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Modern generation of polymer electrolytes based on lithium conductive imidazole salts

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Abstract

In this paper the application of completely new generation imidazole-derived salts in a model polymer electrolyte is described. As a polymer matrix two types of liquid low molecular weight PEO analogues e.g. dimethyl ether of poly(ethylene glycol) of 500 g mol⁻¹ average molar mass (PEGDME500) and methyl ether of poly(ethylene glycol) of 350 g mol⁻¹ average molar mass (PEGME350) were used. Room temperature conductivities measured by Electrochemical Impedance Spectroscopy were found to be as high as 10⁻³-10⁻⁴ S cm⁻¹ in the 0.1-1 mol dm⁻³ range of salt concentrations. Li⁺ transference numbers higher than 0.5 were measured and calculated using the Bruce-Vincent method. For a complete electrochemical characterization the interphase resistance stability over time was carefully monitored for periods of 30 days. Structural analysis and interactions between electrolyte components were done by Raman spectroscopy. Fuoss-Kraus semiempirical method was applied for estimation of free ions and ionic agglomerates showing that fraction of ionic agglomerates for salt concentration of 0.1-1 mol dm⁻³ is much lower than in electrolytes containing LiClO₄ in corresponding concentrations.

Keywords: lithium electrolytes; lithium salts; conductivity; transference number; interfacial stability.

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1. Introduction

Although development of the novel electrode materials for lithium (ion) batteries became widespread (especially for cathode) in the last decade, electrolytes used in these devices are still those created in early 90's. Solvents for the electrolytes, as certain compositions were optimized [1,2], are usually made from a mixture of organic carbonates or from poly(ethylene glycol).

LiPF₆, which is the one of the most frequently used electrolyte salts, is known for years for its corrosive properties (e.g. hydrolysis to HF). Since its introduction, a few new salts were added to the choice for the industry for the wide application in lithium-ion batteries. Apart from the salts known before initiation of the lithium batteries market in 1991 (LiClO₄, LiAsF₆, LiPF₆, LiBF₄ or LiCF₃SO₃), in the last two decades introductions of new anions for lithium salts were limited. Such salts range from imide salts, LiTFSI (LiN(SO₂CF₃)₂) [3], LiBETI (LiN(SO₂C₂F₅)₂) [4], to methide ones, LiC(SO₂CF₃)₃ [5] and LiC(SO₂CF₃)₂(RCO) [6], to orthoborate chelate-type class, like LBBB (lithium bis[1,2-benzenediolato(2-)-O,O']borate) [7-9], LiBOB (lithium bis(oxalate)borate) [10,11] or LiTFAB class (tetrakis(haloacyloxy)borates) [12], phosphate salts, like LiFAP (LiPF₃(CF₂CF₃)₃) [13] and finally to trifluoroborate anions CF₃BF₃ and C₂F₅BF₃ [14]. None of them really got through to the mass production due to different issues. LiTFSI, LiBETI and methide anions were corrosive against Al current collectors [15]. Others, like LiBOB, had problems with a too resistive electrolyte-electrode interphase. Most of them (orthoborate, chelate-type, some of phosphate salts and trifluoroborates) had too low conductivity. Some were not introduced due to their high price (LiTFSI and LiFAP).

Based on the above description there is still a strong demand for salts tailored for use as lithium electrolytes.

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). This particular structure is completely covalently bonded and shows very stable 6 π (or 10 π 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 (~300°C) thermal stability. LiDCTA was successfully tested in PEO matrices systems as a promising, improved electrolyte for rechargeable lithium

batteries [16]. Unfortunately DCTA failed as a component of the EC/DMC 50/50) battery electrolyte [17].

Similar structures as studied in this paper have been previously patented (EP-0 850 933-A) where imidazole ring was bonded to electrophilic groups such as perfluoroalkylsulfonyl or perfluoroalkylcarbonyl. However the presence of oxygen originated from C=O and O=S=O groups limited the salt dissociation and weakened the stability of the overall structure. In the present work the idea of using Hückel type anions has been extended to the salts with CF₃ or C₂F₅ groups.

The goal of the present studies is to precisely tailor the new types of salts applicable (e.g. thermally stable at elevated temperatures and electrochemically useful at the potentials up to 5 V vs Li) as an electrolyte in the electrochemical devices. General concept of the synthesis route was to weaken chemical bonds between anion and lithium cation in order to limit ionic pair formation. Increasing the "free" ions or/and decreasing the aggregates fraction in electrolyte would enhance electrolyte's transport properties e.g. increase cation transference number and conductivity. Especially breaking ion pairs and higher aggregates is important in terms of potential applications in lithium (ion) batteries. Desired properties would be assured by perfluoroalkyl substituents attached to the ring carbon skeleton and additionally modified by H, F, Cl, fluoro or perfluoro alkoxy (1-5 carbon chain length) or alkyl group also fluoro or perfluoro (1-5 carbon chain length). The idea presented here was previously introduced in the French patent application [17] and presently is subjected to the extension procedure in other countries (USA, Japan etc.). Since it is a new scientific path there is still a lack of publications in that area, however synthesis of the 2-trifluoromethyl-4,5-dicyanoimidazole were formerly described by Bukowska *et al.* [18]

Described concept has been recently examined theoretically by computational modeling. Jacobsson *et al.* [19] studied anion oxidation potentials and lithium ion pair dissociation energies of nitrile substituted imidazoles. As expected, the number and position of nitrile groups showed a substantial effect on the anion electrochemical stability and influenced the possible ion pair formation mechanism.

Here we present for the very first time experimental data for two representatives of this kind of lithium structures as constituents of the methyl ether of poly(ethylene glycol) and dimethyl ether of poly(ethylene glycol) based polymer electrolytes.

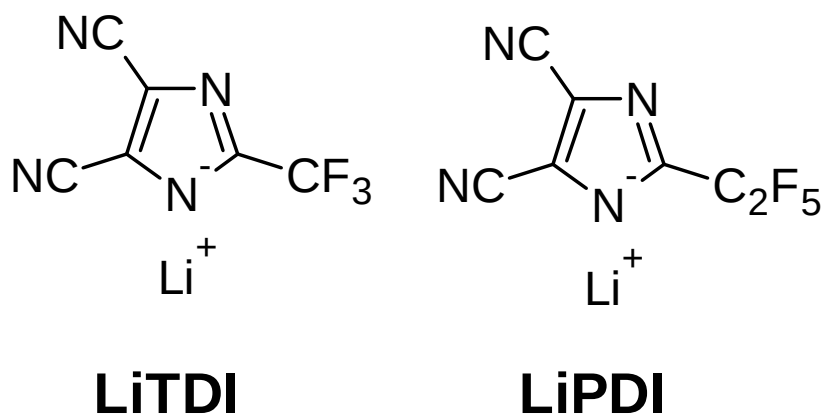


Fig. 1. Structural formula for LiTDI and LiPDI.

2. Experimental

2.1. Sample preparation

Two examples of novel generation salts proposed here as an electrolyte component are: lithium 4,5-dicyano-2-(trifluoromethyl)imidazole (LiTDI) and lithium 4,5-dicyano-2-(pentafluoroethyl)imidazole (LiPDI) (Fig.1) which were dissolved in liquid low molecular weight poly(ethylene glycol)s. Synthesis routes of salts are presented elsewhere [20].

All samples were made using vacuum-dried salts (both LiTDI and LiPDI) in vacuum at 130°C for 4 hours. PEGME350 (methyl ether of poly(ethylene glycol) of average molar mass 350 g mol⁻¹) and PEGDME500 (dimethyl ether of poly(ethylene glycol) of average molar mass 500 g mol⁻¹), used as solvents, were dried on vacuum line at 90°C for 72 hours. Salts were dissolved and samples were prepared in drybox with argon atmosphere containing less than 3 ppm of water, with every operation taking place at 25°C. Lithium metal (1.5 mm thick, 99.9% purity, Aldrich) was used for electrodes for Electrochemical Impedance Spectroscopy (EIS) and cell polarization measurements.

2.2. Electrochemical characterization

2.2.1. Electrochemical impedance spectroscopy - ionic conductivity

Ionic conductivity was measured using electrochemical impedance spectroscopy (EIS) in the temperature range from 20°C to 70°C. Electrolytes were sandwiched between stainless steel blocking electrodes and placed in a cryostat-thermostat system. A Swagelok-type cylindrical cell with electrodes of 13 mm diameter was used for measurements, with electrolyte layer thickness of between 170 and 180 μm (measured each time with 1 μm

precision). All impedance measurements were carried out on the computer-interfaced VMP3 (Biologic Claix France) multichannel potentiostat within frequency range from 500 kHz to 100 mHz with 10 mV a.c. signal.

2.2.2. Electrochemical impedance spectroscopy – Li/electrolyte interfacial stability

Interfacial stability was measured over 30 days. Li/electrolyte/Li symmetric cells were stored at room temperature and impedance spectra within range from 500 kHz to 100 mHz were recorded on VMP3 multichannel potentiostat. All measurements were carried out at 20°C temperature. Spectra were analyzed with Equivalent-circuit 4.55 application developed by Bernard A. Boukamp [21,22] and each spectrum was fitted with an equivalent circuit which allowed to separate resistance contributions between different phenomena. This circuit consisted of three parts connected in series:

1. electrolyte resistance (R_e);
2. parallel combination of charge transfer resistance (R_{ct}) and constant phase element associated with it;
3. parallel combination of passive layer resistance (R_p) and constant phase element associated with it;

2.2.3. Lithium transference number

Transference numbers (t_+) were calculated using d.c. polarization method combined with a.c. impedance method introduced by Bruce and Vincent [23,24]. Impedance spectroscopy measurements were performed on VMP3 multichannel potentiostat with a.c. signal of 10mV in 500 kHz to 100 mHz range. Impedance spectra were analyzed with the Equivalent-circuit 4.55 software [21,22]. Chronoamperometry measurements were executed also on the VMP3 multichannel potentiostat. Polarization with 20 mV potential difference was applied on each sample until current reached steady-state. All measurements took place at the temperature of 20°C.

Polarization method, where $t_+ = I_s / I_0$ (I_0 - initial current; I_s - steady-state current) is working well in assumption of ideal conditions. Under real conditions current flow is affected by passive layer forming, so the adequate correction for resistance changes is needed. For the Li / Li^+X^- / Li cell type, Bruce and co-workers introduced the following correction:

$$t_+ = (I_s (\Delta V - R_0 I_0)) / (I_0 (\Delta V - R_s I_s))$$

where:

ΔV = d.c. voltage applied;

R_0 = initial passive layer resistance;

R_s = steady-state passive layer resistance;

I_0 = initial current;

I_s = steady-state current;

Impedance spectroscopy measurements were taken just before d.c. polarization and immediately after it reached steady-state. The lithium cation transference numbers of the samples were measured at room temperature. Every concentration of each salt was measured on three samples for consistency of data.

Bruce and Vincent method was derived for polymer electrolytes with electrolyte and charge transfer resistances of the similar order. However, the method was also successfully used with liquid non-polymer electrolytes, where differences between electrolyte and charge transfer resistance are similarly large [25]. Moreover, this experimental approach was used in gel electrolytes, e.g. in the systems with very high passive/charge transfer resistance (more than order of magnitude higher than electrolyte one) [26,27]. Bruce and Vincent method was also used in the oligo(ethylene) systems [28]. It was also a practical advantage to use this method. Besides some limitations it is one of the most popular methods and thus very easy to compare with systems studied by other researchers.

2.2.4. Fuoss-Kraus formalism - ionic fractions estimation

Ionic fractions estimation was made using Fuoss-Kraus formalism [29-31] adopted for polymer electrolytes by Vincent et al. [32]. The method consists of limiting conductance measurement, then calculation of ion pair formation constant and triplets (both LiA_2^- and Li_2A^+ , where A is an anion of the electrolyte) formation constants. It is possible then to calculate fractions of triplets, ion pairs and “free” ions. This method distinguishes agglomerates (pairs, triplets) which are bonded by electrostatic forces (also in agglomerates with solvent molecules), as distinct from direct bonds which are the only detected by FT-IR or Raman peak analysis method [33]. All calculations were done on conductivity data collected at the temperature of 20°C.

2.3. Raman spectroscopy - ionic association estimation

Raman spectra were performed on Nicolet Almega dispersive spectrometer. Diode laser with an excitation line at 780 nm was used. The spectral resolution was about 2 cm^{-1} for all measurements. Peak analysis was used for calculation of ionic constituents' fractions

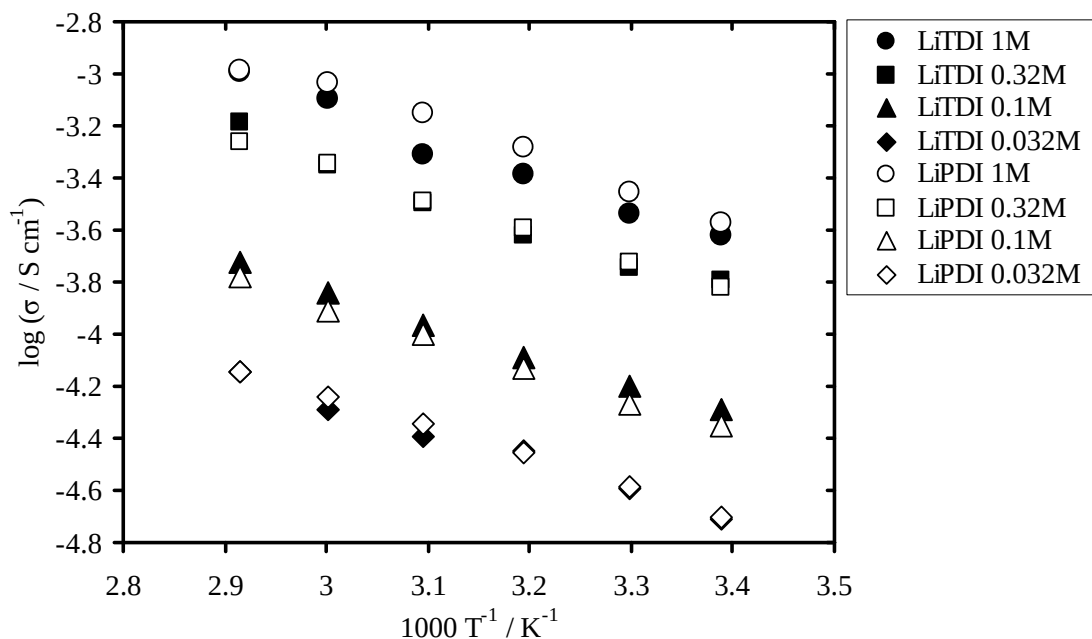


Fig. 2. Temperature dependence of LiTDI and LiPDI in PEGDME500 conductivity for different salt concentrations.

(“free” ions, ion pairs and triplets which are singly charged agglomerates of three ions). This method is based on numerical separation of peaks originated from anion vibrations [33]. After the base line correction, the peaks were fitted automatically and deconvoluted with Galactic Grams Research software using Gaussian-Lorentzian function. Raman experiments took place at room temperature.

3. Results and discussion

3.1. Electrochemical characterization

3.1.1. Ionic conductivity

Ionic conductivity was measured for two salts – LiTDI and LiPDI dissolved in PEGDME500 - in the temperature range between 20°C and 70°C, both for the same four concentrations. Arrhenius plots of these measurements are shown on Fig. 2 (both LiTDI and LiPDI). LiPDI is slightly more conductive with 0.15 mS cm^{-1} and LiTDI with 0.14 mS cm^{-1} at room temperature at high concentration (1 mol dm^{-3}), although difference is negligible. In the studied salt concentration range conductivity for electrolytes based on both salts is increasing with temperature.

A molar conductivity vs. square root of concentration diagram (Fig. 3) has been made for the salt concentration range where ionic pairs and higher aggregates usually form.

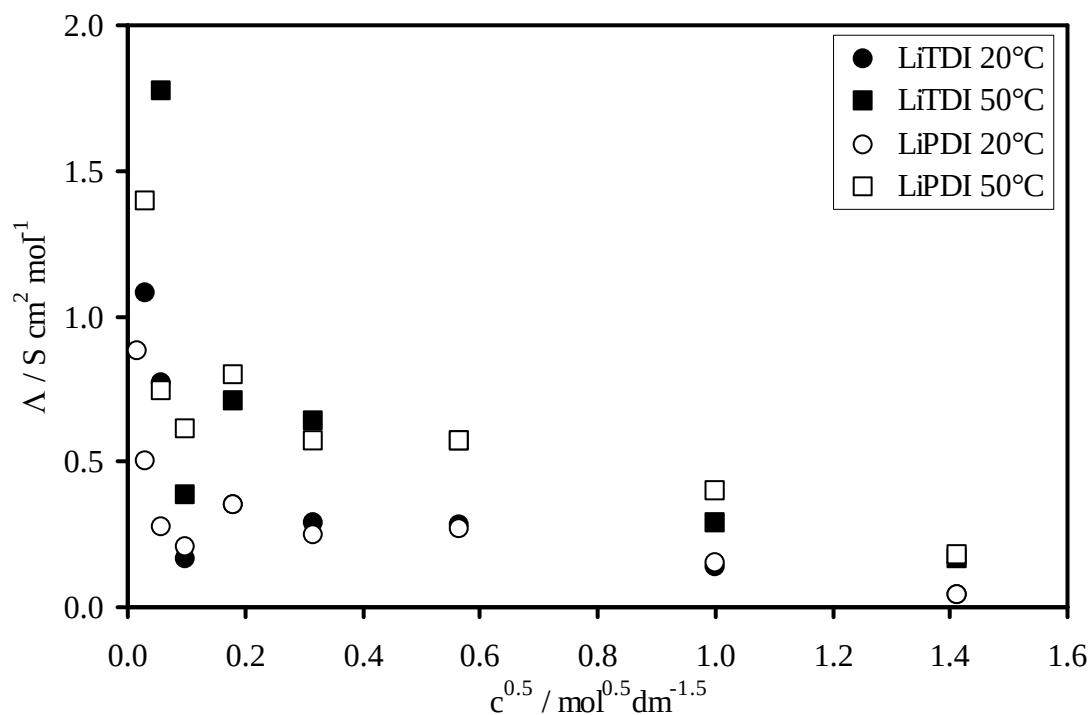


Fig. 3. Concentration's square root dependence of LiTDI and LiPDI molar conductivity in PEGDME500 at 20°C and 50°C.

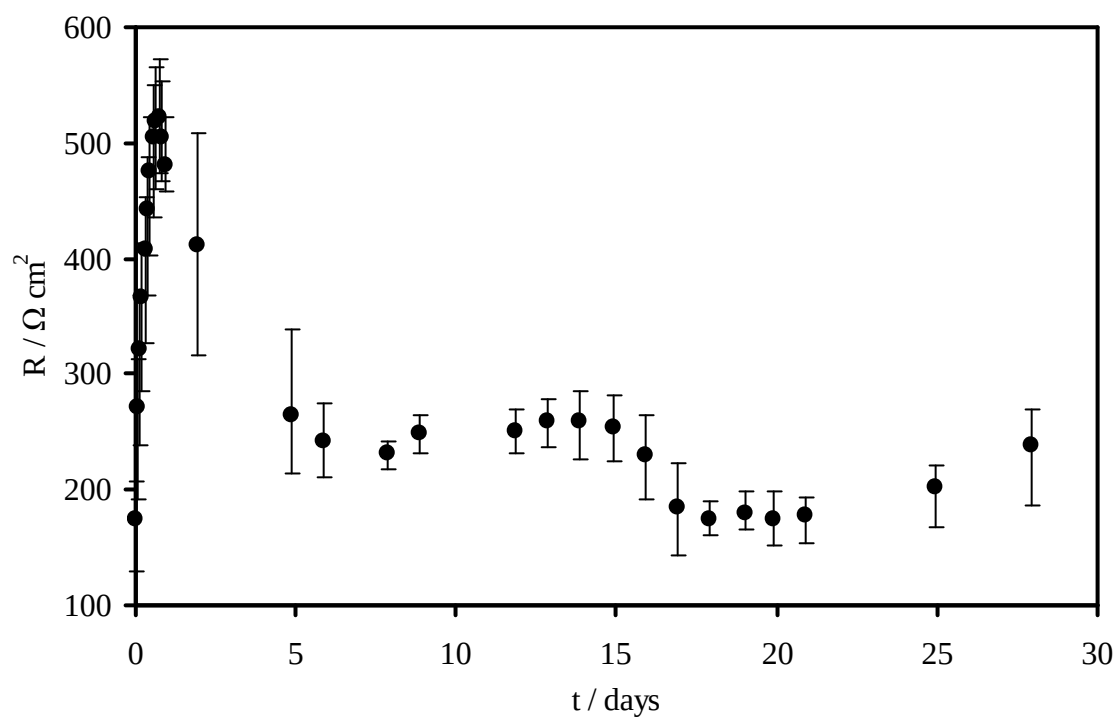


Fig. 4. Interface stability (area specific resistance as time function) of 0.5 mol·dm³ LiTDI in PEGDME500 – consistency of interface behavior averaged for 3 samples – with marked error range.

Exemplary data for 20°C and 50°C were shown. Starting at low molar conductance and with concentration growth there is a drop of molar conductivity when number of ion pairs increase (as the concentration of charge carriers increase the probability of forming associate is getting higher), causing decrease of “free” ions fraction. Note the local minimum is achieved for very narrow salt concentration range (in our case only for 0.05 and 0.1 mol dm⁻³). That would suggest limited ability of ion pair formation for these particular systems which is by the way another prove of concept of using imidazole salts in polymer electrolytes. Above 0.1 mol dm⁻³ triplets form (three ions’ agglomerate), and as a charged ionic constituent, provides rise in molar conductivity, until it reaches maximum at certain concentration.

3.1.2. Interfacial stability studies

Interfacial stability tests for LiTDI in PEGDME500 were carried out at the concentration of 0.5 mol·dm⁻³ (Fig. 4), by monitoring the passivation resistance with equilibria in the cell. For all samples formation and durability of resistive layer was similar, repetitive and stable. After short period of initial conditioning the film resistance reached a steady-state plateau and remained stable until the end of the testing period, a month after assembling. Also, the charge-transfer resistance and electrolyte resistances were stable throughout the investigated period (Fig. 5). The most important observation is that over the whole period of testing any signs of decomposition of electrolyte components haven’t been noticed.

Samples for 0.1 mol·dm⁻³ were also investigated (data not shown here), giving similar results for stability in the month period. Based on the above, it can be assumed that stabilization of LiTDI in PEGDME500 is satisfactory for lithium ion battery application.

3.1.3. Lithium transference number

In Fig. 6 lithium cation transference numbers vs. salt concentration are plotted for LiTDI and LiPDI in PEGDME500 matrix. As expected, new salts showed high lithium transference numbers in comparison to other salts used in similar systems. For the concentration of 0.1 mol·dm⁻³ LiTDI in PEGDME500 the t_+ value reaches 0.35 (Fig. 6). A maximum of t_+ at 0.56 was noticed for 0.1 mol·dm⁻³ LiPDI solution in the same polymer matrix.

Results shows that the maximum of cation transference number is shifted towards higher concentrations for LiPDI (maximum of averaged data at 0.03 mol·dm⁻³) than for LiTDI

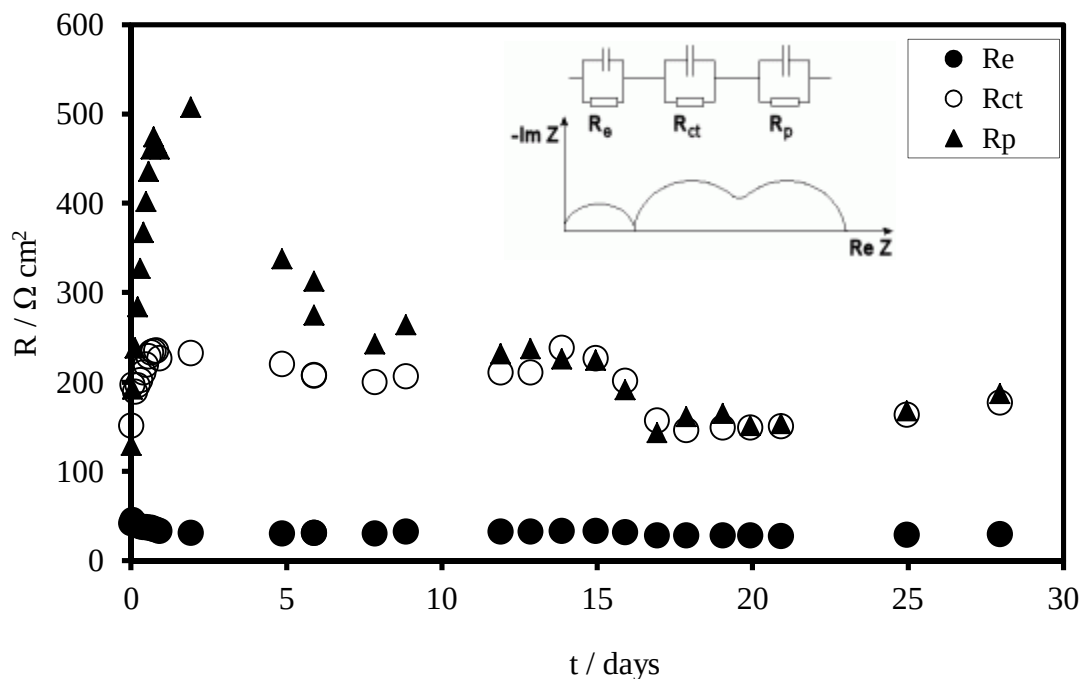


Fig. 5. Example of as interface stability (area specific resistance as time function) - one of three samples - of $0.5 \text{ mol} \cdot \text{dm}^{-3}$ LiTDI in PEGDME500; data obtained from impedance spectroscopy; spectra fitted with equivalent circuit described in text; R_e – electrolyte resistance; R_{ct} – charge transfer resistance; R_p - passivation layer resistance; Insert: scheme of equivalent circuit for data analysis.

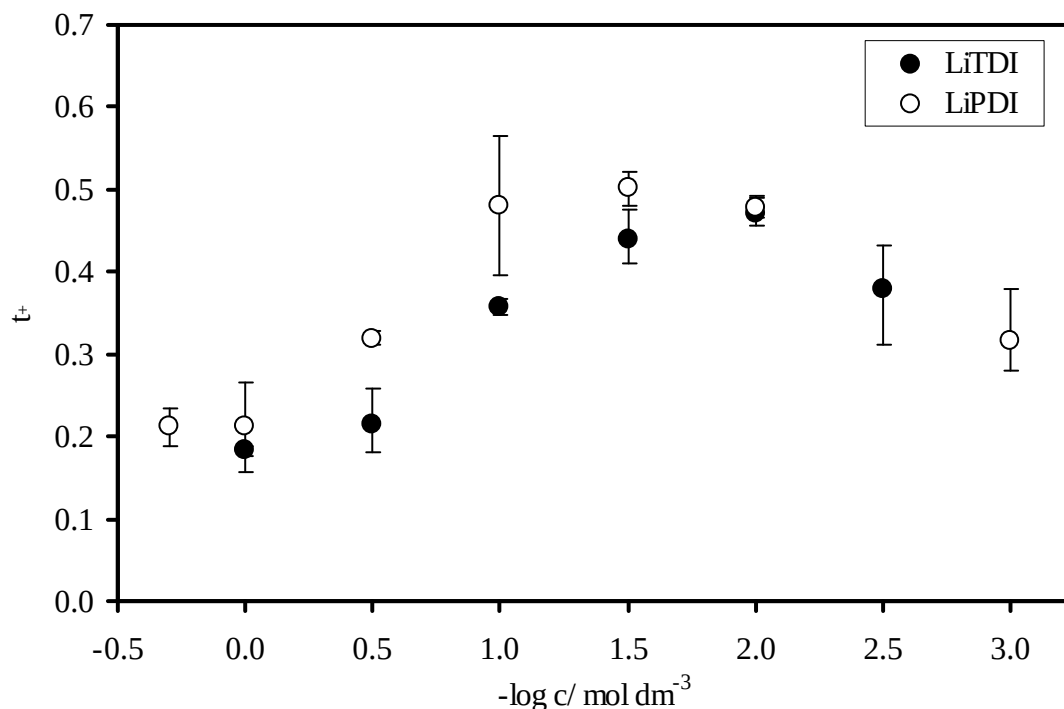


Fig. 6. Transference number dependence of salt concentration – comparison of both investigated salts; transference numbers calculated with Bruce-Vincent method for LiTDI and LiPDI in PEGDME500. Each point averaged over three samples - with marked error range.

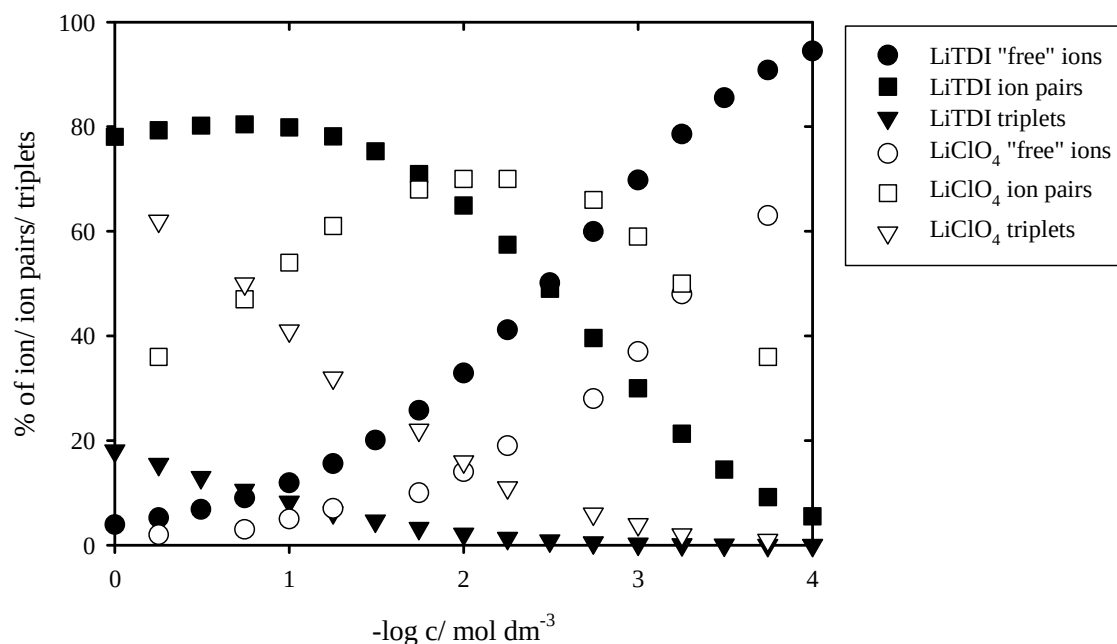


Fig. 7. Calculated ionic fractions for LiTDI in PEGDME500 and LiClO₄ in PEGDME400 at 20°C with Fuoss-Kraus formalism; data for LiClO₄ taken from [32].

(maximum at 0.01 mol·dm⁻³). In addition LiPDI reaches little higher t_+ , which is 0.50 (averaged data), than LiTDI (maximum for LiTDI is 0.47 for averaged data).

When compared to LiTDI in PEGME350 (data not shown here), it can be noticed, that numbers remain almost the same for analogue concentrations (in 1-0.1 mol·dm⁻³ range), even though -CH₃ group was changed on -OH group on the end of polymer matrix chain. So, it would suggest that functional groups on chain end have no or very little influence on the transport mechanism of these salts' ions. This seems to be promising in terms of applicability with variety of solvents.

3.1.4. Fuoss-Kraus formalism - ionic fractions estimation

Ionic fractions were calculated for LiTDI, LiPDI and LiClO₄ in low molecular weight poly(ethylene glycol)s. Data for LiClO₄ were taken from work of Vincent et al. [32]. LiClO₄ was chosen as it is known for its low association. As it is shown on the Fig. 7, for all concentrations useful for battery application (> 0.1 mol·dm⁻³) LiTDI / PEGDME500 has about 2-3 times higher free ions fraction than LiClO₄. Also, much smaller triplets' (4-5 times smaller, at 0.5 mol·dm⁻³ – 15.4% to 62%) fraction at LiTDI solutions is noticeable, assisted by higher ion pair's fraction. Despite a slightly smaller conductivity, which is the result of ions associated in neutral agglomerates, it is still much better than the LiClO₄ case. This

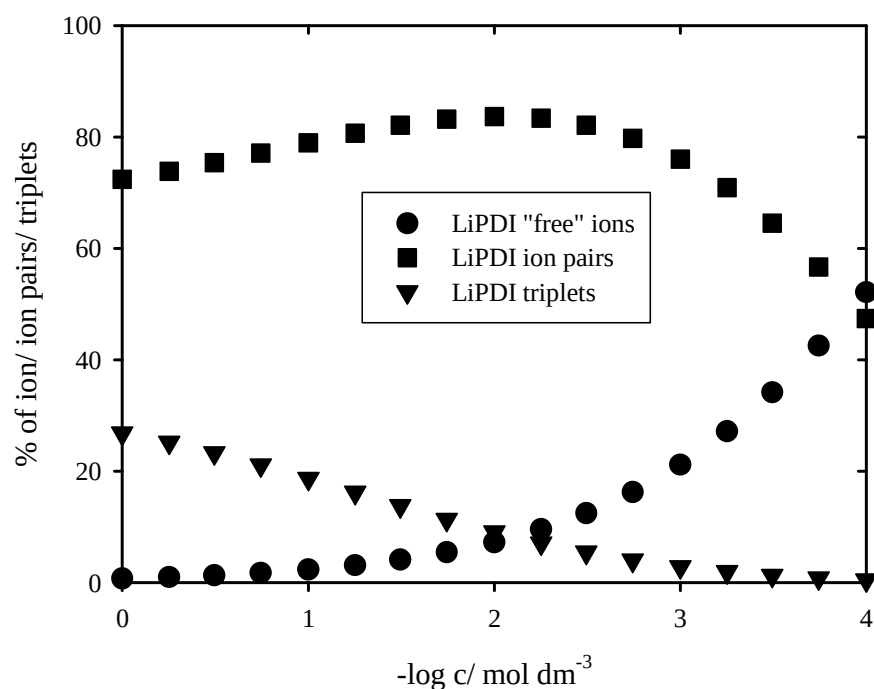


Fig. 8. Calculated ionic fractions for LiPDI in PEGDME500 at 20°C with Fuoss-Kraus formalism.

is because too high triplets concentration is negatively influencing important cell parameters, like interface stability over time and transference number.

Calculations for LiPDI / PEGDME500 electrolyte showed the comparable results with LiTDI / PEGDME500, although it is visible on the Fig 8, that triplets' fraction is a little higher for LiPDI and lower fraction of "free" ions. Nevertheless, LiPDI has still same "free" ions fraction and much lower triplets' fraction (about 3 times) than those of LiClO₄ electrolyte.

3.1.5 Raman spectroscopy - ionic association estimation

Various ionic species present in salt solutions can be distinguished by means of vibration spectroscopy. The new synthesized imidazole salts LiTDI and LiPDI are characterized by highly delocalized charge on the anion. Therefore, we may expect better dissociation in solutions of these salts, than in solutions of conventional salts like LiCF₃SO₃ or LiClO₄.

Through the analysis of the spectra of electrolytes' different concentrations, it was possible to match peak shifts with influence of different ionic constituents. For further calculations, the maximum of ν_{CN} band (2224 cm⁻¹) was chosen, as very strong and solitary

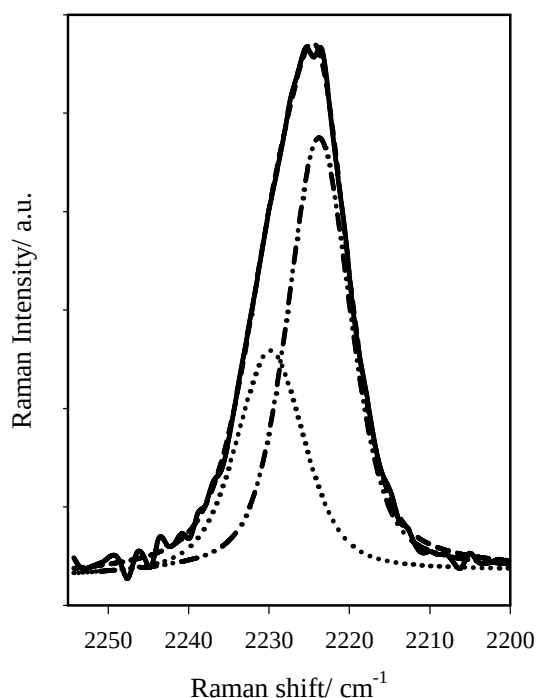


Fig 9. Exemplary deconvolution of the ν_{CN} peak in Raman spectrum for 1M LiPDI in PEGDME500.

in its area. Example of the deconvolution is present at Fig. 9. for 1M salt concentration range. For very diluted solutions one could find only one peak, assumed as the effect of only “free” ions influencing the bond. With the increase of concentration of salts, peak in LiPDI spectra was separating into two peaks with maxima at 2224 and 2230-2231 cm^{-1} with the new peak (2230 cm^{-1}) increasing its intensity with concentration. Deconvolution of these bands and calculating their surface ratio led to obtaining the “free” ion and ionic pair fractions in both LiTDI and LiPDI solutions in PEGDME500. Calculations’ result is shown in Table 1.

3.3. Discussion

When using salts having the charge dislocation in anion, associates are forming more rarely, while the ion bonding between anion and cation is not that strong. It is possible to observe it in Raman study, where actual structure of the electrolyte is revealed. As shown in Table 1, LiTDI in PEGDME500 is completely dissociated and LiPDI in its majority. However, picture of ionic association created exclusively from spectroscopic evidence is oversimplified and the comparison between numerous methods is always recommended. Thus, there was a semi empirical measurement elaborated using a procedure proposed by Fuoss and Kraus. Fuoss-Kraus method in authors’ opinion gave more precise results

Salt concentration / mol·dm ⁻³	“free” ions	Ionic pairs	“free” ions	Ionic pairs
	LiTDI		LiPDI	
1	100	0	65	35
0.5	100	0	83	17
0.32	100	0	84	16

Table 1. Content of ion pairs calculated on the basis of deconvolution of Raman spectra. Solutions of LiTDI (lithium 4,5-dicyano-2-(trifluoromethyl)imidazole) and LiPDI (lithium 4,5-dicyano-2-(pentafluoroethyl)imidazole) in PEGDME500 (dimethyl ether of poly(ethylene glycol) of average molar mass 500 g·mol⁻¹). Peak was resolved using two curves, with maxima at 2224 and 2230-2231 cm⁻¹. “Free” ions content was obtained by calculation of the share of the area of peak at 2224 cm⁻¹.

of estimation of the solvent separated ion pairs and thus gave the most reliable results of the amount of ionic associates. On the other hand it has to be stressed out that percentage of ionic species fraction obtained from Raman results and from Fuoss-Kraus method may differ significantly because Raman spectroscopy cannot distinguish solvent separated ionic pairs from “free” ions, i.e. ionic pairs’ content will be always higher according to Fuoss-Kraus calculations. Additionally, the deconvolution of Raman spectra gives reasonable results if the intensity of the band is high enough, i.e. for higher salt concentration. In contrast, Fuoss-Kraus method is more valid for diluted systems. What is important, both methods give evidence of better dissociation of TDI as compared with PDI.

It is worth mentioning that electrolyte based on LiPDI, although not so spectacular in Fuoss-Kraus calculation as LiTDI electrolyte, has still much smaller fraction – 3 times smaller – of charged agglomerates than LiClO₄ electrolyte, while “free” ions fraction is of the comparable value at high concentrations. It would mean that charge distribution on imidazole-derived anion is more uniform than for ClO₄⁻, which was assumed from the beginning. The smaller “free” ions fraction and a little higher triplets fraction for LiPDI electrolyte compared to LiTDI electrolyte is not necessarily meaning that LiPDI possesses worse association properties in charge distribution terms. It is still always recommended to compare it with complementary results originated from other methods, like Raman spectroscopy, when considering that complicated interactions.

Electrochemical research, using Fuoss-Kraus formalism, gives information on long-distance structure (electrostatic interactions between solvated ions), so it is not negating data obtained through spectroscopic methods. Given the molar

conductivity data (Fig. 3), it can be proved that Fuoss-Kraus method is properly estimating the concentration, at which “free” ions fraction exceeds (when concentration decrease) ion pair fraction – 0.1 mol dm^{-3} . On the molar conductivity figure it is the visible minimum for all temperatures, while on the associates fractions figure it is clear, that crossing of those two lines occurs at the same concentration (0.1 mol dm^{-3}).

Weaker ion bonding between cation and anion was achieved with making the anion small enough, so it would not increase too markedly the local viscosity of the electrolyte. Conductivity tends to decrease when anion of the salt in electrolyte is too large because of its local viscosity increase. On the other hand size of the anion should be somehow compromised in order to guarantee uniform charge delocalization within its structure. The latter is also assured by the symmetry of the anion structure and withdrawing the charge outside the ring by attaching satellite functional groups (e.g. $-\text{CF}_3$) as confirmed by theoretical simulations [19]. Longer perfluorinated alkyl group (consisting of two carbons) should withdraw the charge from the ring even stronger (and thus, increasing charge dislocation) without disturbing the symmetry. The longer, three carbon fluorinated chain, would bend on one side, making the aromatic ring sides unequal in charge density terms. In consequence it would lead to a charge density shift and association more probable, as it is seen in difference between first two analogues in spectroscopic data. That is the main reason why herein the data for only two first analogues ($-\text{CF}_3$ and $-\text{C}_2\text{F}_5$) were presented.

Conductivities of electrolytes based on both investigated salts are sufficient for applications with even the most advanced electrode materials nowadays, because the cathode kinetics are the limiting element in conductivity terms equivalent. The best cathodic materials are capable of conductivity in the range of $10^{-5} \text{ S cm}^{-1}$ [34] at room temperature.

In terms of t_+ value LiPDI seems to be more attractive for practical applications. Optimum of the lithium transference number is reached for slightly lower salt concentration than for LiTDI in analogue system. It was one of the aims of synthesis strategy, to maximize value of lithium transference number. Structure with longer perfluorinated chain with maintained symmetry of the anion lead to the benefit of increased values of $\text{Li } t_+$ due to larger size of anion or the introduction of fluorophilic association of side chains.

4. Conclusions

Experimental results shown in the present work confirmed that new imidazole based lithium salts possess the properties necessary to apply them as electrolyte components

for lithium ion batteries. It has been shown that the conductivity of electrolytes obtained for both salts (LiTDI and LiPDI) is in range of 10^{-3} to 10^{-4} S cm⁻¹ at room temperature for concentrations higher than 0.1 mol dm⁻³. The electrode-electrolyte interface growth monitoring indicates no changes in the passive layer resistance after initial stabilization. All these results were reproducible for different salt concentrations in the electrolytes. Room temperature transference numbers were higher than 0.5 for LiPDI and near 0.5 for LiTDI at 0.1 mol dm⁻³ concentration. Studies on ionic agglomerates forming showed all (LiTDI) or majority (LiPDI) of the electrolyte in dissociated state. Those spectroscopic estimations are in perfect agreement with data from Fuoss-Kraus formalism based method. Comparison of LiTDI and LiClO₄ agglomerates fraction have been shown over 10^{-4} -1 mol dm⁻³ concentration range. Triplets' fractions for LiTDI based electrolytes at high concentrations were about four times smaller than for LiClO₄, with electrolyte sustaining quite high conductivity.

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