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LiTDI and solvent mixture based electrolytes for lithium-ion cells

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Abstract

Electrolyte optimization for both best performance and low use of materials is described in this paper. Electrochemical performance and material utility are reported to achieve the goal of optimal combinations of salt concentration and solvent ratios for several solvent mixtures. A lithium 4,5-dicyano-2-trifluoromethanoimidazolide (LiTDI) salt was used for its thermal stability, ease of handling (stable in the presence of air and moisture) and high ionic conductivity at low concentration in solvents. Solvent mixtures were chosen based on industrial practice and performance at low temperature. The conductivity dependence of salt concentration is reported. In all systems, low concentration onset and a broad range of high conductivity was observed. Lithium cation transference numbers were measured for highly conductive samples and used as the secondary parameter in the optimization procedure. Both high ionic conductivity and transference number values were recorded, even for samples with low salt content: 0.3 mol kg⁻¹ LiTDI in 1EC:2EMC (σ = 4.18 mS cm⁻¹, T_{Li+} = 0.544) and 0.4 mol kg⁻¹ LiTDI in EC:DMC:EMC (σ = 4.69 mS cm⁻¹, T_{Li+} = 0.455). Cycling with anodic material was also carried out, showing good capacity for retention of the mixtures chosen containing average salt concentrations. Hence, material savings in comparison to other commercially available lithium salts is possible.

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1. Introduction

In the last 20 years, lithium-ion (Li-ion) cells have gradually taken over the battery market. More and more devices are using this type of energy storage: electric vehicles, personal electronic devices, and medical and military applications, to mention only a few. Future development of Li-ion cells depends on the ability to use modern electrode materials without compromising stability or a long life of the cell. This ability comes from compatibility between electrode materials and the electrolyte between them. Unfortunately, the existing electrolytes dominating the market are based on lithium hexafluorophosphate (LiPF₆), which has many disadvantages. Among them is lack of compatibility with newly developed electrode materials due to traces of hydrogen fluoride. Other main disadvantages of LiPF₆ are thermal stability only up to 70°C and instability when moisture is present, even at trace levels on the order of ppm [1-3]. To overcome these issues, numerous functional additives have been proposed, for example to increase PF₆⁻ anion stability, absorb impurities, and neutralize the hydrogen fluoride that forms in LiPF₆ solutions. Adding additives to the electrolyte makes it more expensive. This approach to solving these problems also unnecessarily complicates the electrolyte composition due to increased potential for safety hazards and incompatibility with electrodes.

An alternative approach includes using new lithium salts. LiTFSI and LiBETI, known for some time already, are corrosive towards aluminum current collectors [4]. Another candidate, LiFSI, is corrosive towards some battery components [5,6]. Other salts have been proposed by our group in recent years as well [7,8]. Notably, LiTDI salt has been the most successful so far. LiTDI is thermally stable up to 250° C – higher than any solvent boiling point or the stability of LiPF₆. LiTDI is also electrochemically stable up to 4.6 V vs. (Li/Li^+) – far more than is needed for commercially available electroactive materials. It is also fully stable in the presence of moisture. A smaller amount of fluorine in the anion in comparison to LiPF₆ is an additional, environmentally friendly advantage. The higher transference number of LiTDI is an advantage over the market-dominating salt, and is especially beneficial for high-energy applications, such as electric vehicles or grid energy storage. While LiTDIbased solutions lack as high an ionic conductivity as LiPF₆ ones, the former excel at transference number [9]. Thanks to the high lithium cation conductivity value (the transference number multiplied by ionic conductivity) of LiTDI electrolytes, the rate of ion transfer should not be compromised and should be similar to that of LiPF₆. Such a claim has been experimentally confirmed recently by an independent team [10]. Thus, it is important to test this new weakly coordinating salt (anion) application in lithium-ion cell electrolytes. More information on LiTDI properties and basic parameters is available elsewhere [11,12].

Solvents chosen for the electrolyte composition are no less important than other cell components. Depending on the choice of solvents and the ratio of their resulting viscosity, the dielectric constant and solvation of ions all have a large impact on electrolyte performance parameters. Also, as much as the salt choice, its concentration is important. An optimal concentration in concert with properly chosen solvents can mean great results in terms of conductivity, lithium cation transference number and material savings. Such a concept has been proven by experiments of Ding and coworkers in the early 2000s [13-15]. They showed that every salt and every solvent ratio has a different optimal concentration for maximum ionic conductivity. Our group previously showed that similar maxima exist for transference number [9]. We also explained this phenomenon based on studies of adequate ionic associations.

Mixtures that are an outcome of such optimization are important from the application point of view. Industry awaits components that are ready to replace current electrolytes. To meet such expectations, we investigated electrolyte compositions based on the new salt LiTDI as well as popular solvents. The solvents chosen are well-known and industrially proven. Ethylene carbonate (EC) is currently the most popular solvent; it is strongly polar and stable under the conditions inside lithium cells. It is the basis for the vast majority of commercial electrolytes. It cannot be used alone, though, as its melting point is as high as 38°C. Complementary solvents chosen for optimization are also common components of Li-ion cell electrolyte solutions: ethyl methyl carbonate (EMC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) [16].

The most important parameter studied herein is high ionic conductivity together with lithium cation transference number, considered together as lithium cation conductivity. The investigation of solvent mixture choice vs. lithium cation conductivity and half-cell cycling behavior, with a particular focus on materials savings, was the main subject of this study. For easier comparison of the new compositions with the state of the art, we include some basic measurements on a LiPF₆-based commercial electrolyte.

2. Experimental

The chosen solvent ratios in mixtures were based on phase diagrams [17,18] and previous work [19]. The following mixtures were employed as a result: EC:EMC (1:2), EC:DEC:EMC (1:1:1), EC:DMC:EMC (1:1:1) and EC:DEC:DMC:EMC (1:1:1:2). EMC was employed due to its advantageous properties at low temperatures.

Samples were prepared in an argon-filled glovebox with less than 1 ppm of moisture content. Electrolytes with the full range of LiTDI concentration (0.1 mol kg⁻¹ to 1.0 mol kg⁻¹) were made. Salt's concentration range was determined by limiting to the most interesting area from the application point of view (elevated conductivity level range), as well as for the sake of plots consistency, as the salt solubility differs between solvent mixtures.

Ionic conductivity was measured using electrochemical impedance spectroscopy in the -20 to +40°C temperature range. Electrolyte samples were put into a micro conductivity cells with cell constant values of 0.3–0.7 cm⁻¹ calibrated with a precision of 0.3%. Cells were subsequently placed in a Haake K75 cryostat-thermostat system with a DC50 temperature controller. All impedance measurements were carried out on a computer-interfaced VMP3 multichannel potentiostat (Bio-Logic Science Instruments) with the frequency response analyzer option. Electrochemical impedance spectroscopy was performed within the 500 kHz to 1 Hz frequency range with 10 points per decade and 5 mV A.C. signal amplitude. Measurements were repeated at least three times for each concentration for more consistency. Samples for conductivity measurements were prepared in an argon-filled glovebox with less than 1 ppm of moisture content.

Lithium cation transference numbers (t_+) were calculated using the D.C. polarization method combined with the A.C. impedance method introduced by Bruce and Vincent [20]. Details of the method have been described elsewhere [11].

The t_+ determination for each measured composition was performed on three samples for more consistent data. Samples were handled in an argon-filled glovebox with less than 1 ppm of moisture content, then sealed and measured.

Charge-discharge cycling used a Li | electrolyte | silicon-carbon composite (Si/C) halfcell system with a silicon-carbon nanostructured composite thin-film anode obtained through use of microwave plasma assisted chemical vapor deposition (MPCVD). Triethoxy(phenyl)silane was used as precursor. Details of the MPCVD method for nanostructured composite electrode manufacturing are described elsewhere [21]. Cycling voltage was set at the 0.05–1.4 V (half-cell containing Si-C) range. The current was chosen every time in such a way that both discharge and charge would take one hour (1 C current). An Astrol Electronic Bat-Small battery cycler was used for cycling experiments.

To simplify notation, a solvent mixture containing EC and EMC in a 1:2 weight ratio will be written as EC:2EMC. Similarly, a mixture consisting of EC, DEC and EMC in a 1:1:1 weight ratio will be written as EC:DEC:EMC, that of EC, DMC and EMC in a 1:1:1 weight ratio as EC:DMC:EMC and that of EC, DEC, DMC and EMC in a 1:1:1:2 weight ratio as EC:DEC:DMC:2EMC.

3. Results and discussion

The aim of the investigation was to find the golden mean between low salt concentration (material savings) and good electrochemical parameters. In order to narrow the number of concentrations considered, the first step of this search was to determine the ionic conductivity dependence on LiTDI concentration. The dependence of ionic conductivity on salt concentration as well as temperature for all solvent mixtures is shown in Figure 1. As shown, depending on solvent mixture, the concentration dependence of the conductivity varies considerably. The difference between the lowest and the highest conductivity at room temperature (20°C) across a concentration of 0.1–1.0 mol kg⁻¹ was smallest for EC:2EMC (2.15 and 4.87 mS cm⁻¹ at 0.1 and 0.7 mol kg⁻¹, respectively). A similar difference in conductivity was observed in the case of EC:DMC:EMC (2.44 and 5.47 mS cm⁻¹ at 0.1 and 0.7 mol kg⁻¹, respectively).

Conductivity plots of these two mixtures also varied relatively. The first mixture (EC:2EMC, Fig. 1a) at 0.3 mol kg⁻¹ had a conductivity value plateau extending until 1.0 mol kg⁻¹, with only one mildly differentiable point at 0.7 mol kg⁻¹ (a flat maximum). Conductivity of electrolytes based on the other mixture (EC:DMC:EMC, Fig. 1c) increased monotonously from 0.1 to 0.7 mol kg⁻¹ to a maximum and then decreased towards 1.0 mol kg⁻¹. Above 0.4 mol kg⁻¹, the conductivity both increased and decreased slightly (to 0.9 mol kg⁻¹). Very different plots were observed for two other solvent mixtures. The first plot (for EC:DEC:EMC, Fig. 1b) contains a distinct maximum (with a very steep slope) at 0.8 mol kg⁻¹. An initial increase of conductivity. Subsequent values started from a very high value (at 0.5 mol kg⁻¹) and fluctuated until 0.9 mol kg⁻¹, with an abrupt increase visible only at 0.8 mol kg⁻¹. The second plot, for the last solvent mixture (EC:DEC:DMC:2EMC, Fig. 1d), also showed a conductivity increase with concentration to a maximum



Fig. 1. Dependence of ionic conductivity on LiTDI concentration in the -20 to 40°C temperature range, for the 0.1-1.0 mol kg⁻¹ salt concentration range in a following solvent mixtures: a. EC:EMC (1:2 weight ratio); b. EC:DEC:EMC (1:1:1 weight ratio); c. EC:DMC:EMC (1:1:1:1 weight ratio); d. EC:DEC:DMC:EMC (1:1:1:2 weight ratio).



Fig. 1 ad.. Dependence of ionic conductivity on LiTDI concentration in the -20 to 40°C temperature range, for the 0.1-1.0 mol kg⁻¹ salt concentration range in a following solvent mixtures: a. EC:EMC (1:2 weight ratio); b. EC:DEC:EMC (1:1:1 weight ratio); c. EC:DMC:EMC (1:1:1 weight ratio); d. EC:DEC:DMC:EMC (1:1:1:2 weight ratio).

(0.9 mol kg⁻¹), with steep slopes both below and above that concentration. A notable point is the flat local maximum at 0.5 mol kg⁻¹.

The second pair of plots (Figs. 1b and 1d) also exhibited large differences between the lowest and the highest conductivity at room temperature. In the case of EC:DEC:EMC, these were 1.84 mS cm⁻¹ for 0.1 mol kg⁻¹ and 5.86 mS cm⁻¹ for 0.8 mol kg⁻¹. The EC:DEC:DMC:2EMC-based electrolyte exhibited 1.52 mS cm⁻¹ conductivity at 0.1 mol kg⁻¹ (minimum) and 4.77 mS cm⁻¹ at 0.9 mol kg⁻¹ (maximum). These characteristic concentrations on the conductivity plots, such as maxima and low concentrations with relatively high conductivity, were chosen for lithium cation transference number measurements.

A conductivity plot with a varied shape, as observed for DEC-based mixtures, is rare, though not unique. Apart from other DEC-based LiTDI solutions [9], it is found in other mixtures [22]. The fact that these solutions are four- or five-component mixtures (LiTDI and at least three solvents), with every component having different properties, can explain such unusual conductivity behavior. In contrast, DMC-based mixtures have a more standard conductivity plot shape, probably due to the relatively similar properties of DMC and EMC. Also, LiTDI is known for forming a variety of associate and solvate configurations depending on the absolute and relative concentration of solvents [9,23]. As the concentration increases, the electrolyte contains more and more ionic associates, both in terms of amount and diversity. This might also explain the increasing variety of conductivity plot shapes.

The ratio between the minimum ionic conductivity value (at 0.1 mol kg⁻¹ LiTDI) and the maximum is equal to 0.44 in the case of EC:2EMC and EC:DMC:EMC solvent mixtures. For the other two mixtures incorporating DEC (EC:DEC:EMC and EC:DEC:DMC:2EMC), this ratio is equal to 0.31; i.e., the conductivity peaks are sharper in this case. This might be an effect of higher viscosity of DEC than DMC and EMC. The dielectric constant of DEC is also the lowest of the solvents used.

Of the four solvent mixtures, the absolute value of the maximum conductivity was the lowest for EC:DEC:DMC:2EMC, probably due to its having the lowest EC content (0.226 molar fraction in pure solvent mixture). On the other hand, the EC:DEC:EMC-based mixture was the most conductive electrolyte. That solvent mixture had the highest molar fraction of EC in pure solvent mixture, 0.386. The other two solvent mixtures contained EC as a 0.354 (EC:DMC:EMC) and 0.371 (EC:2EMC) molar fraction. We already established EC content and solvation as the most important parameters for good electrolyte conductivity [9]. As the dielectric constant of EC exceeds that of DEC, DMC and EMC, it would be the first



Fig. 2. Dependence of ionic conductivity on ethylene carbonate to lithium cation molar ratio at 20°C for different solvent mixtures.

choice to solvate lithium cations. Initially, conductivity would increase due to the increase in concentration, and such an effect would overcome the viscosity increase. After reaching a maximum, the conductivity would drop when there would no longer be enough EC in the system to fill a solvation layer of lithium cation. The present findings are proof of this concept.

To investigate this concept further, we plotted the conductivity of all solvent mixtures at one chosen temperature (20°C) on a single figure, but instead of concentration, using the molar ratio between EC and lithium cations as the independent variable. The results are shown in Figure 2. Maximum for three solvent mixtures with high EC content are at 5–6 EC molecules per lithium cation. That corresponds to our previous calculations for EC:DEC, EC:DMC and EC:DEC:DMC mixtures, where the maximum occurred at a ratio close to 3. That value should be adjusted by taking into the account the number of EC molecules not taking part in lithium cation solvation — ca. 50% for the 0.6–0.8 mol kg⁻¹ concentration range. Thus, the total EC to lithium cation ratio at the conductivity maximum should fall around 6, as is the case. The only solutions that do not fit this concept are those based on EC:DEC:DMC:2EMC, for which the maximum conductivity is around 2.5 EC molecules per lithium cation. However, a small local maximum is also visible for the 4–5 EC molecules

per lithium cation range, which confirms that the concept serves its role here as well, although to a lesser extent. An absolute maximum at such a low EC to Li ratio (2.5) can be explained by the high concentration of weakly polar solvents in the system. As they are competing for access to lithium cations with EC, their vast excess in the system might shift the ratio at which EC loses its strong binding to the lithium cation. Notably, DEC has already been proven a successful competitor against EC in a solvent layer [9]. As a result, EC solvating molecules have a lower effect on the lithium cation due to their lower ability to fill the solvation layer to a large extent. Thus, conductivity drops faster on the EC-to-Li ratio scale. On all plots, less the EC:DEC:DMC:2EMC, there are drastic conductivity changes visible around 8 EC-to-Li ratio. Presence of such a conductivity change is the confirmation of the solvation explanation described before, as this ratio represents 4 EC molecules in the solvation layer around lithium cation. Additional peaks around 12 EC-to-Li ratio in EC:2EMC and EC:DEC:EMC and their lack in the other mixtures might suggest better shielding from the anion when EMC or DEC are present in the higher concentration in the solvation layer - not necessarily in the first layer. However, when EC is present in the bulk of the electrolyte in the relatively higher concentration (solvation layer is saturated with EC, EC-to-Li ratio over 8), conductivity plots start to be parallel and depend on linear carbonate properties. EMC the middle value of both viscosity and dielectric constant, making it a golden mean between DEC (the lowest dielectric constant of three) and DMC (the lowest viscosity of three). These conclusions might be helpful in the future designing of electrolyte compositions involving weakly coordinating anions, such as TDI. The anion itself and its low affinity to lithium cation are the main reason the solvation layer is shielding cation enough and the presence of linear carbonates in it is also sufficient to dissociate the salt and keep it dissociated even when only 1-2 EC molecules are present in the solvation layer around the cation.

Lithium cation transference numbers (t_{Li+}) were measured for the chosen concentrations and solvent mixtures. Subsequently, the lithium cation conductivity (σ_{Li+}) was calculated for each. The results are summarized in Table 1. For comparison, parameters for LiPF₆-based electrolytes (*i.e.*, the state of the art) from the literature were added. As shown, LiTDI-based electrolytes exhibit similar lithium cation conductivity to those based on LiPF₆ due to the high lithium cation transference number, which is typically twice as high as that of electrolytes containing LiPF₆. This means that in terms of a usable parameter, namely lithium cation conductivity, these electrolytes are fully comparable. Also, such a high lithium cation transference numbers of LiTDI with relatively (to other salts) high

mixture	c / mol kg ⁻¹	$\sigma \ / \ mS \ cm^{\text{-1}}$	t ₊ / -	$\sigma_{Li^+} \ / \ mS \ cm^{\text{-1}}$
LiTDI-EC:2EMC	0.3	4.18	0.54 ± 0.01	2.27
LiTDI-EC:2EMC	0.7	4.87	0.52 ± 0.03	2.52
LiTDI-EC:DEC:EMC	0.3	3.21	0.64 ± 0.05	2.06
LiTDI-EC:DEC:EMC	0.5	4.39	0.44 ± 0.04	1.91
LiTDI-EC:DEC:EMC	0.8	5.86	0.50 ± 0.03	2.94
LiTDI-EC:DMC:EMC	0.4	4.69	0.46 ± 0.02	2.13
LiTDI-EC:DMC:EMC	0.7	5.47	0.43 ± 0.03	2.37
LiTDI-EC:DEC:DMC:2EMC	0.5	3.68	0.62 ± 0.02	2.27
LiTDI-EC:DEC:DMC:2EMC	0.9	4.77	0.51 ± 0.03	2.42
LiPF ₆ -EC:2EMC	0.9	8.0[24]	0.3 ± 0.1 [25-28]	2.40
LiPF ₆ -EC:DEC:DMC:2EMC	1.0	7.7[19]	0.3 ± 0.1 [25-28]	2.30

Table 1. Optimized electrolyte compositions: LiTDI or LiPF₆ concentration, solvent mixture, ionic conductivity, transference number and lithium cation conductivity.

conductivities are confirming low affinity and weak coordination of the TDI anion to lithium cation.

The main goal of the investigation was not only to find suitable electrolyte compositions that would compete with commercial ones, but also to aim for as high of a material savings as possible. Thus, for further measurements, we chose only lower concentrations if there were no huge differences in terms of lithium cation conductivity. Unfortunately, as it is often the case, not every electrolyte with a low concentration of lithium salt gave a stable solid-electrolyte interface. As a result, not every lowest concentration of salt in the electrolyte was examined further.

The final test of electrolytes was half-cell cycling, for which the system Li | electrolyte | Si/C was used. Si/C was used due to the growing interest in silicon-based anodes and the ensuing challenges. Also, it was made with a unique but efficient in-house procedure. The 1C rate was used for cycling, which was presumed to be challenging enough for the electrolyte. Results of cycling experiments on the chosen LiTDI-based electrolytes are shown in Figure 3, together with results for a commercial LiPF₆ electrolyte mixture (LiPF6-EC:DMC, 1:1 weight ratio). Only 0.3 mol kg⁻¹ LiTDI in EC:DEC:EMC exhibits a markedly

a.



Fig. 3. Discharge capacity during cycling of (Si/C | LiTDI-solvent mixture | Li) half-cell for different solvent mixtures: a. 0.7 mol kg⁻¹ LiTDI in EC:EMC (1:2 weight ratio), 0.7 mol kg⁻¹ LiTDI in EC:DMC:EMC (1:1:1 weight ratio) and 1.0 mol kg⁻¹ LiPF₆ in EC:DMC (1:1 weight ratio); b. 0.3 mol kg⁻¹ LiTDI in EC:DEC:EMC (1:1:1 weight ratio) and 0.9 mol kg⁻¹ LiTDI in EC:DEC:EMC (1:1:1:2 weight ratio).

weaker cycling performance. This might be explained by the low concentration of lithium salt. However, the fact that such a low concentration of electrolyte can work steadily for over 20 cycles and at an electrode capacity almost 3 times higher than that of a LiPF_6 -based concentrated electrolyte is a success in itself.

The rest of the LiTDI-based electrolytes performed much better than the commercially available LiPF6 electrolyte. After 100 cycles, they all exhibited at least twice the anodic capacity as 1.0 mol kg⁻¹ LiPF₆-EC:DMC (262 mAh g⁻¹). In the case of 0.9 mol kg⁻¹ LiTDI-EC:DEC:DMC:2EMC, it was exactly two times higher (524 mAh g⁻¹) and at 0.7 mol kg⁻¹ EC:2EMC, it was a little higher still (550 mAh g⁻¹). A 0.7 mol kg⁻¹ LiTDI-EC:DMC:EMC electrolyte exhibited an anodic capacity as high as 737 mAh g⁻¹, with a trend toward an increase. The initial capacity for all LiTDI-based electrolytes was in the range of 680 to 695 mAh g⁻¹, with the exception of LiTDI-EC:DMC:EMC, which trended toward that value but started at a lower one (489 mAh g⁻¹). Thus, 0.7 mol kg⁻¹ LiTDI-EC:2EMC and 0.9 mol kg⁻¹ LiTDI-EC:DEC:DMC:2EMC electrolytes respectively maintained 75% and 81% of the initial capacity after 100 cycles at a 1C cycling rate. Considering their much higher absolute capacity, they are fully comparable to a 1.0 mol kg⁻¹ LiPF₆-EC:DMC mixture, which has 89% capacity retention after 100 cycles under the same cycling conditions. In contrast to all other electrolytes, LiTDI-EC:DMC:EMC exhibited a capacity increase of the anode in the half-cell — there was a 50% capacity gain throughout 100 cycles. This might be an effect of the initial thick solid electrolyte interface layer, which changes during cycling or from a slow but steady penetration of the electrode's superficial pores. Regardless of the reasons and the increase rather than decrease of capacity, this electrolyte achieves an anodic capacity of 737 mAh g⁻¹ after 100 cycles. This is a much better result than for other LiTDI-based electrolytes and is three times the capacity value observed for a LiPF₆-based electrolyte after 100 cycles.

4. Conclusions

LiTDI salt was used for electrolyte optimization in popular battery solvent mixtures such as EC:2EMC, EC:DEC:EMC, EC:DMC:EMC and EC:DEC:DMC:2EMC. LiTDI solutions already reach a high conductivity (3 mS cm⁻¹ at 20°C) at low concentrations (0.2-0.3 mol kg⁻¹, with the exception of EC:DEC:DMC:2EMC). At the concentration where the conductivity increases greatly, the σ_{Li+} is high — 2.27 mS cm⁻¹ for 0.3 mol kg⁻¹ LiTDI in EC:2EMC and 2.27 mS cm⁻¹ for 0.5 mol kg⁻¹ LiTDI in EC:DEC:DMC:2EMC. More importantly, these values are comparable to the industry state-of-the-art salt using the same solvent mixtures (2.4 mS cm⁻¹ for 0.9 mol kg⁻¹ LiPF₆ in EC:2EMC and 2.3 mS cm⁻¹ for 1.0 mol kg⁻¹ LiPF₆ in EC:DEC:DMC:2EMC). However, such values for the industry standard are achievable only at high concentrations: 3 times higher in the case of the EC:2EMC mixture and 2 times higher in the case of the EC:DEC:DMC:2EMC mixture. Thus, there is a possibility of huge savings on material. Finally, half-cell cycling with a new generation of anode shows the superiority of LiTDI-based electrolytes over LiPF₆-based ones.

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