



# Comparison of LiTDI and LiPDI salts and influence of their perfluoroalkyl side-chain on association and electrochemical properties in triglyme

Marek Broszkiewicz<sup>1</sup> · Aldona Zalewska<sup>1</sup> · Leszek Niedzicki<sup>1</sup>

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## Abstract

For the first time, the effect of minor structural changes to the electrolyte salt on solution properties is investigated experimentally. It was achieved by decomposition of the overall changes into individual components. It allowed to obtain information on the contradicting effects influence on the final result. This study is focused on comparison of two lithium salts: lithium 4,5-dicyano-2-(trifluoromethyl) imidazolide (LiTDI) and lithium 4,5-dicyano-2-(pentafluoroethyl) imidazolide (LiPDI). LiTDI is a very promising salt for lithium-ion battery application. PDI<sup>-</sup> anion differs from TDI<sup>-</sup> only in length of perfluorinated alkyl chain. Triethylene glycol dimethyl ether (triglyme) solutions of both salts in a wide range of concentrations were prepared. Triglyme was chosen as a solvent due to number of oxygen atoms which allows for fulfilment of lithium cation coordination sphere. Use of such similar salts in a model system allows us to find the correlation between salt structure and properties of electrolyte. Conductivity, viscosity, lithium transference number, thermal properties and FTIR spectra were measured for all solutions. Ionic fractions were also estimated by Fuoss-Kraus formalism. Obtained results showed that electrochemical properties of electrolyte are result of several opposing factors. Transference numbers are mostly dependent on association. We have also observed interesting correlation between thermal properties and conductivity.

**Keywords** Conductivity · Transference · FTIR · Association · Fuoss-Kraus

## Introduction

Lithium-ion batteries are commercially available for more than two decades and have become the most popular secondary batteries. A lot of studies were dedicated to improving their properties, although majority of them were focused on electrode materials. Electrolytes used in modern batteries are very similar to those used 20 years ago. Such electrolyte consists of lithium hexafluorophosphate (LiPF<sub>6</sub>) dissolved in a mixture of organic carbonates [1].

The electrolyte largely determines cell performance. The choice of salt can strongly influence electrochemical

properties as well as cost and safety of the electrolyte. Apart from previously mentioned LiPF<sub>6</sub>, there are several other salts which were considered for lithium-ion cells application, including LiClO<sub>4</sub> [2], LiBF<sub>4</sub> [3, 4], LiAsF<sub>6</sub> [5] and LiCF<sub>3</sub>SO<sub>3</sub> [6]. Despite its lack of stability in contact with water and poor thermal stability [7], LiPF<sub>6</sub> proved to be so far the best salt for secondary batteries. In years following lithium-ion batteries commercialization, several attempts were made to replace it with another salt of comparable electrochemical properties but better stability. A few promising salts were proposed including LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> (LiTFSI) [6], LiN(SO<sub>2</sub>C<sub>2</sub>F<sub>5</sub>)<sub>2</sub> (LiBETI) [8], lithium bis(oxalate) borate (LiBOB) [9], LiPF<sub>3</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> (LiFAP) [10] and lithium 4,5-dicyano-2-(trifluoromethyl) imidazolide (LiTDI) [11]. The last of these salts synthesised few years ago by our group shows very promising results [12].

Performance of electrolytes depends on different factors such as physical and chemical properties of salt or solvent as well as interactions between them. Parameters which have to be taken into account include solubility, association, conductivity, viscosity and lithium transference number. These parameters are affected by ion concentrations and thus are affected by their character and association. For better

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✉ Marek Broszkiewicz  
mbroszkiewicz@ch.pw.edu.pl

<sup>1</sup> Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

electrochemical performance, less associated electrolytes are preferred. Anion structure affects its mobility and as a result, both solution viscosity and lithium cation transference number ( $T_{Li^+}$ ) [13]. One of the best ways to enhance electrolyte electrochemical performance is to design a new lithium salt. In theory, optimal results should be achieved by salt consisting of bulky anion weakly bound with cation. However, anion size influences viscosity and conductivity of the resulting electrolyte solution. Thus, the anion should be small, so changes to its structure should be restricted to small functional groups. Lithium cation is a hard acid thus we need an anion which would be a soft base. For this reason, we design anions with charge uniformly distributed over all its atoms. Using cyclic anion following Hückel's rule and substituted with electron withdrawing groups, having symmetry axes should be most effective favourably. We would also like to avoid any hydrogen atom. Presence of hydrogen atoms due to ease of their dissociation is detrimental to electrochemical, chemical and thermal stability [14]. However, design of new salt requires knowledge of structural change influence on the electrolyte parameters.

LiTDI anion fulfils all the above criteria. There have been many works regarding LiTDI electrochemical properties [12, 15–18]. There are other works addressing some issues regarding this salt like SEI formation on graphite electrode. Even considering the disadvantages of LiTDI, it is still one of the best candidates for lithium-ion cells application [19]. Several publications addressed the issue of crystal structures containing this salt [20, 21]. In this work, we describe our latest investigation into ionics of the lithium weakly coordinating salts solutions. The main aim of our work is to study electrochemical properties and associations in solutions by means of electrochemical, thermal and spectroscopic methods. Analysis of associates by studying solutions allows for closer approximation of real electrolyte. We use LiTDI and its analogue, lithium 4,5-dicyano-2-(pentafluoroethyl) imidazolidine (LiPDI). Anions of LiTDI and LiPDI differ only in perfluorinated moiety size—one vs two perfluorinated carbon atoms. Such minute difference allows us to study effect of subtle changes in structure on electrolyte properties. This, to our best knowledge, has never been attempted experimentally before in a systematic way. Difference between LiTDI and LiPDI is even smaller than between LiTFSI and LiBETI. It allows us to take advantage of similarities to isolate influence of moiety. We use triethylene glycol dimethyl ether (triglyme) as solvent due to a number of oxygen atoms which should allow for perfect fulfilment of lithium cation coordination sphere [22]. It allows us to create a model solution, which can be described in terms of excess or deficit of oxygen to coordinate lithium. It should give us the ability to find correlation between electrochemical parameters, association, or solvation effects in the solution and anion structure. It will give us a better

understanding of reasons behind changes of certain parameters and allow for the design of new salts based upon predictions rather than pure guesses.

## Experimental

LiTDI and LiPDI salts were prepared according to the synthetic route described in our previous work [11]. Salts were dried at 140 °C under the vacuum for 48 h. Solutions of LiTDI and LiPDI in triglyme (99% purity, Sigma-Aldrich) were prepared. Solutions of 1 to 3, 4, 5, 6, 8, 10, 20 and 50 molar ratio of salt to solvent were prepared. For ionic fractions estimation by Fuoss-Kraus formalism [23–26] solutions of 0.01, 0.005, 0.002, 0.001, 0.0005, 0.0002 and 0.0001 mol/kg of solvent were prepared by dilution of 0.1 mol/kg solution. Precise procedure on how to obtain values for Fuoss-Kraus model was described in our previous work [12]. All solutions and samples were prepared in an argon-filled dry box containing less than 1 ppm of moisture or oxygen.

Conductivity measurements were carried out using electrochemical impedance spectroscopy (EIS) on the computer-interfaced VMP3 (Bio-Logic Science Instruments) multichannel potentiostat with frequency response analyser (FRA) module. Conductivity was measured at 25 °C. Samples were placed in a cryostat-thermostat system (Lauda Ecoline Star edition RE 307). Frequency range was set in 500 kHz to 10 Hz range with 10 points per decade and 5 mV ac signal. Each measurement was repeated six times for higher consistency of the results.

Lithium cation transference numbers were determined using the Bruce and Vincent method [27]. Electrolyte samples were sandwiched between two electrodes of metal lithium foil (0.45-mm thick, 99.9% purity, MTI-XTL) in Swagelok-type cell. All samples were measured at 25 °C. Impedance spectra were measured using computer-interfaced VMP3 multichannel potentiostat. Frequency range was set from in 500 kHz to 100 mHz range with 10 points per decade and 5 mV ac signal. Each measurement was repeated six times for higher consistency of the results. Polarisation measurements were carried out with 20 mV potential. Current data was collected every 2 s with 10 nA accuracy. Current upon achieving of the steady-state was calculated by averaging values for the last 60 s.

Cyclic voltammetry was measured in two-electrode Swagelok type cell in 0.1–5.2 V range with 1 mV scan rate. Platinum plate was used as working electrode while lithium plate (0.45-mm thick, 99.9% purity, MTI-XTL) was used as counter electrode and reference electrode. Computer-interfaced VMP3 multichannel potentiostat was used for these measurements. Two samples of 0.5 mol/kg of solvent of LiTDI and LiPDI in triglyme were used.

Viscosity measurements were carried out with a Physica MCR301 Anton Paar rheometer with a CP40 cone plate and

thermoelectric heat pump base. Experiments were performed at 25 °C. For each sample and temperature, viscosity data was collected with shear rate ranging from 10 to 1000 s<sup>-1</sup>. Viscosity was calculated by extrapolation of viscosity measured for the last 10 points to zero shear rate.

Thermal properties were investigated by differential scanning calorimetry (DSC). Q200 calorimeter (TA Instruments) was used. Samples were heated from -140 to 0 °C at 10 °C/min rate.

FTIR spectra were obtained with Nicolet Avatar 370 DTGS spectrometer (Thermo Electron) with resolution of 1 cm<sup>-1</sup> and 512 scans in 4000 to 500 cm<sup>-1</sup> range. Studies were performed with attenuated total reflection (ATR) accessory at room temperature.

### Results

Figure 1 shows relation between conductivity of LiTDI and LiPDI solutions and salt concentration at 25 °C. Maxima of conductivity for both salts appear at 1:5 molar ratio. Conductivity of LiTDI solutions were slightly higher than those of LiPDI, 4.79 mS/cm and 4.65 mS/cm, respectively, although for 1:10 molar ratio, we can observe a sudden drop in conductivity of LiTDI solution. Error bars for all measurements are smaller than markers.

Electrochemical stability was determined by cyclic voltammetry. Obtained results shown on Figs. S1 and S2. (supplementary information) did not reveal any significant differences to results presented in previous works [11].

In Fig. 2, we can see similar plots showing viscosity of aforementioned solutions. Viscosity grows with salt concentration. Viscosity of LiTDI solutions is lower than viscosity of LiPDI solutions. Difference is very small yet it grows with salt concentration.

Figure 3 presents ionic fractions estimation for LiTDI and LiPDI solutions. Fraction of ion pairs is higher for LiPDI solutions while fractions of “free” ions and triplets are lower.

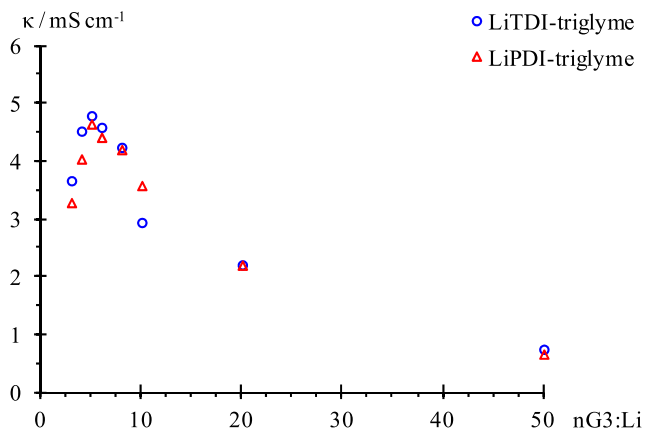


Fig. 1 Conductivity of LiTDI and LiPDI solutions in triglyme

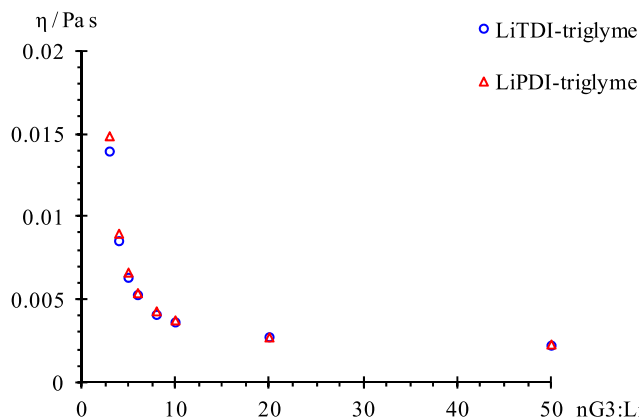


Fig. 2 Viscosity of LiTDI and LiPDI solutions in triglyme

In studied range of molar ratios triplets are dominant charge carriers. Ion pairs constitute vast majority of all compounds for both salts with over 70% content. Triplets content revolves around 20% and free ions constitute for less than 1%.

Results of lithium transference number measurements are presented on Fig. 4a for LiTDI and on Fig. 4b for LiPDI solutions. Transference number for LiTDI solutions seems to be higher than numbers obtained for LiPDI solutions, at least for low salt concentration. It is also worth noticing that these salts exhibit opposite behaviour with concentration change. For LiTDI solutions, transference number increases while for LiPDI solutions it decreases with salt concentration.

Figure 5 shows results of thermal analysis. For pure triglyme melting point was observed at -46.3 °C and glass transition temperature at -105.9 °C. LiTDI solutions crystallise only down to 1:5 molar ratio. Melting point decreases with salt concentration from -43.4 to -56.0 °C. Glass transition temperature exhibits different behaviours depending on salt concentration. For high molar ratio of 1:20 and 1:50, we observe relatively high glass transition temperature of -98.0 °C and -98.6 °C, respectively. It is increasing slightly with

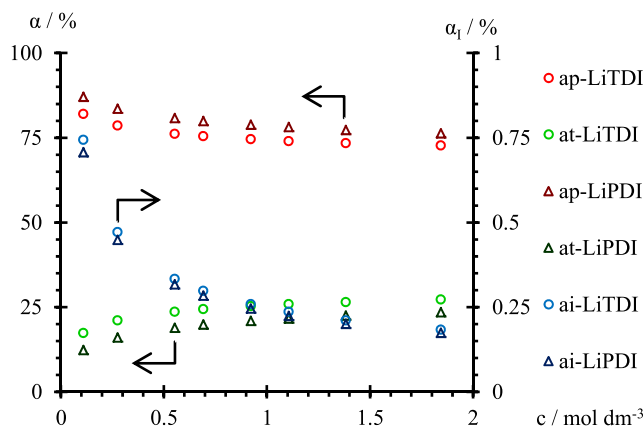
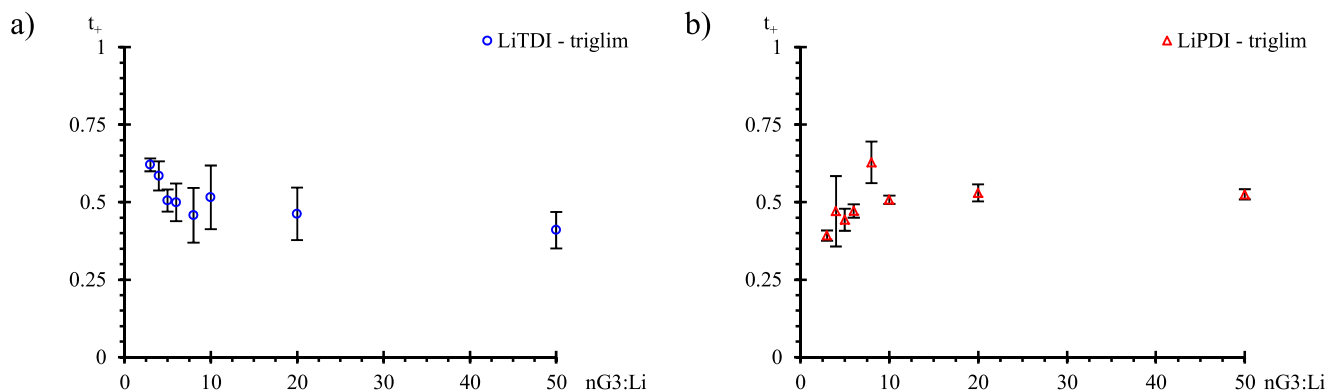


Fig. 3 Ionic fractions of free ions in LiTDI and LiPDI triglyme solutions, ion pairs in LiTDI and LiPDI triglyme solutions, and triplets in LiTDI and LiPDI triglyme solutions calculated with Fuoss-Kraus model obtained from low concentration solutions. Concentrations presented on this figure are equivalent to molar ratios used on other figures

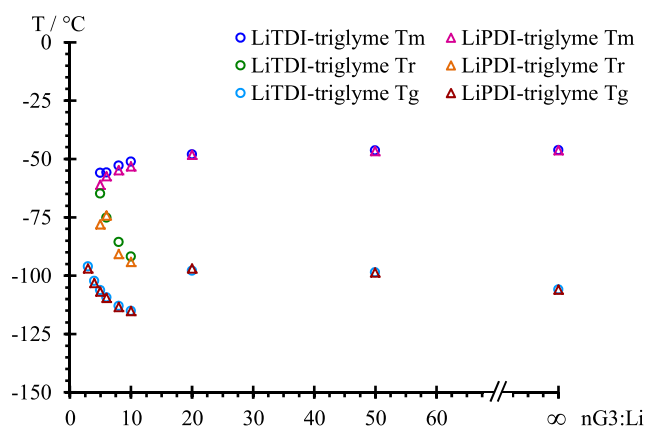


**Fig. 4** Transference number of LiTDI and LiPDI solutions in triglyme

concentration. For lower molar ratios, glass transition temperature is considerably lower, at  $-115.2$  °C for 1:10 molar ratio, yet it rises with salt concentration up to  $-96.2$  °C. Melting point and glass transition temperatures of LiPDI solutions behave similarly; however, they are slightly lower than respective temperatures of LiTDI solutions.

We have chosen few regions of spectra for deconvolution based on previous works, relevance to study of association and ease of deconvolution. There are two main ways to form direct association between  $\text{TDI}^-$  and  $\text{PDI}^-$  anions and lithium cations: one through nitrile nitrogen and another through ring nitrogen with fluorine. Changes in association through nitrile moiety can be observed by changes in relative intensity of peaks in  $\text{C}\equiv\text{N}$  stretching region. We can study association through ring nitrogen and fluorine by changes in relative peak intensities in either C–F stretching or C–F deformation region or C–N–C stretching region. However, only C–F peaks are easy to analyse [21].

Figure 6 is divided into four parts showing fragments of FTIR spectra and diagrams presenting relative intensities of peaks of deconvoluted spectra for LiTDI solutions. On the left side of Fig. 6, we can see selected regions of spectra. On



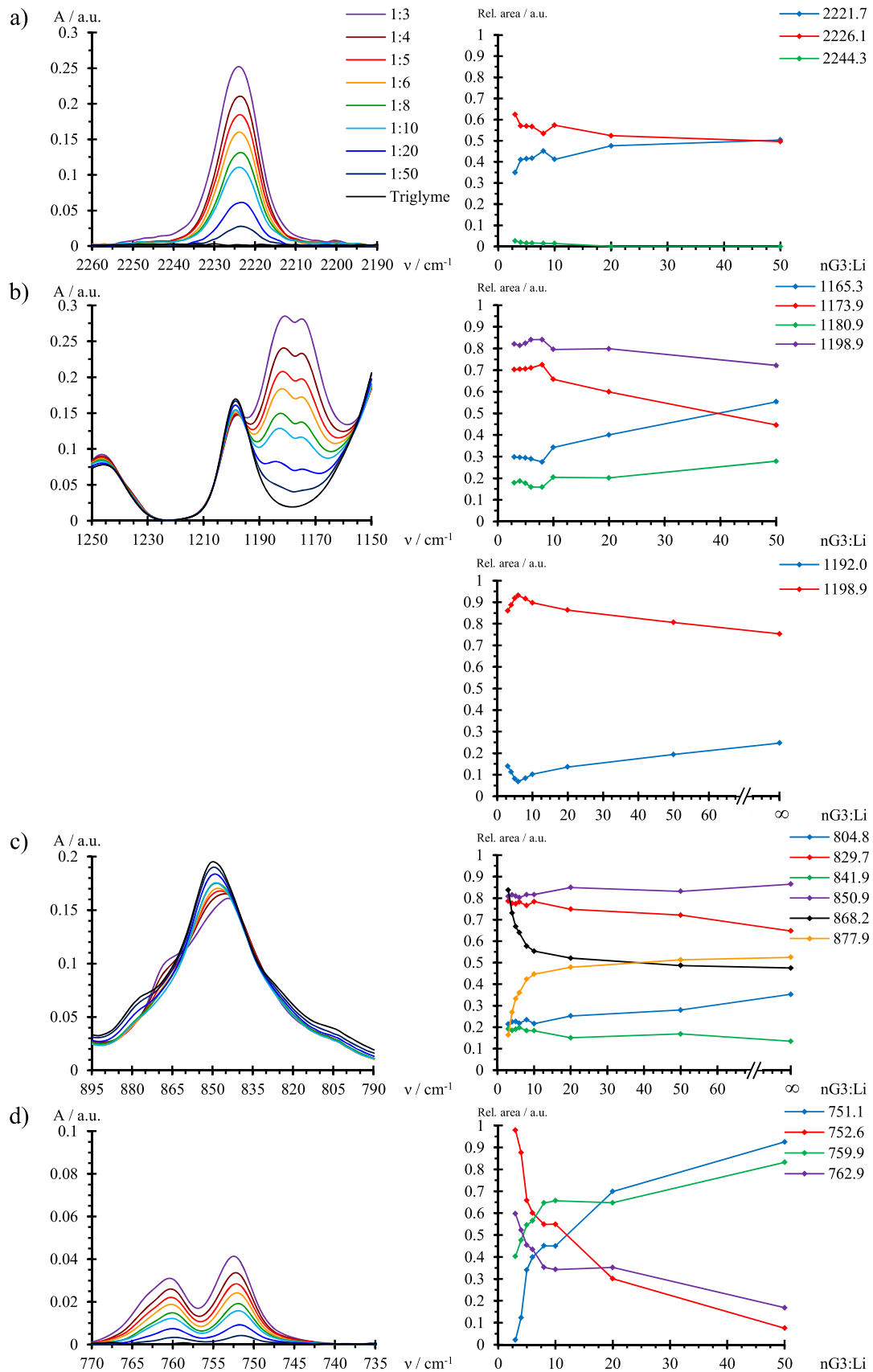
**Fig. 5** Melting point, glass transition temperature, and recrystallization temperature of LiTDI and melting point, glass transition temperature, and recrystallization temperature of LiPDI solutions in triglyme and pure triglyme

the right side, we can see relative intensities of peaks shown on the left side; Fig. 6a =  $2200$   $\text{cm}^{-1}$  region, Fig. 6b =  $1250$   $\text{cm}^{-1}$  region, Fig. 6c =  $850$   $\text{cm}^{-1}$  region and Fig. 6d =  $750$   $\text{cm}^{-1}$  region.

Figure 7 is divided into five parts and present similar data for LiPDI solutions; Fig. 7a =  $2200$   $\text{cm}^{-1}$  region, Fig. 7b =  $1250$   $\text{cm}^{-1}$  region, Fig. 7c =  $850$   $\text{cm}^{-1}$  region, Fig. 7d =  $750$   $\text{cm}^{-1}$  region and Fig. 7e =  $600$   $\text{cm}^{-1}$  region. Figure 7b does not contain deconvolution of spectra. This region was not deconvoluted due to interference of peaks.

In  $2200$   $\text{cm}^{-1}$  region, we can see three peaks at  $2244$   $\text{cm}^{-1}$ ,  $2226$   $\text{cm}^{-1}$  and  $2222$   $\text{cm}^{-1}$  for LiTDI and two at  $2228$   $\text{cm}^{-1}$  and  $2223$   $\text{cm}^{-1}$  for LiPDI solutions. These peaks are attributed to stretching vibration of imidazole nitrile group ( $\nu$  C $\equiv$ N). Relative intensities of peaks at  $2222$   $\text{cm}^{-1}$  and  $2223$   $\text{cm}^{-1}$  decrease with salt concentration, thus they were attributed to free nitrile. Relative intensities of peaks at  $2226$   $\text{cm}^{-1}$  and  $2228$   $\text{cm}^{-1}$  increase with salt concentration so they were assigned to associates. Another peak seems to appear for LiTDI solutions at  $2244$   $\text{cm}^{-1}$ . Its relative intensity grows with salt concentration. It is likely corresponding to higher associates.

In  $1250$   $\text{cm}^{-1}$  region, there are six interesting peaks for LiTDI solutions. Two peaks at  $1199$   $\text{cm}^{-1}$  and  $1192$   $\text{cm}^{-1}$  are assigned to rocking of, respectively, free and coordinated  $-\text{O}-\text{CH}_3$  ( $\rho$   $-\text{O}-\text{C}$ ) in triglyme. Remaining four peaks at  $1185$   $\text{cm}^{-1}$ ,  $1181$   $\text{cm}^{-1}$ ,  $1174$   $\text{cm}^{-1}$  and  $1165$   $\text{cm}^{-1}$  are connected with  $-\text{CF}_3$  stretching vibration ( $\nu$  C–F) of  $-\text{CF}_3$  group of  $\text{TDI}^-$ . These four peaks can be divided into two pairs of  $1185$   $\text{cm}^{-1}$  and  $1181$   $\text{cm}^{-1}$  and  $1174$   $\text{cm}^{-1}$  and  $1165$   $\text{cm}^{-1}$ . Peak pairs are assigned to in plane and out of plane vibrations respectively. First peaks in those two pairs are assigned to free  $-\text{CF}_3$  and second peaks to associated moiety, respectively. In LiPDI solutions, there are most probably five peaks. There are two peaks at about  $1200$   $\text{cm}^{-1}$  and  $1190$   $\text{cm}^{-1}$  corresponding to rocking of  $-\text{O}-\text{CH}_3$  ( $\rho$   $-\text{O}-\text{C}$ ). Three other peaks at about  $1220$   $\text{cm}^{-1}$ ,  $1210$   $\text{cm}^{-1}$  and  $1200$   $\text{cm}^{-1}$  are assigned to  $-\text{CF}_3$  stretching vibration ( $\nu$  C–F). Interference of peaks at  $1200$   $\text{cm}^{-1}$  prevents deconvolution.



**Fig. 6** Fragments of FTIR spectra (on the left) and relative intensities of peaks in that region (on the right) for LiTDI triglyme solutions and pure triglyme in **a** 2200 cm<sup>-1</sup> region, **b** 1250 cm<sup>-1</sup> region, **c** 800 cm<sup>-1</sup> region and **d** 750 cm<sup>-1</sup> region. Lines on the left figures are given to guide the eye

In  $850\text{ cm}^{-1}$  region, there are six peaks for both LiTDI and LiPDI. Peaks at  $878\text{ cm}^{-1}$  and  $868\text{ cm}^{-1}$  correspond to stretching of triglyme free  $-\text{CH}_2-\text{O}-\text{CH}_2-$  ( $\nu\text{ C-O}$ ) and coordinated ( $\nu\text{ C-O}\cdots\text{Li}^+$ ), respectively. Peaks at  $851\text{ cm}^{-1}$  and  $842\text{ cm}^{-1}$  correspond to free and rigid  $-\text{CH}_2-$  scissoring ( $\delta-\text{CH}_2-$ ) while peaks at  $830\text{ cm}^{-1}$  and  $805\text{ cm}^{-1}$  to free and rigid  $-\text{CH}_2-\text{CH}_2-$  stretching ( $\nu\text{ C-C}$ ).

Peaks at  $750\text{ cm}^{-1}$  region are attributed to  $-\text{CF}_3$  deformation ( $\delta-\text{CF}_3$ ). In LiTDI solutions, we can see four peaks at  $763\text{ cm}^{-1}$ ,  $760\text{ cm}^{-1}$ ,  $753\text{ cm}^{-1}$  and  $751\text{ cm}^{-1}$ . Presence of two peaks at about  $750\text{ cm}^{-1}$  is indicated by slight, yet constant shift of maximum of absorption intensity with salt concentration. Peaks in this region correlate in assignment with  $-\text{CF}_3$  peaks at  $1250\text{ cm}^{-1}$  region. In LiPDI solutions, we observe five peaks at  $754\text{ cm}^{-1}$ ,  $753\text{ cm}^{-1}$ ,  $750\text{ cm}^{-1}$ ,  $747\text{ cm}^{-1}$  and  $744\text{ cm}^{-1}$ . There is a much higher relative intensity of pairs of peaks for LiPDI solutions at about  $745\text{ cm}^{-1}$  than those for LiTDI solutions. Correlation between number of peaks from stretching and deformation  $-\text{CF}_3$  vibrations in case of LiPDI would suggest the presence of six peaks. Those two observations makes us believe that there is in fact additional (sixth) overlapping peak at about  $745\text{ cm}^{-1}$  in case of LiPDI solutions.

There are also two peaks at  $628\text{ cm}^{-1}$  and  $626\text{ cm}^{-1}$  for LiPDI solutions which are assigned to coordinated  $-\text{CF}_2-$  deformation ( $\delta-\text{CF}_2\cdots\text{Li}^+$ ) and free  $-\text{CF}_2-$  deformation ( $\delta-\text{CF}_2-$ ), respectively. Those peaks are not present for LiTDI solutions, which is why they were attributed to  $-\text{CF}_2-$  deformation.

## Discussion

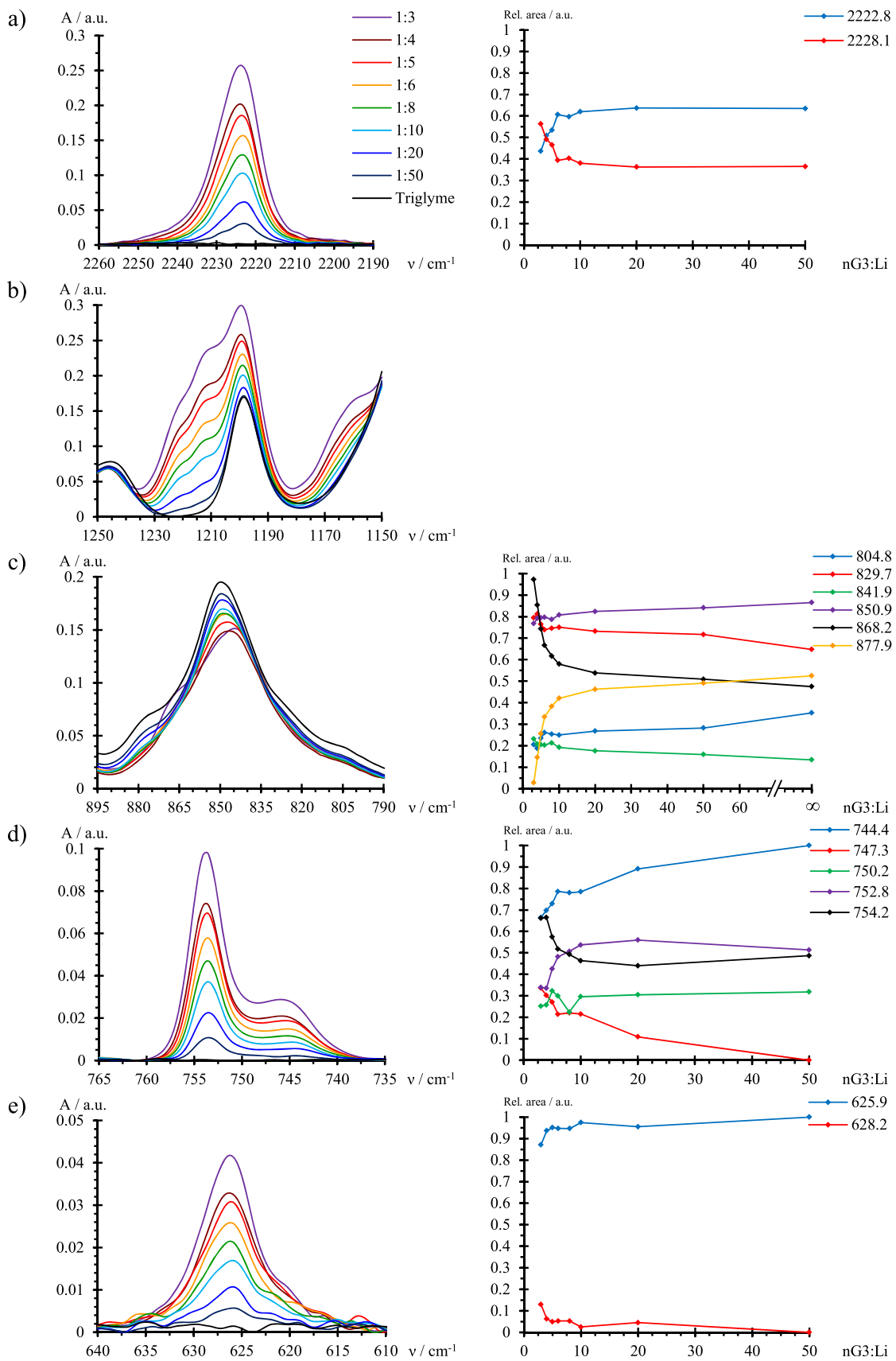
Conductivity of electrolytes depends on several factors like used salt, its concentration, and association. Increase in salt concentration cause increase in amount of charge carriers resulting in increase in conductivity. However viscosity also rises with salt concentration. Maxima of conductivity for both LiTDI and LiPDI solutions are at the same molar ratio which indicates that such a small change in anion structure does not have a significant impact on their position that can be noticed with used resolution of measurements. This position is most likely determined by properties of solvent. In case of triglyme, it is more or less 1:5 molar ratio which corresponds to ca. 20 coordinating moieties per lithium cation. Conductivity of LiTDI solutions is higher than conductivity of LiPDI solutions and differences are more pronounced at higher concentrations which correlates well with viscosity measurements.  $\text{PDI}^-$  anion is bigger than  $\text{TDI}^-$ ; therefore, higher viscosity of LiPDI solutions is justified. However  $\text{PDI}^-$  anion should provide better distribution of charge due to stronger electron withdrawing properties of pentafluoroethyl group than those of trifluoromethyl group. In result, interactions between lithium cation and  $\text{PDI}^-$  anion should be weaker and dissociation

degree should be higher, thus providing higher conductivity. This does not find conformation in conductivity results.

FTIR studies revealed, however, that association phenomena in LiPDI solutions are weaker, both through nitrile nitrogen and ring which is evident by higher relative intensities of peaks related to free anion. It should be noted that for LiPDI association with fluorine from  $-\text{CF}_2-$  moiety should be far more likely than association with  $-\text{CF}_3$  fluorine. In LiTDI solutions, there is also an additional peak observed at  $2244\text{ cm}^{-1}$  related to higher associations. Absence of this peak in LiPDI solutions further supports this claim. We can also see these changes in relative intensities in  $2200\text{ cm}^{-1}$  region to a greater extent for LiPDI than for LiTDI. In  $750\text{ cm}^{-1}$  region, we observe huge changes in peaks' intensities for LiTDI solutions, unlike for LiPDI solutions. It is not surprising, as it was stated earlier,  $-\text{CF}_3$  fluorine should not partake in association for LiPDI in measurable quantity. Interestingly, peaks around  $600\text{ cm}^{-1}$  associated with  $-\text{CF}_2-$  for LiPDI do not exhibit such great changes in relative intensities as peaks around  $750\text{ cm}^{-1}$  for LiTDI. It suggests that not only association for LiTDI is stronger than for LiPDI solutions, but also prefers change in association mechanism. For LiTDI, association through ring nitrogen and fluorine is preferred, while for LiPDI, association through nitrile nitrogen is preferred.

Analysing triglyme interactions with lithium we can see very similar behaviour for both LiTDI and LiPDI solutions. In  $850\text{ cm}^{-1}$  region, there are two peaks related to  $\text{C-O}$  stretching which change considerably alongside salt concentration and two pairs of peaks related to  $\nu\text{ C-C}$  and  $\sigma-\text{CH}_2$  vibrations, which change only slightly. Changes in relative intensities of peaks corresponding with  $\nu\text{ C-O}$  are slightly higher for LiPDI than for LiTDI. It can be explained by stronger solvation for electrolytes containing LiPDI. Less associates results in less anions replacing oxygen atoms in lithium coordination sphere. There are also peaks at about  $1200\text{ cm}^{-1}$ . The relative intensity of peak from free  $-\text{O}-\text{CH}_3$  decreases with salt concentration, which is a result of coordination of lithium cations by triglyme molecules, than down from the molar ratio of 1:6, it increases. Such result is probably related to strengthening association which affects number of free terminal moieties. Increasing concentration reduces number of free  $-\text{OCH}_3$  moieties due to solvation of lithium cations by triglyme molecules. Creation of contact associates causes exchange of some oxygen atoms in lithium coordination sphere for anion moieties. As a result, fraction of terminal moieties become free again. Aforementioned concentration marks border at which direct association effect starts to dominate over concentration effect.

Peaks attributed to  $-\text{CF}_3$  stretching both in  $1250\text{ cm}^{-1}$  region and in  $750\text{ cm}^{-1}$  region exhibit justifiable similarities as they are related to the same moiety. The fact that vibrations in plane in which lithium cation-anion bonds are created are more affected by this bonding is also understandable.



**Fig. 7** Fragments of FTIR spectra (on the left) and relative intensities of peaks in that region (on the right) for LiPDI triglyme solutions and pure triglyme in **a** 2200 cm<sup>-1</sup> region, **b** 1250 cm<sup>-1</sup> region, **c** 800 cm<sup>-1</sup> region, **d** 750 cm<sup>-1</sup> region and **e** 600 cm<sup>-1</sup> region. Lines on the left figures are given to guide the eye

Different number of peaks for LiTDI and LiPDI in both  $1250\text{ cm}^{-1}$  and  $750\text{ cm}^{-1}$  region can be explained by higher degree of freedom for  $-\text{CF}_3$  moiety in LiPDI.

Ionic fractions estimated by Fuoss-Kraus formalism explains why stronger association for LiTDI solutions does not suffice to result in lower conductivity than LiPDI solution. Stronger association for LiTDI solutions results in higher viscosity; however, difference is not big enough to entail higher viscosities than those for LiPDI solutions. On the other hand, predominant charge carriers in those solutions are triplets, while fraction of free ions is negligible. As a result, stronger association causes greater increase in triplets concentration than decrease in free ions concentration. Ultimately, charge carriers concentration is higher for LiTDI than for LiPDI solutions. It should be noted that Fuoss-Kraus formalism accounts for all associates, not only contact ones. Alas, it is only an estimation of ionic fractions with limited accuracy at higher concentrations. Limitations arise from approximations in equations which are appropriate only for low concentrations. Still, it is sufficient for qualitative analysis.

Lithium cation transference number obtained for LiTDI and LiPDI solutions suggests that according to expectations, electrolytes containing LiPDI should have higher numbers due to more bulky anion. However, unexpectedly, lithium transference number for LiPDI solutions decreases with salt concentration. There are several factors that influence transference number: first and foremost, properties of ions—their relative masses, sizes and shapes. Secondly, properties of solvent encompassing also viscosity and ability to coordinate ions. In case of solvents for lithium ion batteries, those would be exclusively cations. Aforementioned properties would determine transference number at infinite dilution. Changes of transference number with salt concentration would be the result of few effects. Firstly, due to difference in sizes and shapes of free anions and cations with their solvation layer, increase of viscosity will differently impact mobility of charged species. The effect should be observed to a greater extent for bulkier particles. Secondly, association will affect transference number, as mobilities of associates are different than those of dissociated ions. Ion pairs influence viscosity only, as they do not migrate in electric field. Mobility of positively and negatively charged triplets will usually vary due to difference in size. Because of associate content, which was discussed earlier, association effect on transference number change in studied concentration should be small as most important change in electrolyte with concentration is ion pair  $\rightarrow$  triplet. Comparison of masses of solvated cation and anion suggest, as mentioned earlier, that mobilities of  $\text{TDI}^-$  and  $\text{Li}(\text{TDI})_2^-$  are higher than mobilities of  $\text{PDI}^-$  and  $\text{Li}(\text{PDI})_2^-$ . Shapes of charged species also suggest similar difference thus viscosity effect will only amplify existing differences in transference number. Experimental results in this case can be explained by association constants.  $\text{PDI}^-$  anions interactions are weaker

than  $\text{TDI}^-$  and  $\text{Li}^+$  interactions strength does not change in both cases. As a result, there is statistically a higher chance to observe  $\text{Li}(\text{TDI})_2^-$  than  $\text{Li}(\text{PDI})_2^-$  and a higher chance to observe  $\text{Li}_2\text{PDI}^+$  than  $\text{Li}_2\text{TDI}^+$ . It entails excess number of free  $\text{Li}^+$  cations in LiTDI solutions and  $\text{PDI}^-$  anions in LiPDI solutions. The number of unbalanced ions in the solution should be correlated with both fraction of triplets and salt concentration in electrolyte.

Melting points and glass transition temperatures obtained by DSC revealed few interesting properties of studied solutions. Lower melting and glass transition temperatures for LiPDI solutions than those for LiTDI solutions can be explained by weaker interactions between cation and anion, which confirms previous assumptions. Interestingly, glass transition temperature exhibits nonlinear behaviour. At low salt concentration,  $T_g$  increases. With sufficient salt concentration, below 1:10 molar ratio, another signal appears on the DSC curve. This is an exothermic signal related to recrystallization of sample. Such new composition has lower glass transition temperature, which results in sudden drop of  $T_g$  with salt concentration. With further growth of salt concentration  $T_g$  increases as a result of viscosity increase causing increased chain stiffness which was already described in previous works regarding poly (ethylene glycol) solutions [28]. Melting point appears for studied solutions only down to 1:5 molar ratio for both LiTDI and LiPDI. More concentrated solutions form fully amorphous systems. Addition of salt results in decrease of melting point. Disappearance of melting point correlates well with maxima of conductivity for both salts. Such correlation could be the result of maximum conductivity appearing at concentration providing optimal fulfilment of lithium cation coordination sphere by solvent molecules. After that, continuous increase of salt concentration leads to amplification of cation-anion interactions which along decreasing number of free solvent molecules, is sufficient to prevent crystallisation. Crystallisation of LiTDI-triglyme system was observed and studied for molar ratios lower than 1:3 [20, 21]. However, these crystal structures ought to be different than those for low salt concentration. Crystals obtained for low salt concentration have melting point slightly below  $-46\text{ }^\circ\text{C}$ , which is a melting point for pure triglyme. It is a much lower melting point than for high concentration crystals. Possibly structure of low concentration crystals is determined by solvent and may resemble its crystal structure.

## Conclusions

To summarise, comparative study of LiTDI and LiPDI solutions showed that functional parameters of electrolytes are results of many different, often opposing, factors. Both salts exhibit very similar parameters despite quite significant difference in anion mass and volume. Conductivity for both



systems encloses within a few percent and positions of maxima are mostly dependent on solvent. Differences in viscosity values are also small. We have demonstrated how association governs electrolyte parameters and is crucial to understand observed changes. It allowed us to understand why  $\text{PDI}^-$ , which is anion of theoretically better properties than  $\text{TDI}^-$ , did not exhibit better parameters in solution. Association is the key parameter for electrolyte optimization, yet it is not always advised to strive to minimize it. If triplets are main charge carriers in electrolyte, obtaining lower association at the expense of other parameters like viscosity is not going to yield a positive effect. Complex nature of interactions affecting transference number, which is very important parameter, was also described. Structure of anion not only determines transference number but also the way it changes with concentration. Together with solvent properties, it constitute position of transference number maximum. Interesting observations were made regarding behaviour of melting point and glass transition temperature, particularly an explanation of nonlinear change with concentration of the latter which is an important factor for electrolyte optimization. These studies have practical implications as well, allowing for knowledge-based design of new salts and electrolytes for lithium-ion batteries.

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### Compliance with ethical standards

**Conflicts of interest** The authors declare that they have no competing interests.

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### References

- Xu K (2004) Nonaqueous liquid electrolytes for lithium-based rechargeable batteries. *Chem Rev* 104:4303–4418
- Marom R, Haik O, Aurbach D, Halalay IC (2010) Revisiting  $\text{LiClO}_4$  as an electrolyte for rechargeable lithium-ion batteries. *J Electrochem Soc* 157:A972–A983
- Matsuda Y, Morita M, Yamashita T (1984) Conductivity of the  $\text{LiBF}_4$ /mixed ether electrolytes for secondary lithium cells. *J Electrochem Soc* 131:2821–2827
- Takata K, Morita M, Matsuda Y, Matsui K (1985) Cycling characteristics of secondary Li electrode in  $\text{LiBF}_4$ /mixed ether electrolytes. *J Electrochem Soc* 132:126–128
- Nanjundiah C, Goldman JL, Dominey LA, Koch VR (1988) Electrochemical stability of  $\text{LiMF}_6$  ( $M = \text{P, As, Sb}$ ) in tetrahydrofuran and sulfolane. *J Electrochem Soc* 135:2914–2917
- Webber A (1991) Conductivity and viscosity of solutions of  $\text{LiCF}_3\text{SO}_3$ ,  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ , and their mixtures. *J Electrochem Soc* 138:2586–2590
- Li W, Campion C, Lucht BL, Ravdel B, DiCarlo J, Abraham KM (2005) Additives for stabilizing  $\text{LiPF}_6$ -based electrolytes against thermal decomposition. *J Electrochem Soc* 152:A1361–A1365
- Gnanaraj JS, Zinigrad E, Levi MD, Aurbach D, Schmidt M (2003) A comparison among  $\text{LiPF}_6$ ,  $\text{LiPF}_3(\text{CF}_2\text{CF}_3)_3$  (LiFAP), and  $\text{LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2$  (LiBETI) solutions: electrochemical and thermal studies. *J Power Sources* 119–121:799–804
- Xu W, Angell CA (2001) Weakly coordinating anions, and the exceptional conductivity of their nonaqueous solutions. *Electrochem Solid-State Lett* 4:E1–E4
- Schmidt M, Heider U, Kuehner A, Oesten R, Jungnitz M, Ignat'ev N, Sartori P (2001) Lithium fluoroalkylphosphates: a new class of conducting salts for electrolytes for high energy lithium-ion batteries. *J Power Sources* 97–98:557–560
- Niedzicki L, Żukowska GZ, Bukowska M, Szczeciński P, Grugeon S, Laruelle S, Armand M, Panero S, Scrosati B, Marcinek M, Wieczorek W (2010) New type of imidazole based salts designed specifically for lithium ion batteries. *Electrochim Acta* 55:1450–1454
- Niedzicki L, Kasprzyk M, Kuziak K, Żukowska GZ, Marcinek M, Wieczorek W, Armand M (2011) Liquid electrolytes based on new lithium conductive imidazole salts. *J Power Sources* 196:1386–1391
- Marcinek M, Syzdek J, Marczewski M, Piszcz M, Niedzicki L, Kalita M, Plewa-Marczewska A, Bitner A, Wieczorek P, Trzeciak T, Kasprzyk M, Łęzak P, Żukowska GZ, Zalewska A, Wieczorek W (2015) Electrolytes for Li-ion transport—review. *Solid State Ionics* 276:107–126
- Scheers J, Johansson P, Szczeciński P, Wieczorek W, Armand M, Jacobsson P (2010) Benzimidazole and imidazole lithium salts for battery electrolytes. *J Power Sources* 195:6081–6087
- Niedzicki L, Karpierz E, Bitner A, Kasprzyk M, Żukowska GZ, Marcinek M, Wieczorek W (2014) Optimization of the lithium-ion cell electrolyte composition through the use of the LiTDI salt. *Electrochim Acta* 117:224–229
- Berhaut CL, Porion P, Timperman L, Schmidt G, Lemordant D, Anouti M (2015) LiTDI as electrolyte salt for Li-ion batteries: transport properties in EC/DMC. *Electrochim Acta* 180:778–787
- Paillet S, Schmidt G, Ladouceur S, Fréchette J, Barray F, Clément D, Hovington P, Guerfi A, Vijh A, Cayrefourcq I, Zaghbi K (2015) Determination of the electrochemical performance and stability of the lithium-salt, lithium 4,5-dicyano-2-(trifluoromethyl)imidazolide, with various anodes in Li-ion cells. *J Power Sources* 299:309–314
- Lindgren F, Xu C, Niedzicki L, Marcinek M, Gustafsson T, Björefors F, Edström K, Younesi R (2016) SEI formation and interfacial stability of a Si electrode in a LiTDI-salt based electrolyte with FEC and VC additives for Li-ion batteries. *ACS Appl Mater Interfaces* 8:15758–15766
- Shkrob IA, Pupek KZ, Gilbert JA, Trask SE, Abraham DP (2016) Chemical stability of lithium 2-trifluoromethyl-4,5-dicyanoimidazolide, an electrolyte salt for Li-ion cells. *J Phys Chem C* 120:28463–28471
- McOwen DW, Delp SA, Paillard E, Herriot C, Han SD, Boyle PD, Sommer RD, Henderson WA (2014) Anion coordination interactions in solvates with the lithium salts LiDCTA and LiTDI. *J Phys Chem C* 118:7781–7787
- Jankowski P, Dranka M, Żukowska GZ, Zachara J (2015) Structural studies of lithium 4,5-dicyanoimidazolide–glyme solvates. 1. From

- isolated free ions to conductive aggregated systems. *J Phys Chem C* 119:9108–9116
22. Henderson WA, McKenna F, Khan MA, Brooks NR, Young VG, Frech R (2005) Glyme-lithium bis (trifluoromethanesulfonyl) imide and glyme-lithium bis (perfluoroethanesulfonyl) imide phase behavior and solvate structures. *Chem Mater* 17:2284–2289
  23. Fuoss RM, Kraus CA (1933) Properties of electrolytic solutions. II. The evaluations of  $L_0$  and of  $K$  for incompletely dissociated electrolytes. *J Am Chem Soc* 55:476–488
  24. Fuoss RM, Kraus CA (1933) Properties of electrolytic solutions. III. The dissociation constant. *J Am Chem Soc* 55:1019–1028
  25. Fuoss RM, Kraus CA (1933) Properties of electrolytic solutions. IV. The conductance minimum and the formation of triple ions due to the action of Coulomb forces. *J Am Chem Soc* 55:2387–2399
  26. Kraus CA, Fuoss RM (1933) Properties of electrolytic solutions. I. Conductance as influenced by the dielectric constant of the solvent medium. *J Am Chem Soc* 55:21–36
  27. Bruce PG, Vincent CA (1987) Steady state current flow in solid binary electrolyte cells. *J Electroanal Chem Interfacial Electrochem* 225:1–17
  28. Stygar J, Zalewska A, Wieczorek W (2000) Studies of ionic interactions in low molecular weight polyether electrolytes. *Electrochim Acta* 45:1437–1441