate salts, e.g. lithium tris[1,2-benzenediolato(2)-O,O']phosphate or lithium tris(oxalato)phosphate. Unfortunately, the first one is too expensive to be applied in commercial cells and the others lacked high conductivity in liquid solvents - again due to the high viscosity of the obtained electrolyte caused by the large anion size.

LiFAP has the ionic conductivity lower than LiPF_6 - in optimized mixture of EC:DMC (1:1) at $0.8 \text{ mol}\cdot\text{dm}^{-3}$ concentration (at 25°C) it has about 80 % of LiPF_6 conductivity ($8.6\cdot 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ of LiFAP vs. $10.3\cdot 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ LiPF_6). One can assume that in solitary solvent, like PC, ionic conductivity of LiFAP would be lower. LiFAP has very simple preparation scheme - through the electrochemical reduction of tris(trifluoromethyl)phosphine oxide:



This method is quite fast (two step process, one solvent), although not exactly easy, due to electrocatalysis usage. Also the substrates are very dangerous, special treatment and extreme precautions are needed due to both phosphine and hydrogen fluoride usage. There is also need of only anhydrous hydrogen fluoride use. Also,

the phosphine is not an inexpensive substrate so to sum it up, given that the reaction yield is not very high (49-74 %), the whole reaction is quite expensive.

A few other ideas appeared along the years, such as using BF_3 compound as an electron-withdrawing group in, among the others, imidazole anions [22]. Low conductivity (much lower than LiPF_6) of such salts applied as the electrolytes is the main drawback of this approach. The problem was, just like in case of borate chelate complexes, too big volume of the anion, making local viscosity big, and hence, decreasing ionic conductivity drastically.

The idea of application of sulfonyl fluorides (like $\text{PhS}(\text{CF}_2)_n\text{SO}_3\text{Li}$) as the new salts for electrolyte systems was also presented [23]. So far the only existing conductivity data for this salt have shown the results only slightly better than for LiTf (LiCF_3SO_3).

There were also other salts, based on other than before mentioned compound classes, that were suggested in the past for potential application in lithium-ion cells, e.g. $\text{LiAl}[\text{OCH}(\text{CF}_3)_2]_4$. None of them was a big success though.

As should be pointed out, the novel salts for application in lithium batteries still are to be discovered. However in most cases the same salt can be dissolved in all three types of solvent under consideration in this report. These new possibilities offered by systems known as organic salts will be discussed in the following sections.

Other simple modifications of liquid electrolytes relay on the application of various types additives which modify safety, ionic transport as well as the properties of electrodes-electrolyte interfaces. Their effect was discussed extensively in the recent review [5] and was also a matter of discussion in previous white papers (on safety issues and on evaluation of lithium battery technology and would not be a matter of discussion here. Interested reader are welcome to use above mentioned references.

Polymer Electrolytes

Among solid ionic conductors (not discussed in this paper as such) there is a class of materials called solid polymer electrolytes. They are "complexes" of electrodonor polymers with various inorganic or organic salts or acids. The main requirements for the polymer to be used as a matrix in polymer electrolyte systems are:

- the presence of an heteroatom (usually O, N, S) with lone electron pairs of a donor power sufficient to complex cations,
- appropriate distances between coordinating centres to insure the hopping of charge carriers, and
- sufficient flexibility in polymer chain segments to facilitate movements of ionic carriers.

In polymer electrolytes ionic transport occurs in a highly viscoelastic (solid) state. The most intensively studied polymer electrolytes are based on poly (oxa alkanes), poly (aza alkanes) or poly (thia alkanes). The present paper deals mainly with polymer electrolytes

based on poly (oxa alkanes) - polyethers and particularly on alkali metal salt complexes with poly(ethylene oxide) (PEO). These various application possibilities have stimulated further investigations of solid polymer ionic conductors. The most important and universal properties of polymeric electrolytes for application in lithium cells are as follows:

- chemical and mechanical stabilities over a wide temperature range,
- electrochemical stability of at least 3-4 V versus a Li electrode; especially important for battery applications
- low activation energies for conduction
- high cationic transport numbers
- good electrode - electrolyte characteristics
- ease of sample preparation.

The range of conductivities required depends on the kind of application and is equal to 10^{-1} - 10^{-2} S/cm for fuel cells and 10^{-3} - 10^{-4} S/cm for batteries; conductivities can be lower for sensors and electrochromic windows applications.

As can be expected from the above list it is not easy to find an electrolyte fulfilling all the desirable properties. Despite a very intensive search there is still a considerable number of unsolved problems connected with the fundamental understanding, synthesis and applications of polymeric electrolytes. This results mostly from the complicated phase structure of the materials. Such a complicated phase structure causes difficulties in the interpretation of ionic transport phenomena in polymeric electrolytes. Therefore the mechanism of conduction in polymeric electrolytes is difficult to establish. Several concepts have been proposed and clearly summarized in recent review papers [24] but none of them is generally valid for the wide range of materials under consideration at the present time.

The advantages of using solid polymer electrolytes in commercial lithium cells (up-to-date systems of choice for mobile applications) compared to liquid electrolytes described above could be numerous:

- non volatility,
- no decomposition at the electrodes,
- no possibility of leaks,
- use of metallic lithium in secondary cells (lithium dendrites growing on the electrode surface would be stopped by the non-porous and solid electrolyte),
- lowering the cell price (PEO is cheaper than organic carbonates; it could be used as a binder for electrodes to improve the compatibility of consecutive layers; moreover fabrication of such a cell would be easier – hence cheaper),
- strengthening of cells thanks to the all-solid-state construction,
- shape flexibility,
- lowering the cell weight – non-volatile, all-solid-state cells don't need heavy steel casing,

- improved shock resistance,
- better overhear and overcharge allowance,
- improved safety.

Berthier et al. [25] have shown that fast ionic transport takes place in the amorphous electrolyte phase in which ionic diffusion coefficients are about three orders of magnitude higher than in the crystalline phases. Berthier's assumption of the crucial role that an amorphous polymer phase plays in ionic conductivity forms the basis for some of the proposed conductivity mechanisms, such as free volume [26], configurational entropy [27,28] or dynamic bond percolation [29-33]. These models are mainly successful in quantitatively describing conductivity mechanisms for simple monophasic amorphous electrolytes and are not valid for multiphase systems.

The assumption of Berthier [25] requires high amorphous phase content for fast ionic transport in polymeric electrolytes. As is demonstrated by configurational entropy and dynamic bond percolation theories the flexibility of the amorphous polymer phase is of crucial importance for conduction since ion and polymer segmental motions are coupled for good conductivity. Therefore a low glass transition temperature (T_g) for the amorphous polymer phase is a desirable property. Unfortunately, the polyether-salt complexes which are the most widely studied systems are those that are highly crystalline at ambient temperatures. Here their conductivities are in the range 10^{-7} - 10^{-8} S/cm which is too low for most applications. The amount of flexible amorphous phase increases on approaching the melting point of the crystalline polymer phase i.e. 65-68°C. However, at temperatures exceeding the melting point the mechanical stability of electrolytes is much lower and membranes often creep under the pressure applied in electrochemical devices leading to shortcircuiting effects.

In spite of all the limitations mentioned above, semi-crystalline PEO still has attracted the highest attention as the best highly viscous polymeric matrix. The main goal of work devoted to polymeric electrolytes is to obtain a stable amorphous system containing a high amount of ethylene oxide molecular repeat units in a main or side chain. The various modifications of PEO based electrolytes can be divided into three main categories.

First, is the preparation of amorphous polymer matrices in which the ether segments consist of 4-15 ethylene oxide monomeric units. These are long enough to effectively complex alkali metal cations but too short to show a tendency towards crystallization. Examples are polymer networks, random and block ethylene oxide copolymers and comb-like systems with short chain ethylene oxide sequences.

Second, is the utilization of an appropriate ionic dopant, one which tends to form complexes having low temperature eutectics with the pristine PEO phase. These are the so called plasticizing salts.

Third is the addition of substances which reduce the crystallizing ability of the polyether hosts.

From the viewpoint of easy preparation as well as commercial application the last idea is the simplest one. Below a main methods of modification of polymeric electrolytes are

briefly described. The reason for spending a bit more space is that polymeric electrolyte were not widely present in the preceding white papers which on the other hand summarize a few concept used to modify liquid systems.

MODIFICATIONS OF POLYMER SOLID ELECTROLYTES BASED ON POLYETHERS

Polymer networks

Crosslinked polymers exhibit a much lower tendency to crystallize and better mechanical properties than linear ones. Most of those that were tested as matrices for polymeric electrolytes were prepared using crosslinking agents (typically isocyanates) with polyether type diols or triols. The reactions with isocyanates lead to the preparation of crosslinked polyurethane structures which were mostly studied by Cheradane's group [34-36]. As was suggested by Cheradane and Le Nest [34] the optimization of the conductivity of a polymer network is achieved for a system with PEG molecular weight equal to $1000n$, containing $2n-1$ mol of lithium ions per mole of PEG units. As can be expected crosslinking with isocyanate reduces the flexibility of the polyether chains which is manifested by an increase in the T_g value. It was generalized by Cheradane [34] that for a variety of networks doped with LiClO_4 , T_g changes according to the following equations:

$$1/T_g = 1/T_{g0} - 7.6 \cdot 10^{-4}C \quad (1) \text{ - for the salt free polymer,}$$

$$\text{and } 1/T_g = 1/T_g' - 2.7 \cdot 10^{-4}C' \quad (2) \text{ - for salt complexed network.}$$

Here, C is the crosslink concentration, T_{g0} is the glass transition temperature at $C=0$, C' is the salt concentration, and T_g' is the glass transition temperature of the salt free network.

The above equations are independent of the kind of crosslinking agents used. This is explained by the fact that the free volume of the network is only a function of the interactions between the salt and polymer chains. In fact the addition of a salt provides additional transient crosslinking in the polymer host. The crosslinking effect of a salt is quite high and equal to one third of that of any crosslinking agent. Increasing the T_g by crosslinking reduces conductivities in spite of the fact that the system is completely amorphous. This observed effect is attributed to the presence of hydrogen bonding and Van der Waals interactions between urethane linkages and the surrounding polyether. Additionally the presence of bulky groups introduced by the addition of isocyanates sterically hindered ionic motion of the electrolyte. Therefore in spite of an improvement of the mechanical stability of PEG based systems chemical crosslinking has a rather negative effect on electrolytes' conductivity. Watanabe and co-workers [37] have studied polyurethane networks based on crosslinked low molecular weight poly(propylene glycols) - PPG. The effect of a crosslinking agent and salt concentration was found to be similar to that described above for PEG based systems. Ambient temperature conductivities of PPG networks were in the range 10^{-7} - 10^{-10} S/cm. The same group [38] also utilized a block PEO- poly(ethylene urethane urea) network. The amount of poly(ethylene urethane urea) was equal to about 30 weight % and provided excellent mechanical stability for the electrolyte. Salt dissolved selectively in the polyether part gave an enhanced conductivity

after approaching the percolation threshold which results in a continuous conduction path [38]. Polyelectrolytes [39] with a cationic part bonded to the network were also prepared but their conductivities were considerably lower. Considering the above mentioned results polymer networks of an enhanced chain flexibility should be introduced.

Triblock copolymers incorporating EO segments were subjected to a crosslinking reaction with isocyanates by Cheradame [34,35] and Gray [40,41]. Cheradame prepared triblock PEO-PPO-PEO copolymers. The role of this system was to reduce the polyurethane crosslink density and hence also to keep T_g in the range typical for polyethers. It was felt that the stiffening effect of the urethane functionals and their role as barriers to ionic mobility could be attenuated if

- PEO oligomers bearing NCO-end groups could be prepared and
- their reaction with OH groups took place away from a branching point.

The synthetic route which opened the way to such novel structures was based on the transformation of commercial PEO diamines into the corresponding diisocyanates by reaction with bis(trichloromethyl)carbonate and subsequent condensation of these bifunctional oligomers with commercial PEO triols [42]. The networks resulting after doping with lithium salts exhibited conductivities in the range 10^{-5} - 10^{-4} S/cm at ambient temperatures.

A Scottish group [40,41] has bonded PEO segments as a central part B of a triblock - [A-B-A]- type copolymer with a styrene - butadiene - styrene copolymer acting as part A. Host materials are of elastomeric form and the triblock system occurs as a self supporting rubber of conductivities of 10^{-5} S/cm at room temperature. Giles [43,44] has synthesized amorphous phosphate esters. After the addition of LiCF_3SO_3 polymer electrolyte samples exhibit ambient temperature conductivities of about 2×10^{-5} S/cm. However, the most pronounced effect of increasing network flexibility was achieved by the incorporation of siloxane units into the polymer framework. Cheradame's group [35,36,45] has studied systems based on poly (dimethylsiloxane). Conductivities of about 10^{-5} - 10^{-4} S/cm at room temperature for the system doped with LiClO_4 were reported and the electrolytes were mechanically stable up to 120°C . Similar results were obtained by Fang et al. [46] and Wnek [47] for their siloxane networks. Ugumi and co-workers prepared crosslinked siloxane based electrolytes via plasma polymerization of tris (2-methoxyethoxy) vinyl silane [48-51]. Such crosslinked systems exhibited ambient temperature conductivities of about 5×10^{-5} S/cm.

It should be stressed that even for a crosslinked system with enhanced chain flexibility it is rather difficult to approach 10^{-5} S/cm for ambient temperature conductivity in network based systems. Therefore in spite of valuable mechanical properties chemically crosslinked polymer networks have conductivities which are still too low for practical applications. It should be mentioned that besides chemical crosslinking, physical process involving gamma, X-ray or UV irradiation have been widely used to produce polymer electrolyte networks. In high molecular weight polymer electrolytes γ -irradiation was used to prevent the recrystallization of the melted electrolytes and stabilize their amorphous structure [52-54]. The polymer electrolytes from PEO- LiClO_4 and PEO- LiCF_3SO_3 systems were melted at 78°C and then subjected to γ -irradiation from a ^{60}Co source. The amorphous structure was only stable for the PEO- LiClO_4 system which in fact was

completely amorphous at the temperatures of melting. The presence of crystalline phases in the PEO-LiCF₃SO₃ structure allows the system to recrystallize after crosslinking.

As can be seen the crosslinking of polymer hosts does not lead to the formation of electrolytes having sufficient conductivities for ambient temperature applications. However, it results in an improvement in the mechanical properties of the polymeric systems that enables them to work even at temperatures higher than the melting temperature of the crystalline PEO phase. Crosslinking is also very useful to ensure the mechanical stability of gel polymeric electrolytes containing high amounts of plasticizer.

Ethylene oxide copolymers

It is well known in polymer chemistry that copolymers usually exhibit a much lower tendency to crystallization than homopolymers. This is why in many laboratories a lot of effort has been made to obtain copolymers containing EO segments long enough to complex effectively cations but too short to form a crystalline phase.

The first totally amorphous copolymers of ethylene oxide (for electrochemical applications) were obtained by Nicholas et al. [55,56] via the condensation of poly(ethylene glycols) with methylene bromide according to the classical Williamson type reaction. In these polymers the ethylene oxide segments of chosen length were separated by single CH₂ groups which was sufficient to stop crystallization. The matrices were very flexible as indicated by the relatively low T_g. For the optimum number of EO units (5) the room temperature conductivity after doping with lithium salts was found to be 1-5x10⁻⁵S/cm. Since the structure of this copolymer is very close to that of PEO this conductivity value is believed to be characteristic for the amorphous phase of PEO.

The linear ethylene oxide - (EO) copolymers with regular lengths of EO segments can also be prepared by ring opening polymerization of appropriate cyclic monomers, like dioxolanes [57], cyclic phosphoric acid esters or 12-crown-4 ethers. However, the number of EO units in repeating units is too short to achieve very high conductivity after doping. At room temperature σ is higher than for the analogous system with PEO, but significantly lower than that expected for the amorphous phase of PEO. Thus these very elegant synthetic methods are of rather no practical importance.

It was demonstrated that random copolymerization of EO with propylene oxide, styrene oxide or epichlorohydrin in the presence of partially hydrolysed organoaluminum compounds produced amorphous products which, at an appropriate composition and after doping with inorganic salts, exhibited higher conductivity than analogous electrolytes based on PEO [58-61]. The best results were obtained for a copolymer with propylene oxide of an average length of EO segments equal to 5. It is interesting that after doping with lithium salts this copolymer exhibits a significantly lower T_g than systems based on PEO. It is equal to about 210K, whereas in PEO electrolytes the T_g values are equal to 240-250K. The maximum room temperature conductivity measured for the copolymer based electrolytes exceeded 10⁻⁴S/cm, which is higher than expected for pure amorphous electrolytes having PEO chains. Furthermore, this copolymer electrolyte had a higher conductivity than pristine PEO at temperatures exceeding the

melting point of the PEO crystalline phase. These observations let us conclude that the copolymerization may lead not only to the elimination of crystallinity but also to an improvement in ionic mobility and thus the conducting properties of the amorphous phase. This probably results from the internal plasticization of the polymeric matrix due to the presence of a small amount of methyl groups introduced by propylene oxide monomeric units.

Detailed studies of the role of the kind and concentration of alkali metal salt on the conductivity of copolymer electrolytes were performed for PEO-PPO system comprising 84mol% of EO monomeric units [61,62]. The temperature dependence of conductivities for samples doped with various lithium salts. The highest conductivities, exceeding 10^{-4} S/cm at ambient temperatures, are measured for copolymers doped with LiBF_4 . However, it is clearly seen that highly conductive fluoroborates and perchlorates flow at temperatures slightly exceeding 40°C whereas iodide and fluoroacetate doped electrolytes are mechanically and thermally stable up to 100°C .

Using the same type of organoaluminum catalysts Ballard et al. [63] obtained a large number of EO copolymers with various co-monomers and prepared many electrolytes with room temperature conductivity above 10^{-5} S/cm. Therefore this relatively simple method of modification seems to be quite general. It is crucial that the differences in co-monomer reactivities in the presence of aluminium based catalysts are not significant. Thus it is possible to prepare a statistical distribution of co-monomers which provided these systems with appropriate lengths of EO segments (4,5,6 monomeric units).

Conductivity of polyether based matrices by introducing highly polar co-monomers like CO_2 or SO_2 was also investigated [64,65]. However, the polycarbonates obtained in the reaction with CO_2 turned out to be very poor conductors in spite of the fact that their low molecular weight analogue cyclic carbonates are regarded as the most suitable aprotic solvents in liquid electrolytes. Polysulphites and poly(ether sulphites) obtained in copolymerisation of SO_2 with EO exhibited only slightly better conducting properties than PEO. DSC studies showed that polysulphites exhibited stronger cation complexing properties than PEO, thus the strong interaction between the chain and cation might reduce the mobility of charge carriers. A similar problem is observed in some matrices comprising polyamines. Polysulphites interact very strongly with PEO chains and hinder its crystallization. Thus mixtures of PEO and polysulphites exhibit very good conducting properties.

Comb-like copolymers form another group of amorphous matrices for polymeric electrolytes. There are systems in which short chain coordinating oligomers are attached to inert polymer backbones. The role of a backbone was to maintain the mechanical stability of a polymer electrolyte whereas short side chain polyglycols [$n=7-22$] complexed cations. At the beginning high T_g metacrylates were used as main chain polymers [66-69]. The highest conductivities achieved in the systems studied are in the range 10^{-5} - 10^{-6} S/cm. Similar conductivities were obtained for comb-like systems utilizing polyitaconates [70] or poly (γ -methyl-2 gluconate) as main chains. Conductivity depends strongly on the length of the pedant chain glycol groups as well as on the kind and concentration of the salt added [71]. The dependence on the structure of the main chain was negligible. It was assumed that substitution of the rigid main chain by flexible polyphosphazene ($T_g=-70^\circ\text{C}$) or polydimethylsiloxane ($T_g=-120^\circ\text{C}$) backbones would provide better ambient temperature conductivities of the comb-like systems.

A series of polysiloxane electrolytes were synthesized by Nagaoka [72], Hall [73] and Smid et al. [74-77]. High conductivity values exceeding 10^{-4} S/cm at room temperature were obtained for all of the samples studied. The electrolytes were prepared in the form of a liquid or wax rather than a solid. For some of the electrolytes recrystallization of side chain polyglycols was evident. The mechanical properties can be improved and recrystallization suppressed by crosslinking which in fact lowers the conductivity by an order of magnitude. Additionally Si-O-C bonds are easy to hydrolyse in the presence of traces of moisture and therefore substantial degradation of the electrolyte structure occurs. The stability of Si-C bonds is much higher than Si-O-C bonds and therefore the comb-like polysiloxanes were also synthesized [78]. Skotheim et al. [79] obtained comb-like polyelectrolytes based on comb-like polysiloxanes of conductivities of 10^{-5} - 10^{-7} S/cm. Nevertheless the liquid-like structure of this group of electrolytes is still a limitation in applications.

Blonsky and co-workers have synthesized a wide range of polyphosphazene based electrolytes by the polycondensation reaction of poly (dichloro- phosphazene) with sodium salt of 2-(2-methoxyethoxyethoxy) ethanol [80,81]. The polymers were doped with various salts showing the strong dependence of the structure on the kind of dopant and its concentration. The structure of polymeric membranes changed from a flexible plastic to a rigid rubber with an increase in salt concentration. This was accompanied by a considerable increase in T_g . Studies of the role of kinds of cations on ionic conductivity and cation transference number were performed [81] for a series of triflate salts and showed that the highest conductivity values are obtained for samples doped with AgCF_3SO_3 ($\sigma = 10^{-5}$ - 10^{-4} S/cm at room temperature, $t_+ = 0.32$). Assuming a very short side chain complexing polyglycol sequence main chain nitrogen or phosphoric atoms seem also to be involved in complexation of cations.

Polyphosphazene based electrolytes usually exhibit a weak temperature dependence for ionic conductivity. The main limitation towards their application in electrochemical devices is related to poor mechanical properties. Linear polyphosphazenes flow under pressure, particularly at temperatures exceeding 70°C . To avoid mechanical instability of the comb-like polymer electrolytes studied several methods of modification have been applied leading to an increase in the mechanical modulus of the polymer host [65-66]. It is now believed that the limitations of polyphosphazene usage are not only due to poor mechanical stability but also due to a low electrochemical stability window for these electrolytes. Cyclic voltammetry experiments showed degradation of the electrolyte at potentials higher than 1.6V versus lithium electrode which is considerably lower than for PEO based systems [82].

To summarize; copolymer based solid electrolytes exhibit high ambient temperature conductivities but their electrochemical stability was not studied. Preliminary studies [60] in a cell utilizing transport lithium electrodes showed similar behaviour to that previously reported for PEO complexes studied above the melting point. The formation of resistive layers at the electrode - electrolyte interface is seen. Poor mechanical stability is a limitation in any application. Furthermore, copolymer matrices of high conductivity are not commercially available.

Single ion conducting polymer electrolytes

Polyelectrolytes are systems in which one of the conducting species (anion or cation) is chemically bonded to the polymer backbone. The counter ion (either positive or negative), which is outside the backbone, makes the system electro neutral. Usually the dielectric constant of the polyelectrolyte is too low to ensure the dissociation of the polyelectrolyte system into separated anions and cations. Therefore an highly polar organic solvent or water is added which increases the dielectric constant of the system and causes dissociation. In polyelectrolytes ionic transport occurs in a quasi liquid phase e.g. counter ions move in a polar solvent trapped in a polymer membrane. A typical example of such a polyelectrolyte is Nafion proton conducting membrane in which anions are bound to the polymer chain and protons are the counter ions. In polyelectrolytes either the cation or the anion transport number is equal to unity. However, special interest is still devoted to the preparation of polyelectrolytes in which ionic transport will occur in a solid state. Such a concept was realized by the blending of polyethers with perfluorinated polyelectrolytes, like Nafion or Flemion reported as alkali metal conductors by Tsuchida [83]. For such systems conductivities of $5 \times 10^{-5} \text{ S/cm}$ at ambient temperatures have been reported.

In standard polymeric electrolytes both the cation and anion are mobile and the anion transference number is usually greater than for the cation. The synthesis of single cation conductive flexible polymer electrolytes is especially important for application in alkali metal batteries. During the long-time performance of a battery (in which both electrodes are transporting against cations but blocking against anions) bulky anions agglomerate near the anode and form a charge layer. This layer interacts with the anode leading to an increase of the overall electrode-electrolyte interface impedance. Moreover the cation transport from the anode to the bulk of an electrolyte is impeded by the layer formed.

In order to obtain a single cation conducting system the counter ions should be sufficiently large or chemically attached to the backbone as in the case of typical polyelectrolytes. However, it was demonstrated by M.Armand et al. [84] that even relatively bulky anions are free to move in the PEO matrix. Experiments on a series of salts of the general formula $\text{LiC}_n\text{F}_{2n+1}\text{SO}_3$ ($n=1-25$) showed that the highest conductivities were obtained for an electrolyte with $n=14$ followed by only a small decrease in conductivity for electrolytes with larger anions. Meyer and co-workers [85] have studied a large group of ionenes as single (cation or anion) polymer electrolytes. Most of the systems studied showed moderate conductivities at temperatures exceeding 100°C due to the stiffness of the main ionene chain as well as due to tight ion pairing occurring in the polyelectrolytes in absence of polar liquid solvents. Many other systems based on the nylon-1 backbone [85], polyphosphazenes [86] or poly(olygo (oxyethylene methacrylate-co-alkali metal methacrylate)) [87,88] or polybrene [89] were studied but their conductivities hardly exceeded $10^{-7}-10^{-8} \text{ S/cm}$ at around 100°C ; far too low for application in electrochemical devices.

Ohno and co-workers [90] have performed systematic studies on the effect of the kind of alkali metal salt cations used on the conductivity of polyelectrolytes based on the poly $[(\omega\text{-carboxy})\text{-oligo (oxyethylene) methacrylate}]$ system. It was shown that conductivity increases with increasing size of the alkali metal cation from lithium to

cesium. Opposite results were reported by Florjanczyk and co-workers for comb-like polyelectrolytes based on half esters of maleic anhydride - styrene copolymer with PEG [58,91]. As one can see in this system an ion-pair is located close to the complexing oxyethylene segments which enables relatively easy dissociation. For the small lithium cation the optimum number of EO molecular units was equal to 6 whereas for the larger potassium cation the optimum number of EO molecular units was equal to 12. The conductivity for some lithium salts is just on the border line of the 10^{-5} S/cm required for practical applications. The easy way of samples preparation and commercial availability of the substrates used is also an advantage of the system proposed.

Plasticized polymer systems and polymeric gels

It is well known in polymer chemistry that the addition of a plasticizer increases the flexibility of host polymer chains. The plasticizer applied should fulfil the following requirements:

- decrease the crystallinity and increase the mobility of the host polymer below its melting temperature,
- be miscible with the amorphous polymer phase to which a dopant salt is added,
- have a low vapour pressure in the temperature range studied,
- be stable against electrode material (this is especially important considering the high reactivity of the lithium electrode)

Low molecular weight polyglycols are often used as plasticizers added to PEO-alkali metal salt electrolytes. Kelly and co-workers [92,93] and Tsuchida et al. [94] have examined the role of the polyether end group on their plasticizing properties and the behaviour of the plasticized electrolyte. It was shown that hydroxyl end capped PEG can dissolve much more salt than end O-acetylated PEG thus giving rise to an increase in conductivity. On the other hand end-hydroxyl groups react with lithium leading to the formation of resistive interface layers [92]. Kelly et al. [93] has suggested the utilization of poly(dimethoxy ethylene glycols) - (PEGDME) which are more stable against lithium than their hydroxyl end capped analogues. The addition of PEGDME to a $(\text{PEO})_8\text{LiCF}_3\text{SO}_3$ electrolyte resulted in an increase in conductivity of up to 5×10^{-5} - 10^{-4} S/cm at ambient temperatures. Wang et al. [95] studied electrolytes of the following general formula; $\text{LiCF}_3\text{SO}_3 (0.5\text{PEO}+0.5\text{Y})$, where $\text{Y}=\text{PEG}$, ($M_w=600\text{g/mol}$), and LiPEG ($M_w=600\text{g/mol}$) and PEGDME ($M_w=400\text{g/mol}$) and PEGDME ($M_w=750\text{g/mol}$). DSC experiments showed a decrease in T_g from -21°C for the non-plasticized $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$ electrolyte to -48°C for plasticized systems independent of the plasticizer used. NMR experiments have confirmed an increase of the segmental mobility of the polymer chains after the addition of a plasticizer. The highest increase of conductivity was measured for electrolytes containing PEG ($\sigma_{\text{rt}}=10^{-5}$ S/cm) and the lowest for samples with the LiPEG additive ($\sigma_{\text{rt}}=10^{-6}$ S/cm).

It should be stressed that electrolytes based on plasticized linear polymers are often of poor mechanical stability. This disadvantage greatly limits the possibility of their application. As was already mentioned crosslinked polymers provided electrolytes of a

much better mechanical stability. Three phase systems consisting of polymer network and a solution of inorganic salt in low molecular weight polar solvents form polymer gels which are currently intensively studied in many laboratories. The gels differ from standard polymer electrolytes since the charge transfer occurs mainly in the plasticizer phase containing the dissolved salt and the polymer plays the role of a supporting flexible matrix. Nevertheless it should be noted that, recent molecular modelling calculations by G. Farrington [96,97] point out that the polymer phase may contribute somewhat to ionic transport in gel electrolytes. The exact nature of polymer-plasticizer-salt interactions is complicated and not easily understood. The effect of the concentration of the salt on the conductivity of gel electrolytes has resulted in some contradictory observations. Some authors reported an increase in conductivity with an increase in the amount of salt added [98,99]. Others stressed the importance of salt to plasticizer ratio [94,100,101]. It was assumed [102] that up to certain critical salt concentrations the conductivity increases and above these concentrations is almost independent of the salt concentration. The value of this critical concentration is strongly dependent on the salt to plasticizer ratio. The highest conductivities can be obtained for plasticizers characterized by low viscosity and high dielectric constant. However, since an increase of bulk viscosity is generally related to an increase in the dielectric constant the later requirement is not easily achieved.

Assuming the crucial role of the liquid phase, the electrical properties of a polymer host are often unimportant. Therefore it is not necessary to utilize ionically conductive macromolecules. Many polymers, like polystyrene, poly(vinyl chloride), poly(vinyl acetate), polyacrylonitrile-(PAN) and poly(vinyl difluoride) (PVdF) [98,100-102] were treated as matrices for polymer gels. It was found that only polymers possessing high dipole moment like PAN or PVdF are suitable candidates. DMF, PC-propylene carbonate, EC-ethylene carbonate, H₂O, PEG were used as plasticizers. Assuming the possible application of polymer gels in lithium batteries only substances stable against lithium are of considerable interest. Therefore PC and EC as well as methoxy endcapped PEG are mostly used as plasticizing agents. The range of conductivity achieved at ambient and sub-ambient temperatures is 10^{-4} - 10^{-3} S/cm. It should be stressed however, that polymer gels suffer from the drawbacks observed in lithium devices utilizing organic lithium electrolytes, like PC-LiClO₄. This is mainly due to the application of viscous highly polar organic solvents, which, as is pointed out in a recent review paper, are unstable when in contact with lithium [103]. Scrosati [104] reported on the formation of dendritic structures in lithium batteries utilizing gel electrolytes which lead to shortcircuiting in the devices. Therefore studies of the electrochemical stability of gel electrolytes is of particular importance.

Hong et al. [105] studied the electrochemical stability of the PAN- (EC + PC)-LiClO₄ system by impedance spectroscopy in a symmetric lithium cell. Interfacial resistance increases during the first two days of experiments and becomes stable. The increase in the interfacial resistance was attributed to the formation of passivating layers which are usually observed after the contact of an organic solvent with lithium. The conductivities achieved were about 10^{-4} - 10^{-3} S/cm at room temperature.

Various groups have intensively studied the so-called MHB electrolyte introduced primarily by Lundsgar et al. [106,107]. The gel was based upon matrices obtained by radiation induced curing of ethylene glycol dimethacrylate or trimethylpropane trimethacrylate. PC, EC or their mixtures were used as plasticizers and LiCF₃SO₃,

LiClO_4 , or LiAsF_6 were applied as dopant salts. It was shown that mixing two plasticizers increases the thermal stability of the gel electrolytes as well as extending their stability window towards the lithium electrode [108]. The widest stability window was obtained for a PC to EC ratio equal 1:1. The gel obtained was only slightly less conductive ($\sigma_{\text{rt}}=8 \times 10^{-4} \text{ S/cm}$) than gels plasticized with pure PC ($\sigma_{\text{rt}}=2.3 \times 10^{-3} \text{ S/cm}$). Even more important, the formation of lithium dendrites was not observed when gel electrolytes based on this plasticizing mixture was used in a microbattery. The mass loss of the described gel electrolytes was found to be less than 35% by weight at temperatures lower than 150°C . The sub-ambient temperature conductivities are still within the 10^{-3} S/cm range. Lithium batteries utilizing such an electrolyte are capable of producing current densities of up to 30 mA/cm^2 for over 1 minute.

Polymeric gels prepared by the polymerization or copolymerization (with various vinyl monomers) of glycidyl methacrylate and carried out in a plasticizer environment were also examined by our group [109,110]. It was shown that various methods of crosslinking lead to different flexibilities of the polymer hosts and therefore to different ionic conductivities. The highest conductivities were obtained for polymer matrices utilizing copolymers of polar substances, such as acrylonitrile or acrylamide crosslinked in reactions with SO_2 [109]. The ambient temperature conductivities of such derivatives exceeded $4 \times 10^{-3} \text{ S/cm}$. It was also recognized that the utilization of lithium triflate as a dopant salt lead to conductivities of about one order of magnitude lower in comparison to complexes of LiClO_4 . Additionally cationic conducting comb-like electrolytes previously studied by us were plasticized with propylene carbonate [110]. The addition of about 30% by weight of the plasticizer lead to an increase of conductivity to $5 \times 10^{-4} \text{ S/cm}$ at ambient temperatures.

To summarize, despite the several advantages of polymer gel technology there are also severe drawbacks in these systems. The main one is the utilization of highly polar organic solvents which are very active in contact with alkali metal electrodes. The chemical and electrochemical processes occurring at the alkali metal electrode (especially lithium) - gel electrolyte interface lead to the formation of passive layers with resistances exceeding the bulk resistance of the electrolyte. As has been already mentioned the formation of lithium dendrites across the cell leading to short-circuiting effects can also not be excluded.

ADDITION OF SPECIALLY DESIGN FILLERS AS A METHOD TOWARDS INCREASE IN LITHIUM TRANSFERENCE NUMBERS

Inorganic fillers with specially designed surface groups

One of the most successful approaches to modify the structure of polyether based electrolytes was to synthesize composite polymeric electrolytes. Originally the aim to use composite polymeric electrolytes was to increase the ionic conductivity of the PEO based system in ambient temperature range. The initial idea of the mixed phase

systems comprising polymeric electrolytes with fillers composed of ceramic fast ionic conductors was based on the expectation to get percolation pathways composed of inorganic fillers grains through the polymeric matrix. Such phenomenon could lead to an increase in ionic conductivity followed, possibly, by an enhancement of the cation transport number while preserving mechanical properties and flexibility of the composite electrolyte prepared in the thin film configuration. This concept was explored by several research groups. Our previous studies on mixed-phase polymeric electrolytes containing conductive fillers such as NASICON [111], β -alumina [112,113] and glassy fillers [113,114] have shown that these fillers do not contribute to the ionic conductivity of the mixed phase systems. Similar results were described by Scrosati and co-workers [115-118] for polymeric electrolytes containing β - and β'' aluminas. However, Skaarup et al. [119,120] reported that for composite systems containing high amounts of conducting fillers (exceeding 85vol%) the conductivity occurs via a dispersed phase and polymers act as binders for ceramic grains. The decrease in conductivity in comparison with pristine ceramic electrolytes is due to the dilution effect of the polymer host. Similar results demonstrating the contribution of the conducting filler to the conductivity of the mixed-phase electrolytes have been obtained by Stevens and Mellander [121] for systems containing PEO and RbAg_4I_5 or KAg_4I_5 as conductive ceramic additives.

Due to the unsuccessful development of the idea of the mixed phase system, the initial idea of composite solid electrolytes introduced by Liang [122] who improved the electrical properties of a LiI solid electrolyte by the addition of finely grained $\alpha\text{-Al}_2\text{O}_3$ was explored by several research teams. Weston and Steele [123] used $\alpha\text{-Al}_2\text{O}_3$ particles (grain size $40\mu\text{m}$) to improve the mechanical stability of a PEO-LiClO_4 electrolyte. Later, it was recognized that the addition of fine inorganic fillers (grain size $1\text{-}3\mu\text{m}$) led to an improvement in the mechanical properties and an increase in the ambient temperature conductivity of the electrolytes studied [124-126]. Scrosati and co-workers have shown that by using electrolytes containing $\gamma\text{-LiAlO}_2$ as fillers properties of lithium electrode polymer electrolyte interface can be greatly improved [118,127-129].

All of the modifications of polymer solid electrolytes presented so far deal an enhancement of ionic conductivity. Below the concept of the use of specially design additives to enhance lithium transference number is briefly presented.

The Lewis acid-base model is also useful for designing fillers which might act as anionic receptors, thus, possibly increasing the cation transport number. Both anions and cations are generally mobile in most of the polymer electrolytes, whereas restricting the mobility of the anions without adversely affecting the lithium cations is desirable for battery applications. The use of inorganic fillers proved to be one of the most effective as demonstrated by Scrosati's group [130,131]. However, despite an increase in the cation transport numbers the values obtained were still much below unity. Recently this group as well as others have developed a new generation of inorganic fillers based on superacid concept having its roots in the catalytic chemistry [132-134,134-138]. Surface modified superacid fillers consisted of particles of oxide grafted with " SO_4^{2-} " groups characterized by high acidity ($\text{H}_0 \approx -15$ on the Hammett scale) [139]. These systems seem to be more efficient in the complexation of anions.

Table 3

Lithium transference numbers for (PEO)₂₀LiClO₄ based composite electrolytes containing 10% by weight of inorganic filler additives

Type of the electrolyte	Type of the filler	Temperature/°C	Lithium transference number
(PEO) ₂₀ LiClO ₄	Filler free sample	40	0.31
(PEO) ₂₀ LiClO ₄	Al ₂ O ₃	40	0.61
(PEO) ₂₀ LiClO ₄	Al ₂ O ₃ (1% ASG)	40	0.66
(PEO) ₂₀ LiClO ₄	Al ₂ O ₃ (4% ASG)	40	0.72
(PEO) ₂₀ LiClO ₄	Al ₂ O ₃ (8% ASG)	40	0.77
(PEO) ₂₀ LiBF ₄	0	70	0.32
(PEO) ₂₀ LiBF ₄	Surface modified ZrO ₂	70	0.81

Table 3 present values of lithium transference numbers measured for PEO-LiClO₄ and PEO-LiBF₄ electrolytes and composite electrolytes based on these model systems with surface modified superacid Al₂O₃ and ZrO₂ additives [137]. The lithium transference number increases with the addition of alumina filler and a further increase is observed for electrolytes with surface modified additives. It should be noticed that the higher the acidic groups concentration, the higher is lithium transference number. Similar observations can be made for composite electrolytes containing ZrO₂ [137].

Boron family receptors

Anion receptors based on boron compounds were applied to the solutions of lithium salts in aprotic (inert) electrolyte based on low molecular weight solvents [140,141] as well as in gel polyelectrolytes [142]. Boron based aza ether compounds (borane, borate complexes) have been studied by McBreen and co-workers [143-146] using mainly Near edge x-ray absorption fine structure spectroscopy (NEXAFS). These studies showed that the degree of complexation of Cl⁻ or I⁻ anions strongly depends on the structure of the boron compounds. Also the dramatic enhancement in ionic conductivity upon the addition of boron compounds has been noticed in these electrolytes.

Wieczorek's group already analyzed properties of triphenylborane (Ph_3B) [147] in polymer electrolyte system and we observed the increase of lithium transference number. This beneficial effect was followed by changes in infrared and Raman spectra confirmed complex formation [146]. Some novel bororganic compound have been also tested in order to verify their stability and application as anion trapping agents [148].

The role of supramolecular additives

Another successful approach leading to enhancement in lithium transference number is to use a boron compound or supramolecular additives as anionic receptors. Several different additives such as boron compounds [149,150], linear or cyclic aza-ether compounds (with electron-withdrawing groups) [151] or calix[4]arene derivatives with various types of active groups in the lower rim were shown to be very effective in complexing anions and, thus, giving lithium transport numbers close to unity [152,153]. However, this effect was quite frequently observed for relatively large fractions of the supramolecular additive which act as a steric hindrance, thus, lowering electrolyte conductivity. Recently some of these limitations were overcome when calix[6]pyrrole was used as an anion trapping group [154].

Table 4 presents values of lithium transference numbers obtained for PEO based electrolytes doped with various type of lithium salts and containing various amounts of calixpyrrole type supramolecular additive. The addition of an even small molar fraction (~ 0.125) of calix[6]pyrrole results in a considerable increase in the lithium transference numbers. (For this supramolecular additive concentration all composite electrolytes seem to be homogenous). The increase in lithium transference number is particularly well seen for PEO- LiAsF_6 and PEO- LiBF_4 electrolytes. A smaller enhancement has been achieved for PEO- LiCF_3SO_3 system and the smallest one for PEO- LiI electrolytes. These observations are in good correlation with computational calculations [155] showing the following preference of calix[6]pyrrole in coordination of anions $\text{BF}_4^- > \text{AsF}_6^- > \text{ClO}_4^- > \text{CF}_3\text{SO}_3^- > \text{PF}_6^- > \text{I}^-$. A further increase in the fraction of calixpyrrole results in only small increase in the lithium transference number.

An important parameter in the characterization of polymer electrolytes is the window of electrochemical stability, especially in view of applications for lithium and lithium-ion allsolid-state batteries. A wide range of electrochemical-stability window allows a large choice of redox couples as electrode materials for the lithium battery. Given that ether-based electrolytes are known to oxidatively degrade at relatively low voltages (2.5-3.5 V vs. Li^+/Li) it was of interest to determine the electrochemical stability of the $\text{LiCF}_3\text{SO}_3:\text{P}(\text{EO})_n$ electrolytes in the presence of C6P and ceramic filler. Some concerns were raised by the possible electropolymerization of calix[6]pyrrole, particularly at high temperatures. Electrochemical stability was tested by linear-sweep voltammetry on a coin cell containing pure and composite electrolytes sandwiched between either two stainless steel electrodes or between stainless-steel working electrode and a lithium counter electrode.

Table 4

Lithium transference numbers for PEO-LiX-Calix-6-pyrrole electrolytes obtained by means of the dc-ac electrochemical experiment

Type of the electrolyte	Molar fraction of calix-6-pyrrole	Temperature/°C	Lithium transference number
(PEO) ₂₀ LiI	0	70	0.25
(PEO) ₂₀ LiI	0.125	70	0.56
(PEO) ₂₀ LiAsF ₆	0	75	0.44
(PEO) ₂₀ LiAsF ₆	0.5	75	0.84
(PEO) ₂₀ LiBF ₄	0	70	0.32
(PEO) ₂₀ LiBF ₄	0.125	70	0.78
(PEO) ₂₀ LiBF ₄	0.25	70	0.81
(PEO) ₂₀ LiBF ₄	0.5	70	0.85
(PEO) ₁₀₀ LiBF ₄	0.25	70	0.95
(PEO) ₁₀₀ LiBF ₄	1	70	0.92
(PEO) ₂₀ LiCF ₃ SO ₃	0	75	0.45
(PEO) ₂₀ LiCF ₃ SO ₃	0.125	75	0.68

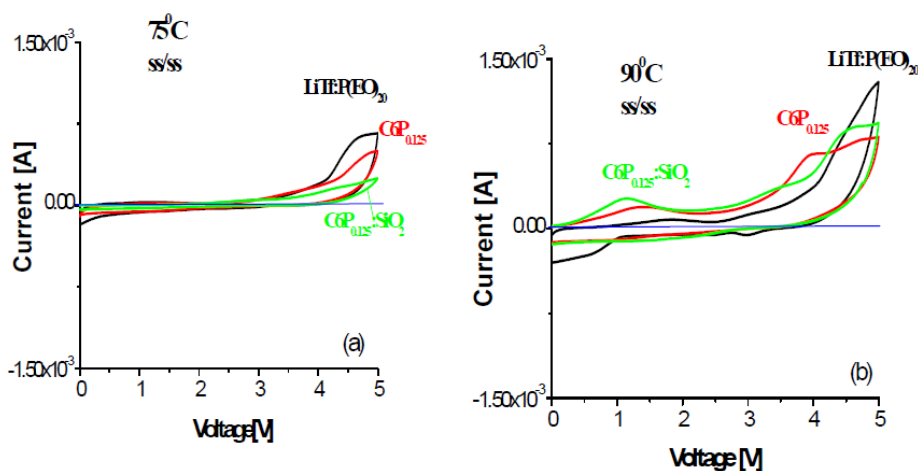


Fig.5 Cyclic voltammograms of LiTf:PEO20 membranes with and without C6P and SiO₂ additives at (a)75°C and (b)90°C over potential range of 0-5.0V using SS/PE/SS cell configuration [156].

As shown from the cyclic voltammograms at 75°C in Figure 5(a), incorporation of the C6P additive had a positive effect on the cell's stability in comparison to the pure polymer electrolyte over a voltage range of 0-4.0V [156]. Supplementary addition of silica caused an even greater electrochemical stability over a larger potential range of 0-5.0V. However, at a higher temperature of 90°C (Fig. 5(b)), an irreversible oxidative instability was detected for all three PEO-based electrolytes. The same system was successfully applied in all solid lithium-ion battery. Li/MoO_xS_y thin-film batteries with pure and modified polymer electrolytes were assembled and tested. Batteries were run over 100 reversible cycles in the temperature range of 75 and 90°C at a low discharge rate of about 0.5C. The capacity loss of the batteries with the double modified polymer electrolytes is lower than those with pure PE and does not exceed 0.4%/cycle at 90°C. At 75°C the capacity is very stable at the first 20 cycles. It has been shown that by proper design of inorganic or organic filler properties affecting ion transport phenomena can be modified in a variety of polyether based electrolytes. The addition of fillers results in an increase in ionic conductivity for amorphous and crystalline polymeric matrices, enhancement in lithium transference number and, on top of this, with the stabilization of lithium electrode – polymer electrolyte interfacial resistivity. Recently developed models [157] tried to relate the increase in conductivity and lithium transference number to the changes in ion-ion and ion polymer interactions caused by the filler. The first class of reactions seems to be particularly important in the explanation of phenomena occurring in polyether based electrolytes.

Ionic Liquids in lithium batteries

IONIC LIQUIDS AS SOLVENTS

In the search for more safety, the present choice of organic carbonates and LiPF_6 as solute has to be questioned, and new electrolyte concept have to be considered. The main drawback of such solvent is the runaway reaction from exfoliation (\ominus electrode) or oxidation or O_2 release (\oplus electrode) leading to the expulsion of flammable vapours, and in frequent case of self-ignition, to toxic chemicals (HF) release. Ionic liquids are considered to provide an answer to this problem.

Ionic liquids are fluids composed solely of ions and, and by consensus, have a melting point below 100 C. Of course, the focus here is on room- or below room-temperature liquids. ILs are the focus of interest of a growing community for their unusual properties

- No vapour pressure,
- High conductivity up to 20 mScm^{-1} at room temperature,
- Non-flammability,
- High thermal stability,
- Exceptional solvent behaviour,
 - Almost all organic reactions ("green" solvents),
 - Previously quasi-untractable polymers (cellulose, starch, silk fibroin...),
- Salts for electrolytes and supercapacitors,
- Very high resistance to oxidation.

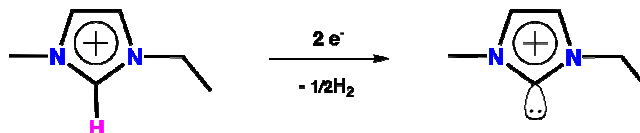
The lack of flammability has been the main attraction for battery electrochemists, solving the most urgent problem of battery electrolyte, and it is hoped that their resistance to oxidation would allow the use of high voltage electrode materials (e.g. $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_2$ at 4.5 V).

The family of ILs, now with innumerable representatives, stems from the study of chloroaluminates (AlCl_4^- , Al_2Cl_7^-) of the delocalized cations based on imidazolium derivatives (right). The Al-Cl bond it however too fragile in terms of redox (Al (plating at +1.3 V vs. $\text{Li}^+/\text{Li}^\circ$) stability and hydrolytic (evolution of HCl) to have any application in the battery field, where they also induce cationic chemistry in the solvents. The advent of "neutrals" ILs, with the classical anions of organic solvents, BF_4^- , CF_3SO_3^- , PF_6^- and imidazolium cations has given large visibility to the field in the early 1990's.

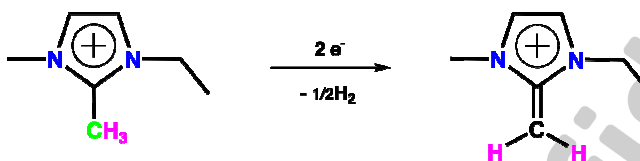


While a large number of metals (Cu, Ag, Au Pd, Al, Fe, Ni, Co possibly Nb and Ta...) and non-metals like Si and Ge, important for solar applications can be easily plated, the question of having graphite or even lithium deposition working in ILs became a

temptation. The limitation of these new ILs is was found however no longer due to the anion, but the imidazolium cation



The acidity of the C2 proton is estimated to $pK_a = 24$, and this corresponds to a reduction potential of 1.5 V vs. Li^+/Li° , which is observed in practice. The methylation of the C2 proton still leaves possibility for reduction, and ≈ 300 mV are gained:



Thus, the imidazolium-based cations, for the negative side, are always in the metastable zone, and thus rely on the formation of an SEI below 1.2 V 1.5 V vs. Li^+/Li° .

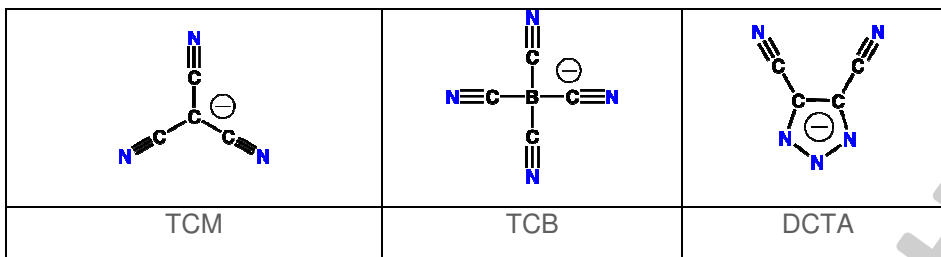
The introduction of the TFSI $[(CF_3SO_2)N]^-$ in 1995 has considerably broadened the scope of ionic liquids, as the soft, flexible anion could now give ionic liquids with very low freezing point (or low T_g s) and not restricted to the imidazolium derivatives. In particular, quaternary ammonium salts, which are appreciably more resistant to reduction as compared with azoles, were now giving low melting salt.

$n = 0$: MPPy; $n = 1$: BMPy	DEMME or 1,2,2,2O1

Despite higher viscosities and lower conductivities, either pristine or with added low-lattice energy lithium salts, the quaternary ammonium either based on the compact 5-membered pyrrolidinium cycles (MPPy, BMPy) or those whose side arm flexibility is enhanced through an ether linkage (1,2,2,2O1) are now the focus of most applications in the battery field. However, the 0-800 mV domain is still dependent on an SEI.

With the same approach to "soft anions", i.e. delocalization and the presence of N or C centres has even further broadened the scope and temperature of operation of ionic liquids:

TFSI	FSI	DCI



These anions tend to give lower melting points and/or viscosities as compared with conventional PF_6^- or BF_4^- . However, the very positive voltages >4.5 V can only be reached with the fluorine containing anions, TFSI and FSI. FSI is considered as the most promising in terms of conductivity, low rise in viscosity with Li salt addition. In addition, FSI has been shown to provide the ad hoc SEI layer to allow dendrite-free cycling of lithium metal at the point of reconsidering this anode as a viable alternative for high energy batteries.

The non-fluorinated anions on the other hand are stable up to a maximal +4V cut-off but have the advantage of being more recyclable and possibly less expensive. It is not known if, then under what conditions, these anions under thermal stress can release HCN but studies are planned. Obviously, such electrode materials are in the right potential range for LiFePO_4 cathodes and it have been shown that they behave quite well with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes. DCl and TCA do give also smooth deposits of lithium metal.

ILs based on anions that give corrosion of Al current collector (TFSI) in “normal” carbonate solvents are far more tame under the for of ILs, and 4+ volt operation has been demonstrated. Here again FSI with its labile S–F bond (similar to the P–F bond in LiPF_6) gives a passivating SEI.

IONIC LIQUIDS AS ADDITIVE

A non-obvious property of ILs is to induce non-flammability to organic solvent beyond a threshold composition. For instance carbonates solvents and LiPF_6 with 20-50% addition of an IL become flame retardant. This is a mixed benefit because in case of runaway reaction, the organic solvent vapours may distil-off and catch fire outside the battery. The vapour pressure however is lower, and the addition of ILs can be done on high boiling cyclic carbonates alone (EC and PC) omitting the more volatile dimethyl or ethyl-methyl carbonate. Conductivity values are kept at reasonable values even without the low-viscosity diluents. Graphite electrode operation has been show to be feasible in such mixtures of solvents.

Ionic liquids, as a whole, are a fast moving field where the rate of progress is very high. It is very clear that the battery community cannot ignore this option for safe operation of batteries. Ragone Plots show that the performances (C rates) are still slightly below that of conventional solvents, the difference is now marginal with for instance FSI base ILs.

Emerging electrolyte systems for Li technology

So far, generally small changes, usually by the use of various types of additives which may influence performance of electrolytes in lithium and (or) lithium ion cells were reported. Below the ideas leading to fundamental changes in the designing of new electrolytes are presented.

CRYSTALLINE POLYMER ELECTROLYTES

Conductivity in polymer electrolytes has long been viewed as confined to the amorphous phase above the glass transition temperature, T_g , where polymer chain motion creates a dynamic, disordered environment that plays a critical role in facilitating ion transport. Crystalline polymer-salt complexes were considered to be insulators until the discovery of ionic conductivity in $\text{PEO}_6:\text{LiXF}_6$ ($X=\text{P}, \text{As}, \text{Sb}$) (fig.6) [158,159]. It is the unique structural features of these complexes that promote ionic conductivity [160,161]. Pairs of PEO chains fold to form cylindrical tunnels within which the Li^+ ions are located and coordinated by the ether oxygens, providing pathways for the movement of cations. The anions are located outside these tunnels in the interchain space and do not coordinate the cations (Fig. 7). It has been shown that the current is solely carried by Li^+ cations, transport number $t_+=1$.

Ionic conductivity of pristine crystalline polymer electrolytes formed by LiXF_6 salts dissolved in PEO is too low for applications, however, it can be increased by several orders of magnitude by isovalent and aliovalent anionic doping, modifying the ends of the polymer chains or glymes, varying the average molecular weight and dispersity of the polymer, Fig. 6 [162-166].

Ionic conductivity in crystalline polymers is not unique to the 6:1 complexes formed with LiXF_6 salts. Recently several new crystalline polymer electrolytes containing different alkali metal salts (Na^+ , K^+ and Rb^+) [167]. The structures of $\text{PEO}_8:\text{YAsF}_6$ ($Y=\text{Na}, \text{K}, \text{Rb}$) also contain tunnels but, unlike the $\text{PEO}_6:\text{LiXF}_6$ structures, each tunnel is formed by a single PEO chain folding into a helix. The anions, however, are also located outside the polymer chains and do not coordinate cations (fig.8). The ionic conductivity at and above room temperature of the best conductor $\text{PEO}_8:\text{NaAsF}_6$ discovered so far, is 1.5 orders of magnitude higher than that $\text{PEO}_6:\text{LiAsF}_6$ (fig.9). Rocking-chair batteries were constructed using $\text{Na}_{0.44}\text{MnO}_2$ electrodes and $\text{PEO}_8:\text{NaAsF}_6$ electrolyte. As can be seen in Fig. 10, cycling may be sustained, thus demonstrating that the electrolyte can be used in cells.

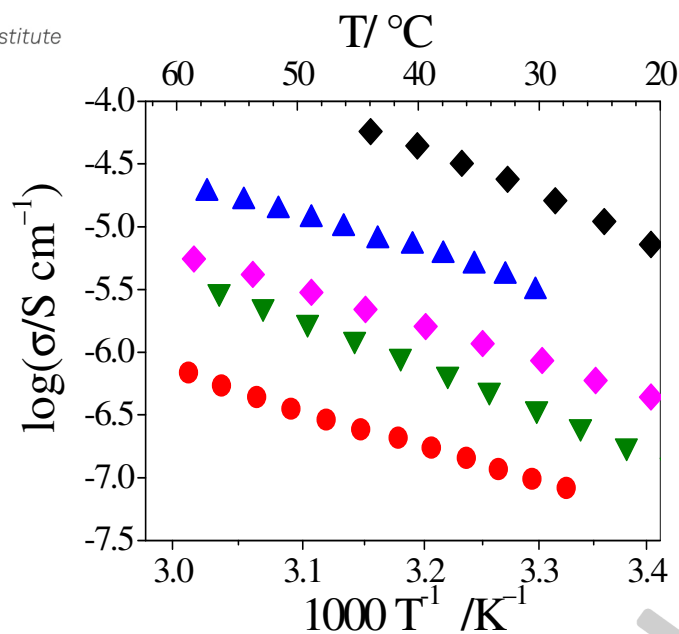


Fig.6 Conductivity of crystalline polymer electrolytes. Red - $\text{PEO}_6:\text{LiAsF}_6$; green - $\text{PEO}_6:\text{Li}(\text{AsF}_6)_{0.9}(\text{SbF}_6)_{0.1}$; magenta - $\text{PEO}_6:(\text{LiSbF}_6)_{0.99}(\text{Li}_2\text{SiF}_6)_{0.01}$; blue - $\text{PEO}_6:(\text{LiAsF}_6)_{0.95}(\text{LiTFSI})_{0.05}$; black - $(\text{PEO}_{0.75}\text{G}_{40.25})_6:\text{LiPF}_6$, G4 – tetraglyme, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3$.

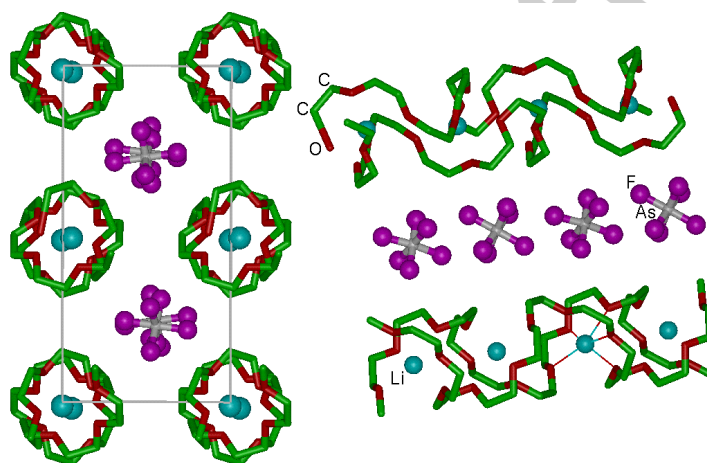


Fig.7 The structure of $\text{PEO}_6:\text{LiAsF}_6$. *Left*, view of the structure showing rows of Li^+ ions perpendicular to the page. *Right*, view of the structure showing the relative position of the chains and their conformation (hydrogens not shown). Thin lines indicate coordination around the Li^+ cation.

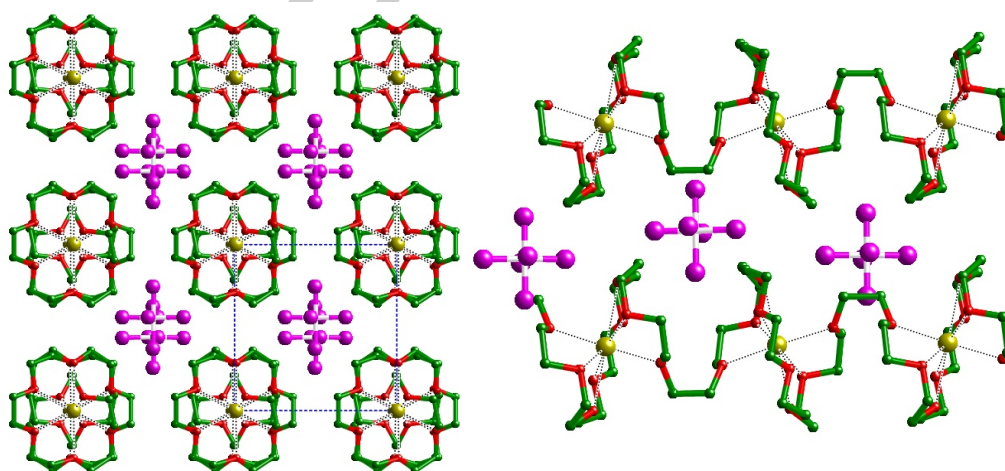


Fig.8 The structure of $\text{PEO}_6:\text{NaAsF}_6$. *Left*, view of the structure showing rows of Na^+ ions perpendicular to the page. *Right*, view of the structure showing the relative position of the chains and their conformation (hydrogens not shown). Thin lines indicate coordination around the Na^+ cations.

SMALL-MOLECULE ELECTROLYTES

Crystalline small-molecule electrolytes form a new class of ionic conductors that are different from ceramic or polymer electrolytes. They are soft solids, unlike ceramic electrolytes, yet, unlike polymer electrolytes, they are highly crystalline, of low molecular weight, and have no polydispersity (distribution in chain length) or chain entanglement. They are solid coordination compounds in which the cations of a salt are coordinated by small molecules, glymes $\text{CH}_3\text{-O-(CH}_2\text{CH}_2\text{O)}_n\text{-CH}_3$ $1 \leq n < 15$ (hereafter denoted Gn). They do not exhibit plasticity and are therefore distinct from plastic crystalline ionic conductors. Crystalline polymer electrolytes form the same crystal structures over a very wide range of molecular weights, from greater than ~ 500 to several million Da.

On reducing the molecular weight below 500 Da, a rich variety of crystal structures is observed [168-173]. A number of the salt/small-molecule complexes, e.g. $(\text{G4})_{0.5}:\text{LiBF}_4$, $\text{G3}:\text{LiAsF}_6$, $\text{G4}:\text{LiAsF}_6$, show appreciable levels of ionic conductivity, greater than the undoped polymer electrolytes, Fig. 11 [172,174]. In addition, $\text{G3}:\text{LiAsF}_6$ (fig.12) and $(\text{G4})_{0.5}:\text{LiBF}_4$ (fig.13) electrolytes have high values of the cation transport number, t_+ , 0.80 and 0.66, respectively. As in the case of polymer electrolytes, it is the specific structural features that determine higher conductivity and greater t_+ values. Higher conductivities and cation transport values are found in those small-molecule electrolytes whose structures feature convenient pathways for the cations to move.

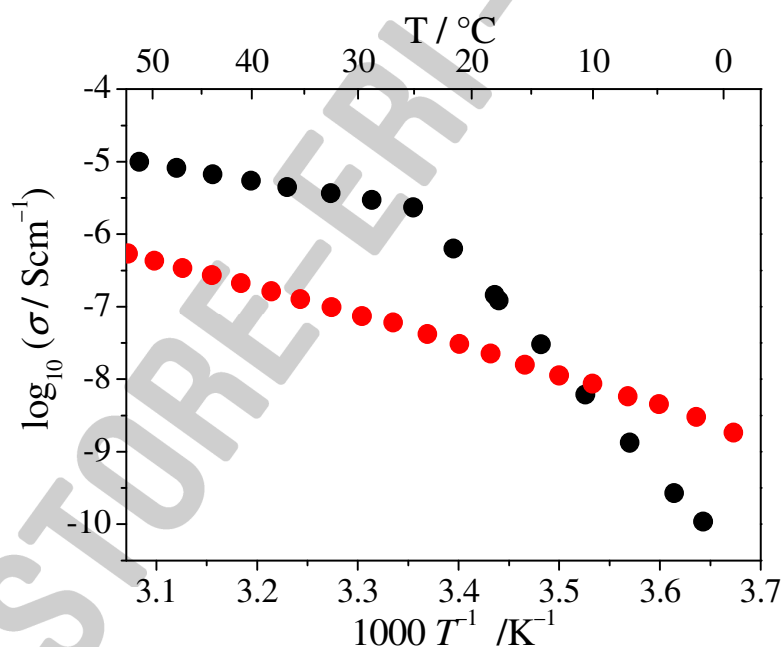


Fig.9 Conductivity of $\text{PEO}_6:\text{LiAsF}_6$ (red) and $\text{PEO}_8:\text{NaAsF}_6$ (black).

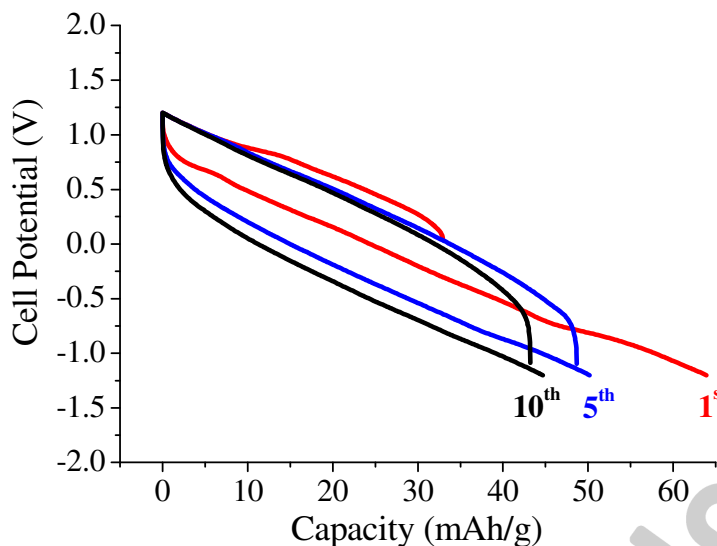


Fig. 10 Charge and discharge curves for the first, fifth and tenth cycles of a $\text{Na}_x\text{MnO}_2/\text{PEO}_8:\text{NaAsF}_6/\text{Na}_x\text{MnO}_2$ cell ($x_0=0.44$) at 45°C between -1.2 and 1.2V at a rate of $\text{C}/6$.

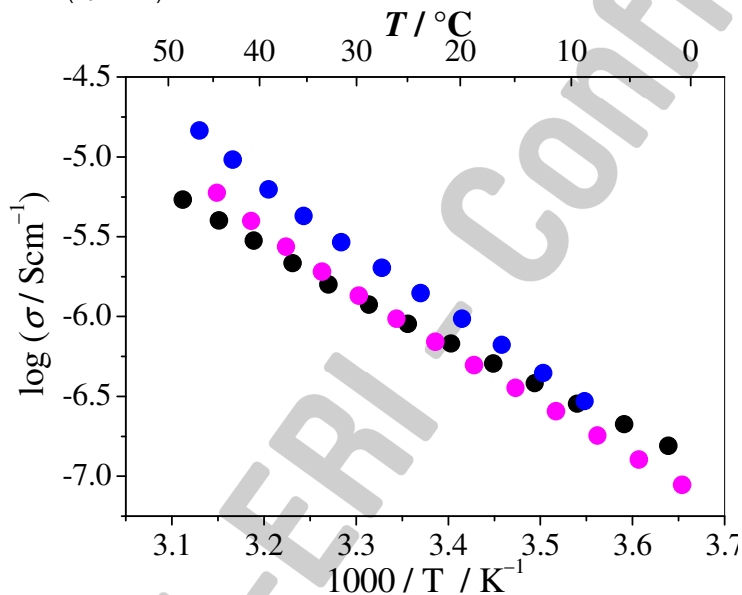


Fig.11 Conductivity of $\text{G3}:\text{LiAsF}_6$ (black), $\text{G4}:\text{LiAsF}_6$ (magenta) and $(\text{G4})_{0.5}:\text{LiBF}_4$ (blue).

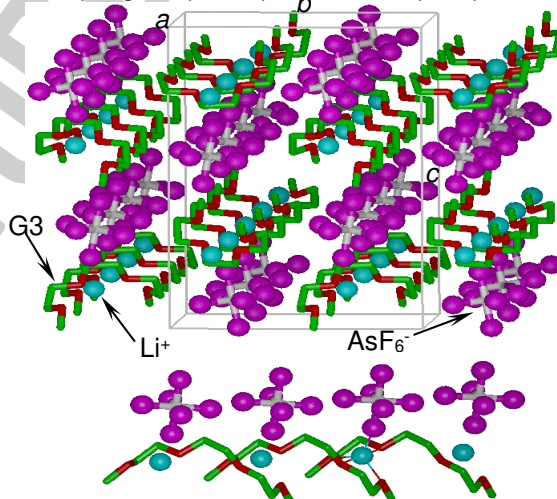


Fig 12 The structure of $\text{G3}:\text{LiAsF}_6$. *Top*, view of complete structure. *Bottom*, fragment of the structure showing one tunnel.

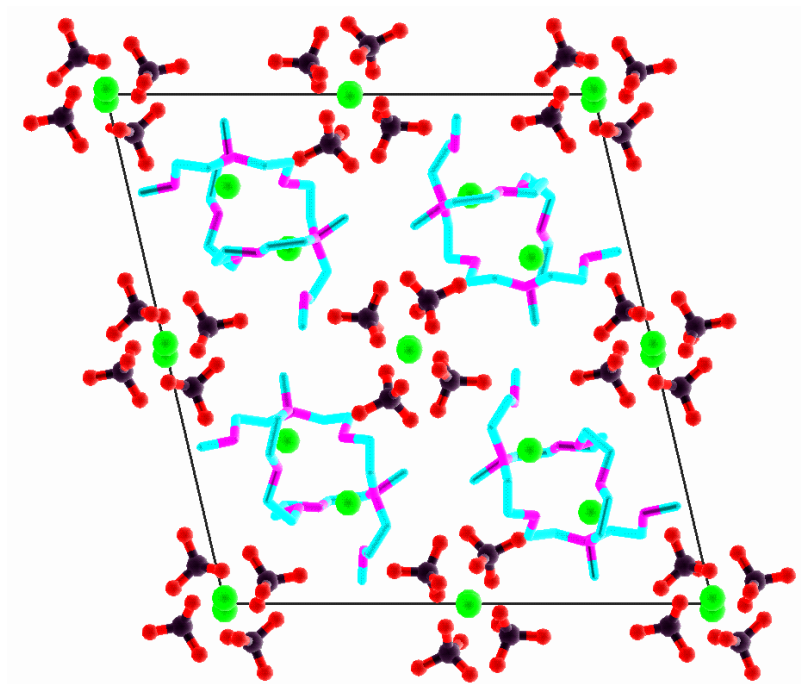


Fig. 13 The structure of $(G4)_{0.5}:LiBF_4$ showing rows of Li^+ ions (blue) perpendicular to the page coordinated either by anions or ether oxygens in the

THE CONCEPT OF THE SYNTHESIS OF NOVEL FAMILY LITHIUM SALTS APPLICABLE FOR LIQUID, POLYMER AND IONIC LIQUID TECHNOLOGIES.

Liquid systems

After almost 20 years of applications of lithium-ion cells there is still a lack of potential substitutes for $LiPF_6$, which is definitely not flawless. Among the most important drawbacks of the $LiPF_6$ use in electrolyte system is the formation of HF in the cell, which destroys the cell from inside after certain time, but also $LiPF_6$ and HF toxicity.

The constant seek for more cheap, environment-friendly and easy to handle materials made a gap to fill. List of parameters for lithium salts to fulfill in order to become new predominant salt on market of lithium-ion cells is not very long, but no existing salt fulfills it. Transference number above 0.5 (or at least better than $LiPF_6$ that in optimized carbonate solvent mixtures has transference number of 0.3-0.4), conductivity higher than $1 \text{ mS}\cdot\text{cm}^{-1}$ ($10^{-3} \text{ S}\cdot\text{cm}^{-1}$), no decomposition in range of 0-4.5 V vs. Li and no aluminum corrosion in this range, low price (at least lower than $LiPF_6$, but the lower, the better), non-toxicity, moisture-proof (and air proof – stability in room atmosphere – easiness of handling), thermal stability up to at least 100°C and low association rate (lower than $LiPF_6$ or very weakly associating $LiClO_4$) is what is necessary to obtain by researchers.

With this in mind, in this work the new “tailored” anions especially for application as lithium electrolytes in lithium-ion cells have been designed and investigated. Main idea was to design structure that would not have disadvantages of big bulky anions causing high viscosity when dissolved in organic solvents, therefore a decrease in conductivity. Also, ions of new salts should not form agglomerates after dissolution, due to ion pairs’ and triplet’s negative effect on conductivity of an electrolyte, mechanism of lithium cations insertion into the electrodes (in both charging and discharging process) and transference number of a lithium cation.

The novel, promising concept of the application of new anions is based on the application of so called “Hückel anions”. The name came from the transposition of the Hückel rule predicting the stability of the aromatic systems. One of the most common examples of this type of anions is 4,5-dicyano-triazole (DCTA) (figure 14). This particular structure is completely covalently bonded and shows very stable 6π (or 10π electron if CN bonds are involved in calculations) configuration. It can be produced from commercially available precursor and even more importantly does not comprise fluorine atoms. Salts of this type of anion were found to exhibit high ($\sim 300^\circ\text{C}$) thermal stability. LiDCTA was successfully tested in PEO matrices systems as a promising, improved electrolyte for lithium-ion batteries [175]. Unfortunately DCTA failed as a component of the EC/DMC (1:1) battery electrolyte.

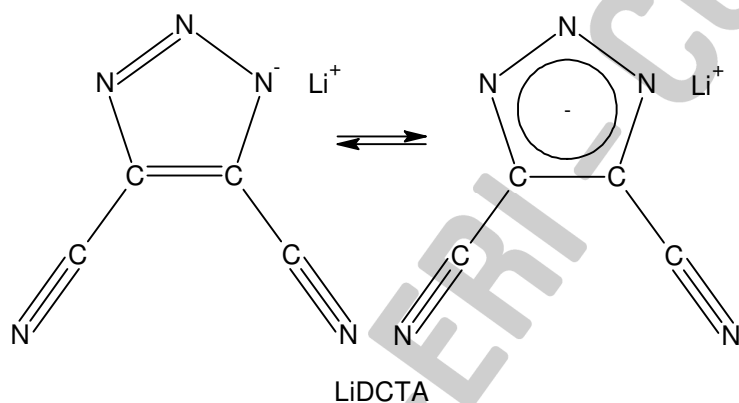


Figure 14. LiDCTA - Hückel type salt: LiDCTA - lithium 4,5-dicyano-1,2,3-triazole.

Basing on LiDCTA example, novel imidazole derivatives salts were synthesized, using the procedure shown below:

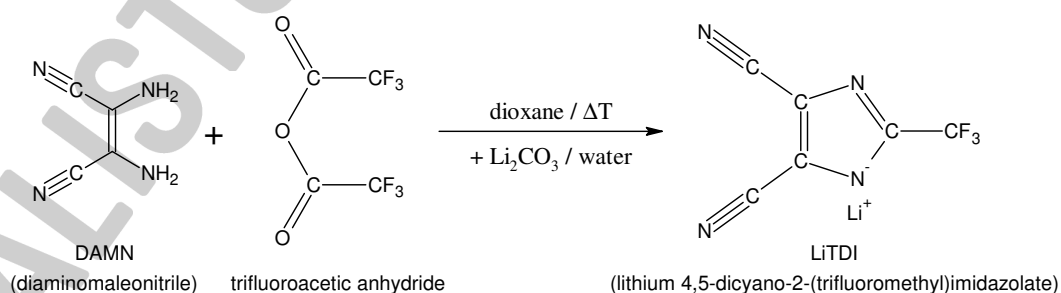


Figure 15. Synthesis scheme for LiTDI.

Molecular modelling studies showed that benzimidazolidine and imidazolidine anions show a typical behaviour of heterocyclic anion alternatives to PF_6^- : if tailored correctly they offer more dissociative lithium ion pairs compared to LiPF_6 , but are not as electrochemically stable. The latter is, however, not crucial as long as the anions exceed the stability window for the intended application, for Li-ion batteries ~ 4.2 V.

The data obtained for the benzimidazolidines, indicate that with very small alterations, such as the positioning of $-\text{CN}$ substituents on the heterocycle, ion pairing can be changed drastically. With equal predicted properties for analogous imidazolidines and benzimidazolidines, the difference in anion size is an important variable for choosing an appropriate lithium salt.

Overall the potential of using cyano chemistry to create new lithium salts with excellent electrochemical stabilities and ion pairing properties is evident. The previously recognized improvement of both the electrochemical stability and the lithium ion pair dissociation ability, by increasing the number of cyano groups, is apparent also for the benzimidazole salts and further strengthened by the predictions made for $\text{P}(\text{CN})_6^-$. However, an increase in the number of $-\text{CN}$ groups leads to a larger anion size and require increased synthesis efforts. The tetracyano benzimidazolidines are the most promising candidates of the explored families of anions, but as of present neither of the benzimidazole lithium salts nor $\text{LiP}(\text{CN})_6$ has been reported experimentally.

Another important characteristic of the electrolyte is its applicability in cells that can provide high current during discharging (up to the capacity of a cell) and then again be able to charge without big loss of capacity. This type of test was made with Li / electrolyte / LiMn_2O_4 coin cells containing LiTDI-EC-DMC, LiPDI-EC-DMC and LP30 (LiPF_6 -EC-DMC). On Figure 16 results of such investigation are shown. Capacity of charging was visualized as percentage of capacity that of charging after C / 10 discharge rate. While capacity changes (related to C / 10 rate) after discharging with C / 20, C / 5 and C / 2 rates are negligible (less than 1 %), beginning with 1 C rate differences are starting to show up. At 1 C rate highest capacity had a cell with LiTDI, although with small advantage over LiPF_6 (99 % over 98 % of capacity). After 2 C discharge rate cell with LiPF_6 had the highest capacity but only a little better than LiTDI (LiPF_6 – 90 %, LiTDI - 88 %, LiPDI - 83 %). Finally, with the highest discharge rate in the investigated range, 5 C, cell with LP30 has the highest capacity (52 %) with LiTDI and LiPDI much lower – 37 % and 29 %, respectively.

Additional test to study charging profile of LiTDI- and LiPDI-containing coin cells was performed (fig.17). 4.3 V cut-off was fixed for this study. Curve is of the same shape and values for both salts throughout the experiment with the exception of the starting voltage. Charging voltage starts with “empty” cell at about 3 V (2.95 V in case of LiTDI and 3.07 V in case of LiPDI), increasing rapidly and after charging ca. $2 \text{ mAh}\cdot\text{g}^{-1}$ increase slows down at the level of 3.95 V, increasing slowly and linearly towards maximum capacity at 4.3 V cut-off obtaining capacity of $119 \text{ mAh}\cdot\text{g}^{-1}$. In the final $7 \text{ mAh}\cdot\text{g}^{-1}$ (before maximum capacity) charging voltage speed up again.

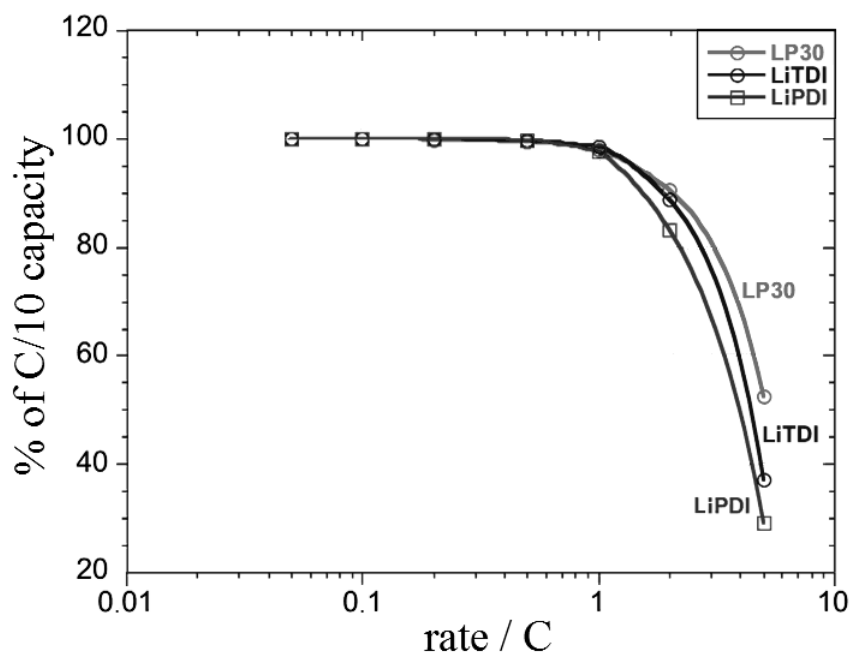


Figure 16. Cell charge capacity against discharge rate of 1 M LiTDI-EC-DMC, 1 M LiPDI-EC-DMC and 1 M LiPF₆-EC-DMC (LP30) electrolytes in Li / electrolyte / LiMn₂O₄ coin cell.

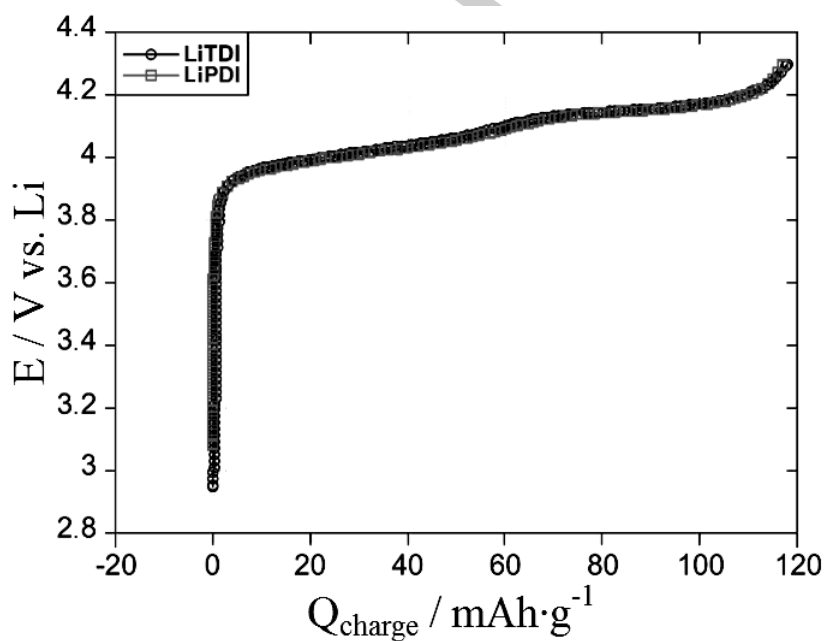


Figure 17. Charging profile with 4.3 V cut-off of 1 M LiTDI-EC-DMC, 1 M LiPDI-EC-DMC and 1 M LiPF₆-EC-DMC (LP30) electrolytes in Li / electrolyte / LiMn₂O₄ coin cell with aluminum charge collector.

Polymer-based systems

PEO-based membranes with LiTDI (lithium 2-(trifluoromethane)-4,5-dicyanoimidazolate) and LiPDI (lithium 2-(trifluoromethane)-4,5-dicyanoimidazolate) salts were prepared by solvent-free hot-pressing method. PEO of average molecular weight of 600 000 g·mol⁻¹ (Aldrich) dried under vacuum at 40°C for 72 hours was used for preparation. LiTDI and LiPDI were dried under vacuum for 36 hours at 110°C. Dried components were mixed (in 1:20 Li:O ratio – 1 salt molecule per 20 monomer units of polymer) in a mortar and put into aluminum mold. At the temperature of 90°C (which is above melting point of PEO) hot-pressing was performed on the mixture powder with 1 tone of pressure applied for 30 minutes, 2 tones for 20 minutes and 3 tones for 10 minutes. As a result two membranes were obtained: PEO₂₀-LiTDI and PEO₂₀-LiPDI (PEO₂₀-LiX means 1:20 Li:O ratio).

On the Fig. 18 there is linear voltammetry scan of both membranes showed. Super P carbon was used as a working electrode and metallic lithium as reference and counter electrode for this measurements. Solid electrolytes with LiTDI and LiPDI were stable up to 4.0 V vs. Li.

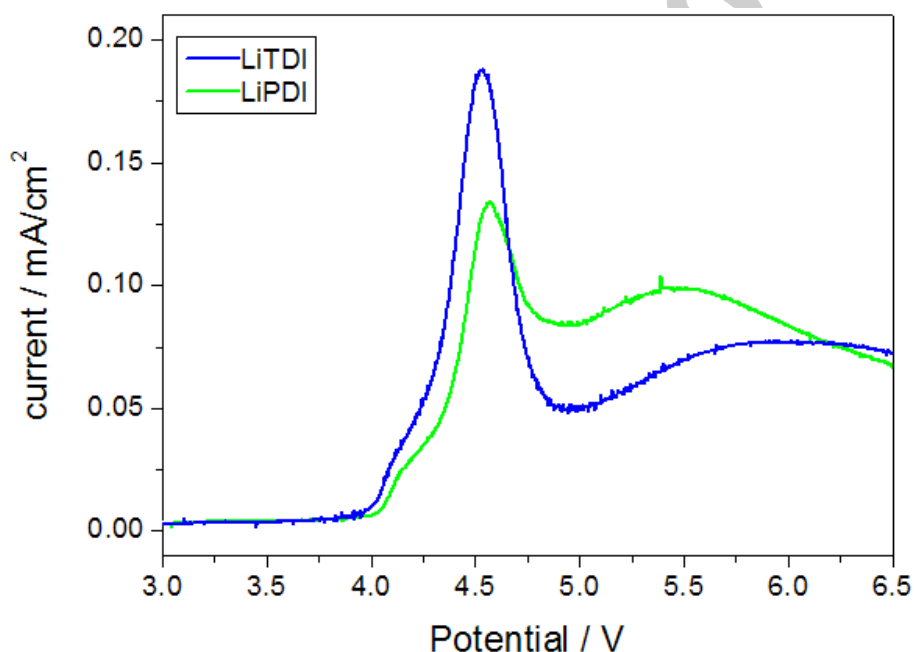


Fig. 18. Electrochemical stability of PEO₂₀-LiTDI and PEO₂₀-LiPDI electrolytes.

Fig. 19 shows Arrhenius plot of the PEO₂₀-LiTDI and PEO₂₀-LiPDI solid electrolytes conductivity. Conductivity results were obtained by EIS (Electrochemical Impedance Spectroscopy) measurements in a Swagelok-type cell with two Stainless Steel blocking electrodes. Temperature of samples was controlled by thermocouple in direct contact with the cell and the conductivities were measured during cooling scan from 120°C to 20°C (LiPDI) and from 100°C to 20°C (LiTDI). PEO-LiTDI and PEO-LiPDI membranes have a similar conductivities throughout the temperature range, starting with 1,2·10⁻³ S·cm⁻¹ (LiTDI) and 1,3·10⁻³ S·cm⁻¹ (LiPDI) at 100°C and 0,6·10⁻⁴ S·cm⁻¹ at 45°C for both salts.

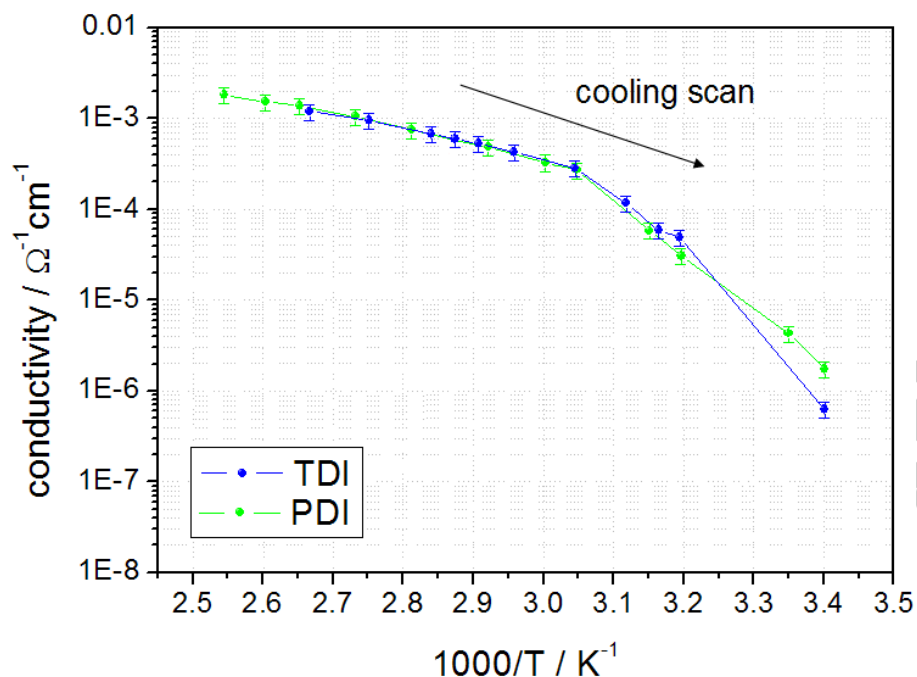


Fig. 19. Ionic conductivity of $\text{PEO}_{20}\text{-LiTDI}$ and $\text{PEO}_{20}\text{-LiPDI}$ electrolytes.

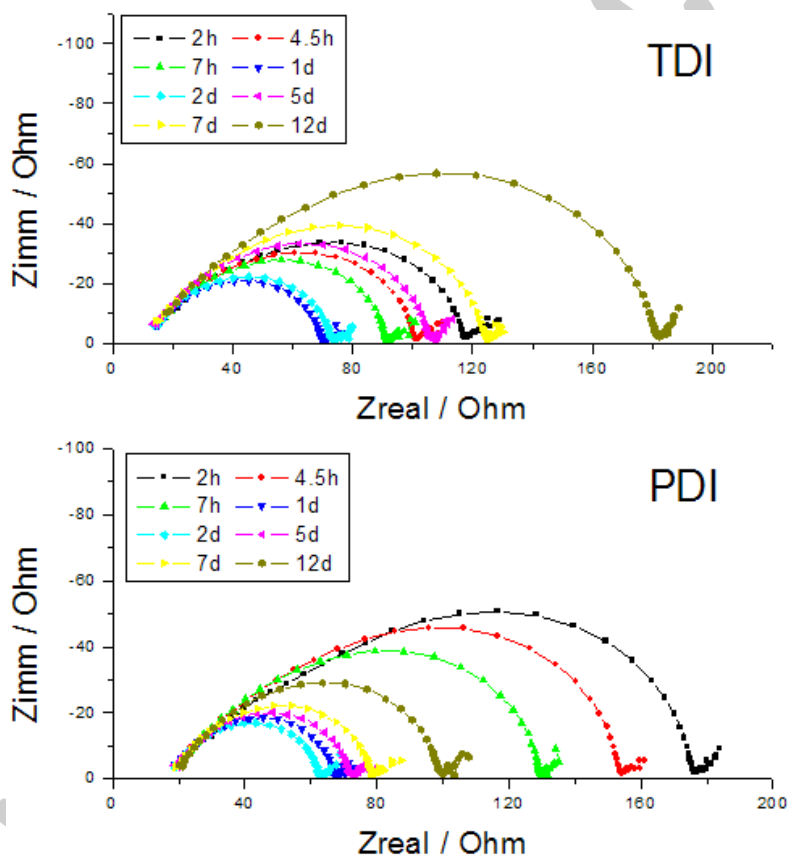


Fig. 20. Interfacial resistance of $\text{PEO}_{20}\text{-LiTDI}$ and $\text{PEO}_{20}\text{-LiPDI}$ electrolytes.

On the Fig. 20 there is showed Interfacial stability of both PEO₂₀-LiTDI and PEO₂₀-LiPDI polymer electrolytes. Measurements were evaluated through EIS (100kHz-100mHz measurement range) of the Li / PEO₂₀-LiX / Li systems kept at 90°C temperature during 12 days period. Electrodes surface was 0,785 cm². It is notable, that both LiTDI and LiPDI systems are similar in the passivating behavior. After fast initial decrease of resistance during first day and stabilization for the next day, there is a slow increase of interfacial resistance. Although LiPDI-PEO system starts with a little higher initial resistance and both salts stabilize at the same level (about 40 Ω), but then it has much more stable interfacial resistance during rest of the period (10 days) showing minimal increase.

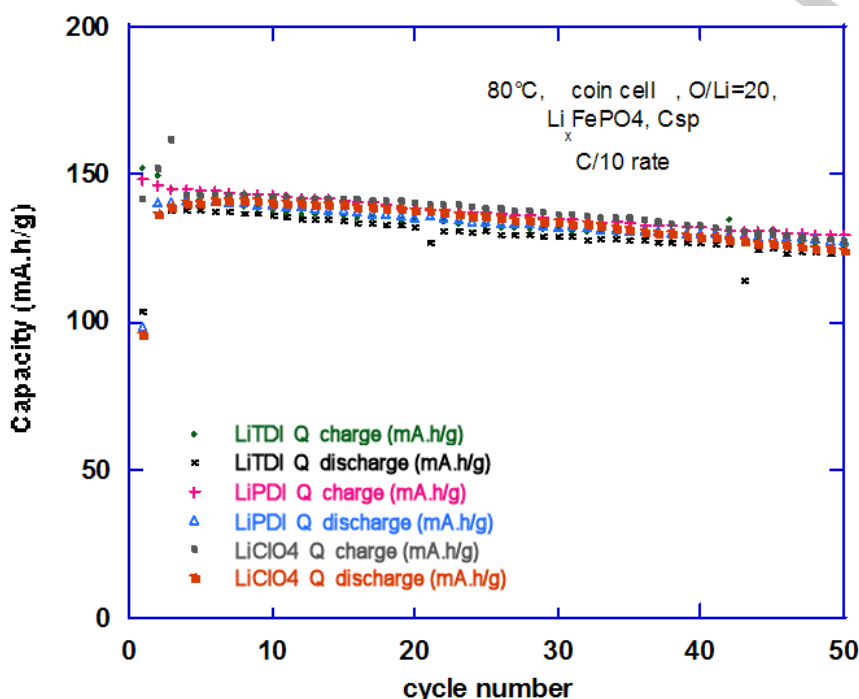


Fig. 21. Cycling of PEO₂₀-LiTDI and PEO₂₀-LiPDI electrolytes.

Cycling results in the Li_xC / PEO₂₀-LiX / Li_xFePO₄ system is shown on the Fig. 21. Also, cell capacity dependence of discharge rate was shown on the Fig. 22. Other salts (LiClO₄ – lithium perchlorate, LiTFSI – lithium bis(trifluoromethanesulfonyl)imide, LiC(CN)₃ – lithium cyanofornate and LiDCTA – lithium dicyanotriazole) were used also for comparison. For other salts there has been same conditions of measurements used, i.e. same system (just as membrane contents ratio and preparation method) and 80°C temperature throughout the measurements. It is visible, that both new salts (LiTDI and LiPDI) has the same efficiency as LiClO₄ in both cycling and discharge rate capacity, and even better than LiTFSI and LiDCTA in terms of discharge rate capacity at higher rates (5C).

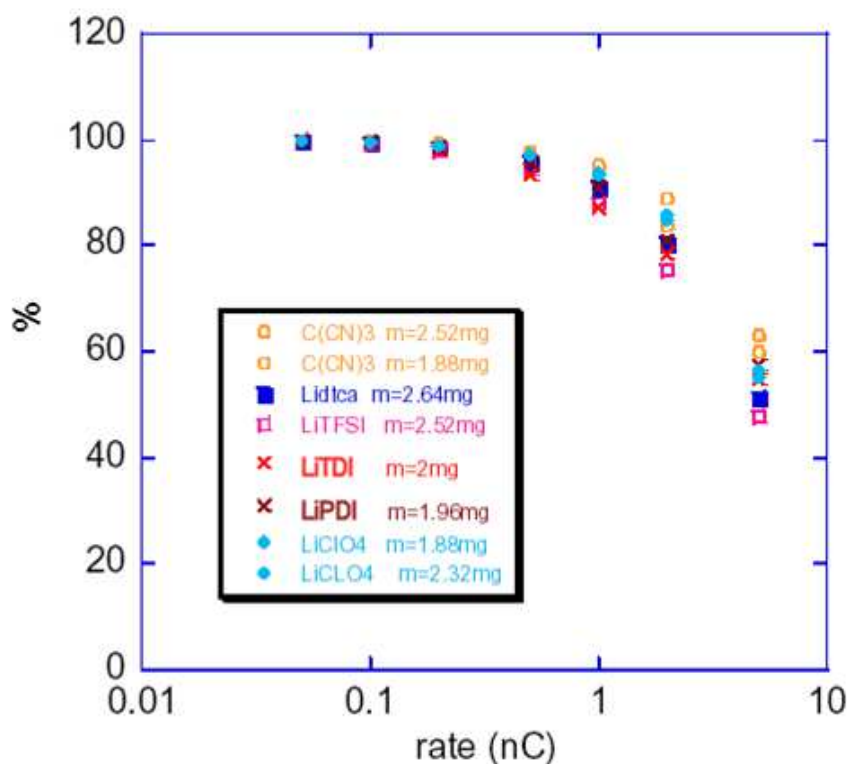


Fig. 22. Discharge rate dependence of cell capacity of PEO₂₀-LiTDI and PEO₂₀-LiPDI electrolytes.

It has been demonstrated that LiTDI and LiPDI are successfully applied in lithium batteries. Based on *ab initio* calculations new members of the Hückel anion family are to be synthesized and studied for battery applications.

POLYMER IN SALT SYSTEMS

An effective approach to achieve polymer electrolytes having single cation conductivity in a solvent free configuration appears that directed to the synthesis of so-called polymer in salt systems, in which a large amount of salt is mixed with a small fraction of polymer to induce mechanical integrity of the final membrane [176,177]. It is well known that some of pristine lithium salts of low T_g values exhibit ambient temperature conductivity in the range 10^{-2} – 10^{-3} S/cm, i.e. values which are suitable for battery applications. However, the addition of the polymer component usually results in a considerable decay in conductivity [178]. In previous studies poly(acrylonitrile), poly(1-vinyl pyrrolidone) and poly(N,N-dimethyl arylamide) were mostly used as polymer matrixes [178-180]. The highest ambient temperature conductivity exceeding 10^{-6} S/cm was reported for poly(acrylonitrile) based electrolytes in which lithium triflate was used as a dopant [180]. In our opinion this unfavorable effect of reduction in conductivity upon the addition of polymer can be suppressed by a proper choice of the functionality

of polymer chain. To confirm this expectation, we have prepared and characterized novel polymer in salt electrolytes based on poly(acrylamide). Turns out the polyacrylamide is a very efficient in the complexation of lithium salts. FT-IR and Maldi-ToF experiments confirm formation of salt-polymer associates and possibility of fast ion transport via exchange of lithium between neighboring associates [181]. The interesting concept of polymer in salt system has not been further explored most probably due to unsatisfactory mechanical properties of the system studied.

A way ahead. Is there any winner?

In the preceding sections the summary of the status quo of electrolytes used in lithium and lithium-ion battery technology has been given for all three types of electrolytes utilizing organic liquid solvents, polymers and ionic liquids as solvents. Currently in the most of lithium ion batteries solution of LiPF_6 in carbonate mixture is used alone or entrapped in the polymer matrices (PVdF, PAN) [182] forming gel type electrolytes. Environmental and safety concerns apart of technological limitations are major drawbacks towards extension in liquid electrolytes technology. On the other hand all solid state lithium batteries remain one of the major goals for research in the field because they offer a step-change in safety and higher energy density. Solid electrolytes are the necessary pre-requisite and true solid polymer electrolytes (solvent free systems) are one of the most attractive options. Polymeric electrolytes, including gels solid amorphous and crystalline, along with some ionic liquids open the doors to using Li metal as an anode which would further increase the energy density of batteries. The currently used liquid and gel electrolytes prohibit the use of Li metal as an electrode because of dendrite formation on charging. Dendrites of lithium lead to battery failure and significantly compromise safety. Polymeric electrolytes and some ionic liquids do not form dendrites during the battery operation and can be used as electrolytes on their own or as polymeric/ionic liquid mixtures. However the low ambient and particularly sub-ambient temperature conductivities together with lithium transference number close to 0.1-0.2 are serious limitations of true solid polymer electrolyte systems.

In the former sections we've tried to highlight various ways of modification applied for liquid and polymeric systems. In the case of liquid solutions work performed was dedicated to search for new solvents or solvent salt combinations. In the case of new solvents it is difficult to quote any major break through compared with the existing ones. The same conclusions can be drawn when considering application of various types additives used to enhance safety of batteries regulate the formation and stabilization of SEI or modifying ionic transport. Very often the progress in one area is associated with negative effect of certain additive on another property of liquid electrolyte. On the contrary searching for the new salt, which in fact seems to be a central issue for all three types of solvent discussed in this report seems to open new possibilities. Despite the fact that so far none of the proposed salt satisfy all desired requirements the variety of possible choices of the salt synthesis together with the modification of the structure of existing ones open new possibilities for each technology under consideration. Ideally

the salt of choice should be inexpensive, easy to prepare and environmentally friendly. It should also fulfil the expectations listed in previously in this report. Various families or organic salts are of choice for application in lithium or-and lithium ion batteries. In this case molecular modelling approach can be very helpful in designing new organic salts and reduce expensive and time consuming synthetic work for the systems which do not theoretically offer any advantages compared with existing ones.

Two anions based on this concept were introduced in 2003, with the dicyanotriazolate $C_5N_4^-$ (TADC) [175,183] and the bis(trifluoroborane)imidazolidine $C_3N_2(BF_3)_2^-$ (Id) [184]. The latter of these anions was intended for Li-ion batteries and presented the highest conductive alternative of several synthesized lithium salts, based on the same concept [185]. Tested in a Li-ion cell, the LId salt showed results comparable to $LiPF_6$, with a high ambient temperature conductivity, good solubility, and good electrochemical stability (> 4.8 V vs. Li^+/Li^0) [184]. Highlighting the favourable synthesis aspects of this salt, LId was advocated as a low-cost alternative to $LiPF_6$. However, the B-F bond poses a potential problem, although not as severe as for the P-F bond in PF_6^- , of possible decomposition or hydrolysis with the resulting formation of LiF or HF [186]. Related to this is the partial disproportionation of the Id anion into BF_4^- at a temperature of $85^\circ C$ [187], with a negative effect also on the overall conductivity.

LiTADC was originally aimed at polymer electrolytes [175]. Parallel to the experimental work on the LiTADC salt theoretical efforts resulted in several suggestions for synthesis of related azoles, including imidazoles [188]. Although many of these salts were predicted to have improved lithium ion dissociation qualities over TADC, practical difficulties in obtaining the proposed salts have so far hindered experimental explorations of their potencies [189]. Therefore, attention has instead been directed towards other heterocycles with more facile synthesis routes.

Two anions brought to focus very recently are the 4,5-dicyano-2-trifluoromethyl imidazole (TDI) and its 2-pentafluoroethyl analogue (PDI). The lithium salts of these anions have by some of us been characterized in model polymer electrolytes [190] and stressed as "tailor made" salts for lithium battery applications [191]. Of these salts, the synthesis of LiTDI has been shown to be the most facile. The first report of this salt appeared five years ago [192], when it was prepared in good yield in connection with the finding of a new, improved synthesis route for the protonated (uncharged) form of TDI, known since the mid 70's [193].

The Chalmers group [194] used LiTDI and LiPDI as templates and screen for further synthesis candidates by means of computational *ab initio* methods. New anions are proposed by first extending the heterocyclic imidazole ring to a benzimidazole ring, with two or four cyano groups symmetrically positioned on the ring, and secondly by also looking at alternatives where the fluoroalkyl substituent is replaced by a smaller, less flexible group. Ion pair configurations and dissociation energies, together with anion stabilities towards oxidation are evaluated. Information is obtained about the sensitivity of these properties with respect to ring size (imidazole or benzimidazole), the number and positioning of $-CN$ groups, and the choice of substituent ($-CF_3$, $-C_2F_5$, or $-CN$) at position 2 of the heterocyclic ring. Particularly cyano substituted benzimidazoles were found to be a very promising candidates from the viewpoint of possible application in the battery technology. However they are more difficult to synthesize than their imidazole cousins. Successful finishing of the synthetic procedure will give us more information about the reaction yield and possibilities of scaling it up.

In the preceding section example of performance of LiTDI and LiPDI in all solid as well as in liquid electrolyte based batteries were shown. Although, the preliminary results are promising further studies in various electrode configurations need to be performed. It should be emphasized that the use of organic salts will extend the range of possible solvent combinations which can lead to the improvement of safety as well as reduction of environmental impact. It is also worth to mention that organic salts can be used as components in the synthesis of ionic liquids. In such a case no additional lithium salt will be required as a component of electrolyte. So far addition of the salt reduces the conductivity range of ionic liquids based electrolytes. As was shown before [190,191] addition of TDI to PEO based polymer electrolytes enhances the ambient temperature conductivity of these systems. However, as it can be concluded on the basis of the review of properties of modified polymeric electrolytes it is hardly to achieve the level of conductivity exceeding 10^{-4} S/cm at ambient temperatures. Moreover, what also should be emphasized is the fact that most of the method of electrolyte modification were developed in late 80-ties or early 90-ties. Since that time small modifications of particular procedures are described in literature but it will be difficult to talk about the major breakthrough of this area. It is quite common to see the papers repeating data published before the internet area especially among American labs and Universities. Currently the use of polysiloxane based electrolytes seems to undergo a renaissance (papers 1O-04 and 2O-05 presented at PBFC Conference held in 2009 in Yokohama). More detailed report are however needed to see whether the performances obtained are in fact much better than data presented by Japanese groups in the 1980-ties. An interesting concept of the use of crystalline electrolytes developed by Prof. Bruce group and described briefly above is still in the phase of laboratory testes.

Table 5 summarizes the properties of each class of electrolyte discussed. In spite of the increase of the safety of electrolytes utilizing ionic liquids in terms of less flammability compared with liquid electrolytes (also mentioned in the Table) recent report highlights quite extensive thermal effect in the batteries utilizing ionic liquids (paper 2O-02 presented at PBFC 2009).

Table 5 Comparison of the properties of various types of electrolytes used in lithium-ion battery technology

Type of solvent	r.t. Conductivity [mS/cm]	t_{Li+}	Electrochemical stability range vs Li	Concerns on safety and environmental hazardous
Liquid	1-10	0.2- 0.4	0 to 6 V	High
Polymer	Up to 0.1	0.1- 0.3	0 to 4.5 V	Low
Ionic liquid	1-10	Up to 0.3	1.5-6 V	Moderate

It should be quoted that for some polymeric electrolytes or polymer type ionic liquids synthesized in the form of polyelectrolytes or utilizing anion trapping additives higher lithium transference numbers are reported usually connected with considerable reduction in ambient temperature ionic conductivity.

To summarize the choice of particular electrolyte for lithium or lithium-ion battery would depend on the application of the devices. It will be difficult to quote the winner among the contenders however Alistore-ERI approach of introduction of new salt systems useful for all type of solvents might enable killing three birds with one stone. At the very end we would like to draw industrial partners attention to the newly developed concept of using mixed system (porous ceramic sponge filled with liquid form of polymeric electrolyte) [195]. Figure 23 presents very preliminary testes of the battery using such type of electrolytes. The results are quite promising even if the system was randomly chosen and not optimized in any respects.

Electrodes: metallic Li (-), NiO-C composite (+) deposited on the electrolyte support
Electrolyte: 1M LiClO₄/PEODME500 supported by anodised alumina membrane (200nm pore size)
Coin cell (CR2032) configuration, $t = -15^{\circ}\text{C}$, C/5 rate between 1.5 and 0.1V (floating at 0.1V and 1.5V)
 → Q charge vs. cycle number → Q discharge vs. cycle number #

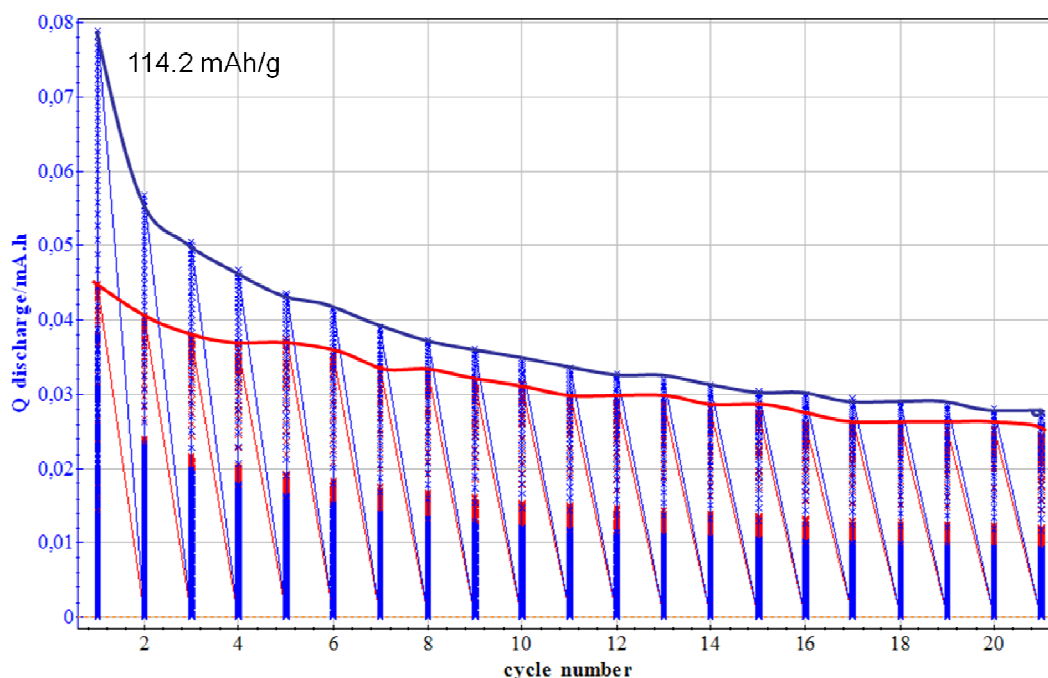


Figure 23. Charge and discharge capacity of the first cell prepared.

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