



## Liquid electrolytes based on new lithium conductive imidazole salts

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### ABSTRACT

In the present paper new generation of imidazole-derived lithium salts (LiTDI—lithium 4,5-dicyano-2-(trifluoromethyl)imidazolide, LiPDI—lithium 4,5-dicyano-2-(pentafluoroethyl)imidazolide and LiHDI—lithium 4,5-dicyano-2-(n-heptafluoropropyl)imidazolide) applied in a model liquid electrolyte, with propylene carbonate used as a solvent, is described. Room temperature ionic conductivities measured by Impedance Spectroscopy are as high as  $10^{-2}$  to  $10^{-3}$  S cm<sup>-1</sup> for the 0.1–1 mol dm<sup>-3</sup> salt concentration range. Lithium cation transference numbers calculated using the Bruce–Vincent method exceed 0.4 at salt concentration equal to 1 mol dm<sup>-3</sup>. Interface resistance measurements showed good stability at high—0.5 mol dm<sup>-3</sup> or low—0.01 mol dm<sup>-3</sup> salt concentrations. Ionic associations were estimated using Fuoss–Kraus semiempirical method revealing relatively low association rates. The effect of anion structure on ionic interactions and electrochemical characteristics of the studied electrolytes is discussed.

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### 1. Introduction

Lithium-ion batteries that supply energy for electric engines in cars and other devices are mostly based on electrolytes using LiPF<sub>6</sub> (lithium hexafluorophosphate) as the salt. However, this particular salt exhibits corrosive properties. This is mostly because it is an easy subject to hydrolysis (e.g. with the presence of traces of moisture) with release of HF (hydrogen fluoride) [1–3]. Therefore, special attention is needed to assure high purity of electrolyte for its proper work. Synthesis conditions for obtaining battery-grade LiPF<sub>6</sub> are also quite demanding. Although these are well known facts for years, still, there is almost no other salt used in the battery industry. Salts used before initiation of the lithium batteries market in 1991 were too toxic for application (LiAsF<sub>6</sub>), too volatile with cathodic materials (LiClO<sub>4</sub>)—also being considered as an explosive, had unsatisfactory low ionic conductivity (LiCF<sub>3</sub>SO<sub>3</sub>) or formed highly resistive SEI—Solid Electrolyte Interface (LiBF<sub>4</sub>) [4].

For the last twenty years there were only few new lithium salts introduced to the real life systems, none of them successful enough to be widely used by lithium battery manufacturers. Imide salts (e.g. LiTFSI—LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> [5], LiBETI—LiN(SO<sub>2</sub>C<sub>2</sub>F<sub>5</sub>)<sub>2</sub> [6]) and methide salts (e.g. LiC(SO<sub>2</sub>CF<sub>3</sub>)<sub>3</sub> [7]) appeared to be corrosive against Al current collectors [8]. Orthoborate chelate-type class salts (e.g. LiBOB—lithium bis(oxalate)borate [9]) formed too

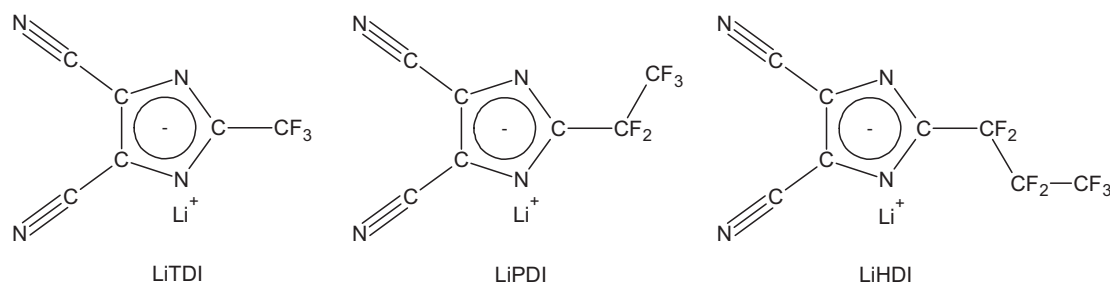
resistive SEI and their conductivity in liquid and (or) solid solvent was too low for practical applications. LiTFAB—class salts (lithium tetrakis(haloacyloxy)borates [10]) and phosphate ones (e.g. LiFAP—LiPF<sub>3</sub>(CF<sub>2</sub>CF<sub>3</sub>)<sub>3</sub> [11]) suffer from expensive synthesis when in mass production.

To sum it up, there is still an urgent need for a better conducting inexpensive salt to be used in lithium batteries.

To this end, new lithium salts, directly “tailored” for the lithium and lithium-ion cells application were synthesized [12]. These salts were based on stable structure of imidazole aromatic ring with covalently bonded electrophilic groups. Unlike many structures proposed by other researchers [13,14], in our approach the imidazole ring is connected to electrophilic groups via carbon, instead of nitrogen atoms. Such structure is even more electrochemically and thermally stable. Also, as the effect of superior charge dislocation in the anion, anion–cation interactions weaken, and so are the association constants. All of these increase the ionic mobility of the salt, regardless its anion size. As a result of these tailored structures syntheses, three new salts—LiTDI (lithium 4,5-dicyano-2-(trifluoromethyl)imidazolide), LiPDI (lithium 4,5-dicyano-2-(pentafluoroethyl)imidazolide) and LiHDI (lithium 4,5-dicyano-2-(n-heptafluoropropyl)imidazolide) [12,15] have been obtained.

Lithium salts have to fulfill or surpass numbers of requirements in order to be used in lithium batteries. The most important are: solubility in a given solvent (at least up to conductivity maximum), high ionic mobility (conductivity), electrochemical stability in wide potential window (at least 0–4 V vs. Li), chemical stability against all

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**Fig. 1.** Structures of LiTDI (lithium 4,5-dicyano-2-(trifluoromethyl)imidazolide), LiPDI (lithium 4,5-dicyano-2-(pentafluoroethyl)imidazolide) and LiHDI (lithium 4,5-dicyano-2-(n-heptafluoropropyl)imidazolide).

other cell elements (solvent, electrodic materials, charge collectors, etc.), thermal stability (up to 70 °C), high transference number and low association rate at high concentrations. Electrolytes obtained by dissolution of these new salts in PEO-oligomers have ionic conductivity and lithium cation transference number sufficient for the lithium-ion cells application [16].

It has been shown that new salts have thermal (up to 250 °C, proved by TGA, DTA and DSC measurements) and electrochemical (preferably up to 4.8 V vs. Li) stability. Up to 250 °C there was also no melting point, no sign of flame in air atmosphere or signs of decomposition under both argon or air atmosphere (both dry and moist) [12]. Salts are also non-hygroscopic, but also stable in wet atmosphere or even water solutions.

The present paper covers our latest research on the modern imidazole-class salts, showing how these new salts fulfill and exceed most of the requirements listed above when dissolved in propylene carbonate.

## 2. Experimental

### 2.1. Sample preparation

All three new salts, LiTDI, LiPDI and LiHDI (Fig. 1) were prepared according to the synthetic route described elsewhere [12]. Prior to the dissolution in propylene carbonate all salts were vacuum-dried at 130 °C for 4 h. Propylene carbonate was used as provided (anhydrous, 99.7%, Sigma–Aldrich). All preparation steps were carried out in an argon filled drybox containing less than 3 ppm of water, with all operations taking place at 25 °C. Lithium metal foil (1.5 mm thick, 99.9% purity, Aldrich) was used for electrodes in lithium cation transference number and interfacial stability measurements. Polypropylene separators soaked with electrolyte were used for lithium metal symmetrical-cell assembly.

### 2.2. Electrochemical characterization

#### 2.2.1. Electrochemical impedance spectroscopy—ionic conductivity

Ionic conductivity of propylene carbonate solutions was measured for all salts in the concentration range of 4 decades (from 1 to  $3.3 \times 10^{-4}$  mol dm<sup>-3</sup>). Measurements were performed using electrochemical impedance spectroscopy (EIS) in the temperature range from 20 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 film 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 40 days for 0.01 mol dm<sup>-3</sup> salts concentration and 80 days for 0.5 mol dm<sup>-3</sup> salts concentrations. 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 [17,18] and each spectrum was fitted with an equivalent circuit which allowed to separate resistance contributions between different phenomena. This circuit consisted of two parts connected in series:

1. electrolyte resistance ( $R_e$ );
2. parallel combination of interfacial resistance ( $R_i$ ) and constant phase element associated with it.

In order to verify the reproducibility of obtained results, each solution was tested on four samples.

#### 2.2.3. Lithium transference number

Lithium cation transference numbers ( $t_+$ ) were calculated using d.c. polarization method combined with a.c. impedance method introduced by Bruce and Vincent [19]. Impedance spectroscopy measurements were performed on VMP3 multichannel potentiostat with a.c. signal of 10 mV in 500 kHz to 100 mHz range. Impedance spectra were analyzed with the Equivalent-circuit 4.55 program [17,18] as described above. Polarization measurements were also executed on the VMP3 multichannel potentiostat. Polarization with 20 mV potential difference was applied on each sample until current reached steady-state (defined as a state where current difference in the last 10 min was lower than 1% relatively). All measurements took place at the temperature of 20 °C. The  $t_+$  for every concentration of each salt was measured on three samples for higher consistency of data. Then the lithium cation transference number was calculated as:

$$t_+ = \frac{I_s(\Delta V - R_0 I_0)}{I_0(\Delta V - R_s I_s)}$$

where:  $\Delta V$ —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.

Resulting individual  $t_+$  values were calculated with error always smaller than 0.02. Standard deviation of results at each concentration was always smaller than 0.06.

#### 2.2.4. Fuoss–Kraus formalism—ionic association estimation

Ionic fractions quantitative estimation was done using Fuoss–Kraus formalism [20] adopted for polymer electrolytes by Vincent and co-workers [21]. The method consists of limiting conductance measurement, then calculation of ion pair and triplets

(both  $\text{LiA}_2^-$  and  $\text{Li}_2\text{A}^+$ , 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 bonding which is the only detected by FT-IR or Raman peak analysis method [22]. All calculations were done on conductivity data collected at the temperature of 20 °C.

Calculation of the ionic fractions based on the Fuoss–Kraus formalism starts with the assumption, that ion pair, CA (C stands for the cation, A for the anion) can dissociate both to the free ions,  $\text{CA} \rightarrow \text{C}^+ + \text{A}^-$ , as well as forming triplet:  $\text{CA} \rightarrow 1/3\text{C}_2\text{A}^+ + 1/3\text{CA}_2^-$ . That defines hypothetical electrolyte  $\text{C}_2\text{A}^+\text{CA}_2^-$ , which is equivalent to the CA, but necessary for obtaining the equivalent factor between those structures (triplets and ion pairs). All these assumptions lead us to calculate association constants equations:



$$K_I = \frac{[\text{CA}]}{[\text{C}^+][\text{A}^-]} = \frac{1 - \alpha_I}{\alpha_I^2 c} \quad (4)$$

$$K_T = \frac{[\text{CA}_2^-]}{[\text{CA}][\text{A}^-]} = \frac{[\text{C}_2\text{A}^+]}{[\text{CA}][\text{C}^+]} = \frac{\alpha_T}{\alpha_I c (1 - \alpha_I - 3\alpha_T)} \quad (5)$$

$K_I$  and  $K_T$  stand here for the ion and triplet forming constants, respectively,  $\alpha_I$  and  $\alpha_T$  for the “free” ions and triplets fraction, respectively. We can transform Eqs. (4) and (5) to derive fractions:

$$\alpha_I = \frac{-1 + \sqrt{1 + 4K_I c}}{2K_I c} \quad (6)$$

$$\alpha_T = \frac{K_T \alpha_I (1 - \alpha_I) c}{1 + 3K_T \alpha_I c} \quad (7)$$

$$\alpha_P = 1 - \alpha_I - \alpha_T \quad (8)$$

$\alpha_P$  stands here for the ion pairs fraction, which we assume to be the rest of the electrolyte. That way, we assume, that no higher charged multiplets than triplets exist in the electrolyte. If no influence on the ions’ electrostatic fields would be taken into consideration, the total molar conductivity of the electrolyte could be written as:

$$\Lambda = \alpha_I \Lambda_0^I + \alpha_T \Lambda_0^T \quad (9)$$

Here,  $\Lambda_0^I$  and  $\Lambda_0^T$  stand for the limiting molar conductivity of the ions and triplets, respectively. If  $\alpha_I$  and  $\alpha_T$  have small values, Eq. (9) can be transformed and simplified to the following form:

$$\Lambda \sqrt{c} = \frac{\Lambda_0^I}{\sqrt{K_I}} + \frac{\Lambda_0^T K_T c}{\sqrt{K_I}} \quad (10)$$

The  $\Lambda \sqrt{c} = f(c)$  plot should be linear for diluted electrolytes (near the infinite dilution). So, after linear regression ( $y = ac + b$ ,  $a$  stands for the shift,  $b$  for the slope), the linear equation coefficients would be equal to  $a = \Lambda_0^T K_T K_I^{-1/2}$  and  $b = \Lambda_0^I K_I^{-1/2}$ . We can transform those equations to derive constants:

$$K_I = \left( \frac{\Lambda_0^I}{b} \right)^2 \quad (11)$$

$$K_T = \frac{a \sqrt{K_I}}{\Lambda_0^T} \quad (12)$$

The only remaining unknown values are now the limiting molar conductivities of ions and triplets, but  $\Lambda_0^I$  is equal to the  $\Lambda_0$ , because

at the infinite dilution we do not expect any triplets (we cannot have any ion–ion interactions), and  $\Lambda_0^T/\Lambda_0^I$  ratio is usually assumed to be 2/3 [21]. Now there is only a need to obtain  $\Lambda_0$ , which was calculated by fitting of the conductivity points with the Fuoss–Onsager equation:  $\Lambda = \Lambda_0 - S\sqrt{c} + E \cdot c \cdot \log(c) + J \cdot c$ . Given that, we can calculate ionic fractions.

### 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  $2 \text{ cm}^{-1}$  for all measurements. Peak analysis was used for calculation of ionic constituents’ fractions (“free” ions, ion pairs and triplets which are singly charged agglomerates of three ions). This method is based on numerical deconvolution and fitting of peaks originated from anion vibrations. This data processing routine was presented in details in our previous works [22]. 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

### 3.1. Ionic conductivity

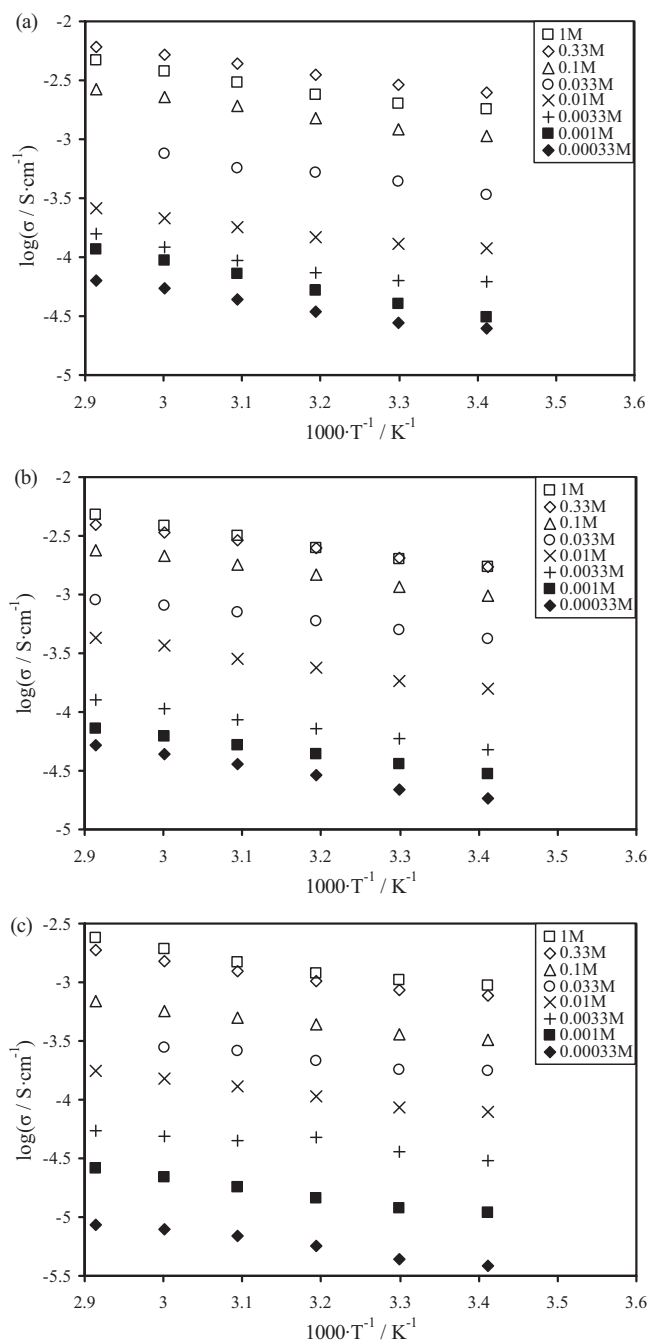
As it is shown in Fig. 2a, b and c, the highest conductivity at 20 °C is reached for LiTDI electrolyte, but ionic conductivities of electrolytes based on other salts do not differ dramatically from the LiTDI level. Maximum room temperature (20 °C) conductivity is reached at the very distinct maximum at  $0.33 \text{ mol dm}^{-3}$  concentration in case of LiTDI-PC (Fig. 2a), within  $0.33\text{--}1 \text{ mol dm}^{-3}$  concentration range for LiPDI-PC (Fig. 2b) electrolyte. Distinct maximum at  $1 \text{ mol dm}^{-3}$  concentration is noticed on the plot of the ionic conductivity against the concentration in case of LiHDI-PC (Fig. 2c). At the 20 °C temperature the highest ionic conductivity is equal to  $2.50 \text{ mS cm}^{-1}$  for LiTDI-PC,  $1.72 \text{ mS cm}^{-1}$  for LiPDI-PC and  $2.11 \text{ mS cm}^{-1}$  for LiHDI-PC.

Molar ionic conductivity dependence of logarithm of concentration plotted in Fig. 3 shows visible difference between LiHDI salt solutions and the two others electrolytes. The behavior of LiTDI-PC and LiPDI-PC electrolytes is typical for weak electrolytes with distinct (although shallow) minima, which appear in the range of  $0.0033\text{--}0.033 \text{ mol dm}^{-3}$  (for LiTDI and LiPDI) followed by the maxima at 0.1 (LiTDI) and  $0.01 \text{ mol dm}^{-3}$  (LiPDI) concentration. The same plot obtained for the LiHDI-PC electrolyte does not show neither a conductivity maximum, nor a minimum, even at lower concentrations than shown on Fig. 3.

### 3.2. Interfacial stability studies

Interfacial stability tests against lithium metal anode for LiTDI, LiPDI and LiHDI were monitored for the PC solutions at  $0.01 \text{ mol dm}^{-3}$  concentration. Results are shown in the Fig. 4a. In the figure it is clear that LiHDI-PC electrolyte is perfectly stable throughout the whole experiment period of 42 days. LiTDI-PC solution was stable up to 500 h (21 days) and LiPDI-PC remains stable only up to about 150 h (6 days). Difference between LiTDI-PC and LiPDI-PC electrolytes was that LiTDI-PC interfacial resistance increased its value quickly (5 times during 200 h) and LiPDI slowly (3 times during 600 h). The interfacial resistance value during experiment for LiHDI-PC electrolyte started from  $792 \Omega \text{ cm}^{-1}$  (after 2 h) and reached  $1101 \Omega \text{ cm}^{-1}$  (after exactly 1000 h).

LiTDI and LiPDI based electrolytes were tested again at  $0.5 \text{ mol dm}^{-3}$  salt concentration in PC (Fig. 4b). At this concentration SEI for both electrolytes was stable up to 220 h—interfacial

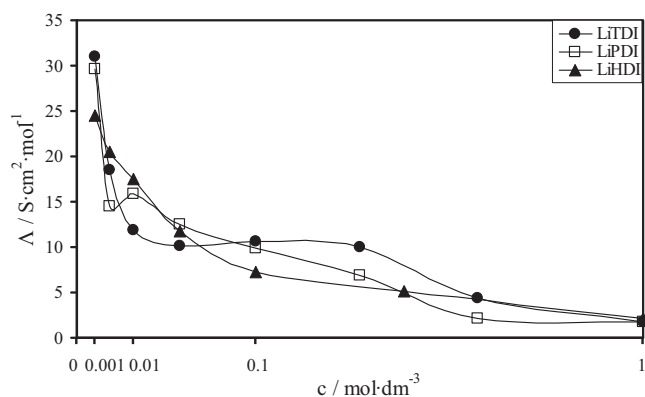


**Fig. 2.** Temperature dependence of conductivity for different salt concentrations of propylene carbonate-based electrolytes: a) LiTDI; b) LiPDI; and c) LiHDI.

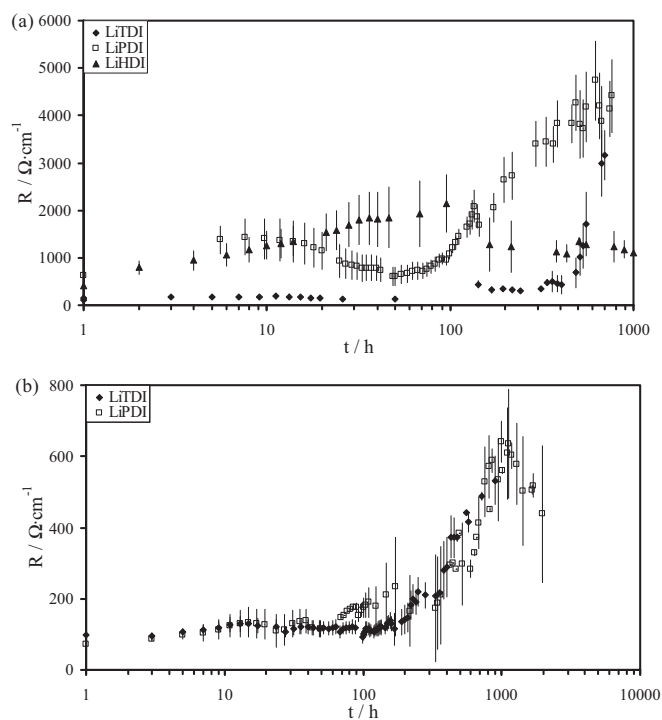
resistance changed from 95 to  $147 \Omega \text{ cm}^{-1}$  for LiTDI-PC and from 88 to  $166 \Omega \text{ cm}^{-1}$  for LiPDI-PC. After growth and peaking 533 and  $644 \Omega \text{ cm}^{-1}$  (LiTDI-PC and LiPDI-PC, respectively) after about 800 h (equal to 33 days), SEI resistance for both salts in PC has stabilized for over 300 h and started to drop slowly towards the end of experiment at 2000 h (83 days). Calculated average interfacial resistance of LiPDI-PC at the end of the experiment was  $438 \Omega \text{ cm}^{-1}$ .

### 3.3. Lithium transference number

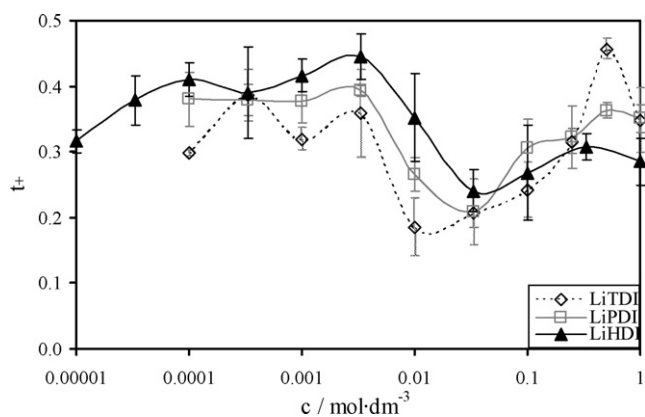
In Fig. 5 lithium cation transference numbers vs. salt concentration are plotted for all salts solutions in PC. One local maximum of  $t_+$  occurs at the  $0.5 \text{ mol dm}^{-3}$  concentration for all three types of electrolytes studied. Second local maximum is also common



**Fig. 3.** Molar conductivity dependence of concentration of LiTDI, LiPDI and LiHDI in propylene carbonate at 20°C. Lines are given to guide the eye.



**Fig. 4.** Interface stability (interfacial area specific resistance dependence of time) of LiTDI, LiPDI and LiHDI in PC. Each point is averaged over four samples with marked error range; a)  $0.01 \text{ mol dm}^{-3}$ ; b)  $0.5 \text{ mol dm}^{-3}$ .



**Fig. 5.** Transference number dependence of salt concentration—comparison of all investigated salts; transference numbers calculated with Bruce–Vincent method for LiTDI, LiPDI and LiHDI in PC. Each point is averaged over three samples—with marked error range. Lines are given to guide the eye.



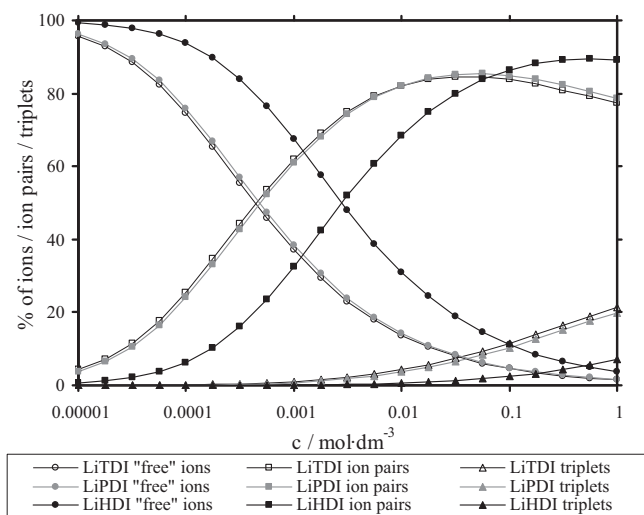


Fig. 6. Calculated ionic fractions for LiTDI, LiPDI and LiHDI in PC. Lines are given to guide the eye.

for all of the systems at the  $3.3 \times 10^{-3} \text{ mol dm}^{-3}$  concentration. Lithium cation transference number decreases with the concentration below  $3.3 \times 10^{-4} \text{ mol dm}^{-3}$  for LiTDI and LiHDI. The highest  $t_+$  value for LiTDI-PC is 0.46 at  $0.5 \text{ mol dm}^{-3}$ , and for LiPDI-PC  $t_+$  is 0.36 for the same salt concentration. Maximum for concentrated solutions of LiHDI-PC is 0.31 at  $0.33 \text{ mol dm}^{-3}$ .

#### 3.4. Ionic fractions estimation

Fractions of “free” ions and ionic aggregates were calculated for all salts in the concentration range between  $1 \times 10^{-5}$  and  $1 \text{ mol dm}^{-3}$  with four points per decade. Results of these calculations are presented in the Fig. 6. Plots for all three salts in PC have a similar shape (slopes and maxima levels). Fraction of ions and ionic aggregates calculated for LiPDI-PC and LiTDI-PC are similar, with fraction of ions in LiTDI-PC slightly higher when compared at the same concentrations. Fraction of ions in LiHDI-PC is much higher than for both its previous analogues in the same solvent at the entire salt concentration range. “Free” ions (without any direct bonding to anion) at  $1 \text{ mol dm}^{-3}$  are 1.46% fraction of ionic constituents in LiTDI-PC solution, 1.53% in LiPDI-PC and as much as 3.65% in LiHDI-PC. Maximum of the ion pairs’ fraction for LiTDI-PC is 84.67% at  $0.032 \text{ mol dm}^{-3}$  concentration, for LiPDI-PC is 85.47% at  $0.056 \text{ mol dm}^{-3}$  and for LiHDI-PC is 89.54% at  $0.56 \text{ mol dm}^{-3}$ . The highest level of triplets (at the  $1 \text{ mol dm}^{-3}$ ) for LiTDI-PC is 21.28%, for LiPDI-PC is 19.92% and for LiHDI is only 7.19%. Association constants used for these calculations are presented in Table 1.

#### 3.5. Raman studies

Comparison of the Raman spectra of LiTDI, LiPDI and LiHDI solutions in PC (high dielectric permittivity solvent) and DMC (dimethyl carbonate) solvent allowed to match specific bands to the certain ionic constituents influence on the spectrum. DMC was selected as

a low relative permittivity reference. As the most distinct band, the  $\nu_{\text{CN}}$  band was chosen for ionic constituent fractions spectral analysis. Such analysis using deconvolution of the bands showed 100% of “free” ions’ fraction for the whole concentration range (from 1 to  $0.01 \text{ mol dm}^{-3}$ ) of all salt solutions in PC.

## 4. Discussion

Combined results of transference numbers measurement, ionic associations and conductivity confirms the excellent properties of synthesized new salts in the PC solutions.

High  $t_+$  value of 0.4 obtained for the one-solvent electrolyte (with no additives) containing salt at the applicable concentrations for all the studied salts can be considered as promising in terms of applications in electrochemical devices. It is important to note that the high  $t_+$  values were obtained without compromising ionic conductivity (which still exceeds  $1 \text{ mS cm}^{-1}$  at room temperature).

Molar conductivity shapes (Fig. 3) are in concert with ionic pairs and triplets formation. Molar conductivity minimum is usually at the point with maximum fraction of the ionic pairs. Consequently a maximum of the molar conductivity at higher concentration is mainly explained by increased amount of the higher aggregates. That observation leads us to the conclusion of the limited association rates of the investigated electrolytes. LiHDI-PC plot of molar conductivity vs. concentration is completely different than corresponding plots of LiTDI-PC and LiPDI-PC electrolytes. A reason for that is simply because of much lower association constants calculated for LiHDI-PC electrolyte (Table 1, Fig. 6). In our cases calculated ionic fraction levels of triplets and ion pairs are much smaller compared to the other systems studied previously [21,23,24].

Very small differences in ionic conductivity in broad ranges of concentration in case of LiTDI-PC and LiPDI-PC can be explained as the effect of ionic association. Presence of steep slope on the molar conductivity plot (molar conductivity decreases ten times within a concentration decade) effects in no particular changes of ionic conductivity. Fast change of molar conductivity within concentration is the effect of slope in ionic fractions plots in this concentration range in both cases. LiHDI-PC different behavior is also the effect of association rates. “Free” ions’ and triplets’ fractions slopes on the plot are inverted in this concentration range, compensating much of the molar conductivity potential change. As molar conductivity changes slowly within a concentration decade, it effects as a bigger change of ionic conductivity.

Unfortunately, much higher (compared to the LiTDI-PC and LiPDI-PC electrolytes) “free” ions fraction of LiHDI-PC does not result in an increase of ionic conductivity as it should. More “free” ions at the same concentration should affect ionic conductivity and it does not. It is due to fluoroalkyl group, which is long enough in LiHDI molecule to go out of the aromatic ring plane, providing extra volume to the anion that way. In both previous analogues fluoroalkyl group is shorter and rigid, so it keeps in one plane with the rest of the anion. So LiHDI, as a salt with bigger anion volume than its smaller analogues, makes the local viscosity higher on the molecular level, having lower mobility of the anion as a result. Most probably because of that, LiHDI-PC, although being least associative of the compared salts, has similar ionic conductivity to its analogues.

Raman spectroscopy used for the ionic association estimation also showed that basically whole association in these solutions is based on the electrostatic interactions. If there were any direct bonding in these, it would affect Raman spectra. It can be assumed that ionic interactions are not so strong if they lack direct bonding. Raman spectroscopy ionic association estimation results are not surprising, given that in PEG (solvent with very low relative permittivity) direct bonding association was already very weak [16].

Table 1

Limiting molar conductivity of salts in PC as well as ion forming and triplet forming association constants used for Fuoss–Kraus calculations, presented with error range for LiTDI-PC, LiPDI-PC and LiHDI-PC.

	$\Lambda_0/\text{S cm}^2 \text{ mol}^{-1}$	$K_I/\text{dm}^3 \text{ mol}^{-1}$	$K_T/\text{dm}^3 \text{ mol}^{-1}$
LiTDI-PC	$64.82 \pm 0.01$	$4599 \pm 76$	$41.89 \pm 0.69$
LiPDI-PC	$65.51 \pm 0.03$	$4180 \pm 50$	$33.52 \pm 0.40$
LiHDI-PC	$50.65 \pm 0.04$	$720 \pm 17$	$2.63 \pm 0.06$

Hence, Raman spectroscopy was used here mainly for the confirmation of previous results and as a complementary method to Fuoss–Kraus estimation method for distinguishing direct and indirect association.

During passivation experiment LiHDI-PC solution has been forming stable SEI at low concentration. Stability of SEI tends to be faster and obtained at the lower resistances with the increase of the concentration because of the passive layer growth mechanism [25]. Stable SEI formation of LiHDI-PC already at low concentrations could be explained by its association constants. There are few times more lithium “free” cations (not connected electrostatically to the anion) in the bulk (Fig. 6) in LiHDI-PC solutions, when compared to LiTDI-PC and LiPDI-PC. It is possible then, that LiHDI-PC passivation properties are much more similar to higher concentration electrolytes. Concentration of lithium cation is affecting the passivation kinetics in the rate-determining step where the propylene carbonate molecule is complexed by lithium cation [26]. The same applies to the explanation of the different behavior of LiTDI-PC and LiPDI-PC at low and high concentrations (0.01 mol dm<sup>-3</sup> vs. 0.5 mol dm<sup>-3</sup>).

It is important to highlight that local maximum (or global maximum in case of LiTDI-PC) of lithium cation transference number of all perfectly overlaps with the ionic conductivity maximum in case of all salts. Even more importantly these maxima occur not at the highest concentrations, so much less salt is needed for the optimal parameters of the electrolyte, compared to other salts. Typical technological concentrations are at 1 mol dm<sup>-3</sup> or higher. Here, LiTDI-PC and LiPDI-PC have this optimal concentration at 0.1–0.33 mol dm<sup>-3</sup>. As a result, electrolytes with these new salts would be more reasonable alternative from the economical point of view. Ionic conductivity and  $t_+$  maxima matching is a brilliant result in the context of commercial applications. Finally in the described systems it was quite straightforward to trim the system toward finding the optimal concentration/conductivity properties. By that fact we avoid compromising between good charge–discharge cycle efficiency and high current density. All above shows a considerable advantage to LiTDI salt family and a huge potential for their applicability in the commercial cells.

## 5. Conclusions

In this paper we present the very recent research progress on the imidazole-derivatives class of lithium salts. Results prove this is an interesting alternative to the presently used salts in the battery systems. High conductivity and transference numbers values followed by weaker association tendencies are the key primary success fac-

tors in these systems. Secondary these new electrolytes form stable SEI layers on metallic lithium anode. Better properties of the new electrolytes substantially reduce the amount of the salt needed to assure desired electrochemical performance of the systems. From the laboratory point of view we conclude electrolytes based on the new salts have complete set of attributes to potentially fulfill market requirements for application in lithium cells.

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