Research paper

LiTDI based lithium-ion cells electrolyte compositions

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A B S T R A C T

Electrolyte compositions for future lithium-anode batteries involving silicon-composite anodes are studied in this paper. The lithium salt of TDI (4,5-dicyano-2-trifluoromethanoimidazole) was used due to its high lithium cation conductivity, the low concentrations needed for good electrolyte performance (material savings), as well as its extraordinary stability against high temperatures, electrochemical potentials, and moisture, which is unmatched by other commercially available salts. A systematic investigation of the dependence of ionic conductivity on the concentration of SEI-stabilizing additives in LiTDI-based electrolytes was performed. Subsequently, the best conductive electrolyte compositions were used in half-cells involving silicon composite anodes and tested in long-term high-rate charge-discharge cycling.

For all the studied systems, including electrolytes at low concentrations ($0.31 \, mol \, kg^{-1}$), the ionic conductivity at room temperature ($20\,°C$) was above $4 \, mS \, cm^{-1}$. Lithium cation transference numbers were measured for the most promising samples, almost exclusively exhibiting values above 0.5. Pure electrolytes, 0.31 and $0.63 \, mol \, kg^{-1}$ LiTDI in EC:DMC (1:2 weight ratio), have shown anode discharge capacities as high as 1500 and $900 \, mAh \, g^{-1}$, respectively. In particular, a $0.63 \, mol \, kg^{-1}$ concentration left little room for improvement, showing very good stability by maintaining the same (or higher) capacity for the first 125 cycles. SEI-stabilizing additives improved the cycling stability in terms of plot smoothness.

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1. Introduction

Lithium-ion cells are advancing towards greater and greater energy densities. This trend is mostly thanks to the development of anodic materials, with a prominent role being played by silicon and tin [1–3]. New anodic materials call for a revolution in electrolytes. LiPF₆, the most popular salt on the market (if not the monopolist), lacks stability, both thermally and against moisture [4–6]. It also works quite poorly with silicon and tin materials [3], most probably due to the unavoidable presence of hydrogen fluoride (even if only in trace amounts) in every LiPF₆ solution [7].

The solution for silicon-based (or based on other innovative materials) lithium-ion cells might be the new lithium salt, LiTDI. It is stable both thermally and with respect to moisture [8], thus it does not introduce any handling or stability disadvantages in comparison with LiPF₆. The lithium cation conductivities of both salts are similar [9]. LiTDI's low optimal concentration with respect to parameter optimization has a potential for huge material savings [9,10]. LiTDI exhibits electrochemical stability against a

lithium metal anode of greater than 4.7 V and does not corrode aluminum at the same potential [8], in contrast to LiTf (lithium trifluoromethylsulfonate) and LiTFSI (lithium bis(trifluoromethylsulfonyl)imide) salts. These two salts, although popular within the research sector, are known to corrode aluminum at potentials as low as 2.8–3.5 V vs Li [11,12]. LiTDI also successfully passed preliminary tests with some anodic and cathodic materials with promising results. Thus, it is time to test this salt in applications with novel and prospective battery materials, where other salts fail.

Our previous work on the optimization of LiTDI salt concentration and searching for the best solvent mixture to use with LiTDI resulted in the formulation of a few recommended electrolyte compositions. Of these solutions, the most important were two based on an EC:DMC (1:2 weight ratio) solvent mixture. One contained $0.31 \, mol \, kg^{-1}$ LiTDI and the other $0.63 \, mol \, kg^{-1}$ LiTDI. These two were employed for further research (this work), due to their extraordinarily high lithium cation conductivity (σ_{Li+}). This parameter is the product of high (in case of LiTDI) lithium cation transference number (t_{Li+}) and relatively high ionic conductivity (σ). The lithium cation conductivity of LiTDI in solutions is comparable (almost equal) to that of LiPF₆ solutions, based on the

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same solvent mixtures. As LiTDI has a lower total ionic conductivity than LiPF$_6$, comparability of lithium cation conductivity is possible thanks to the low lithium cation transference number of LiPF$_6$. It is worth noting that this is another disadvantage of LiPF$_6$, as t$_{Li+}$ is a parameter responsible for charge-discharge cycle efficiency [13].

As silicon anodes are very demanding towards electrolyte stability and especially SEI stability, we introduced the most commercially popular SEI-stabilizing additives into our electrolyte compositions. Fluoroethylene carbonate (FEC) and vinylene carbonate (VC) were added in different amounts to our electrolytes. The aim was to check whether cycling stability would be enhanced in comparison to pristine electrolytes, and if so, to what extent. Those two additives were chosen due to their established position in the lithium-ion battery industry, as well as their beneficial effect on the SEI, especially with silicon-based anodes [14–17].

As the industry needs specific solutions for battery/cell components and ready-to-use products, here we propose precise compositions. The recommended compositions are based firstly on a detailed study of the effect on ionic conductivity of the incorporation of functional additives into LiTDI-based electrolytes. Such studies narrow down the usable range of additive concentration, ensuring that it does not negatively affect the parameters of the initial electrolyte. Subsequently, we show results of the investigation of cycling performance and the compatibility of our electrolytes with silicon-carbon composite anodes in half-cells. Silicon composites are the most promising anode materials currently under worldwide investigation, and, in our opinion, the closest to the commercialization phase. Hence, it is important to take them as the benchmark for new electrolyte compositions. Finally, we show lithium cation transference numbers measured for the most promising electrolytes. Thus, we show that there is no compromise between static electrochemical parameters and good cycling performance in LiTDI-based electrolytes.

2. Experimental

LiTDI was synthesized using method described previously by us [8]. LiPF$_6$ was obtained from Sigma-Aldrich (battery grade). EC, DMC, VC and FEC were obtained from BASF.

The chosen additives initial concentration ranges were based on research by Lucht et al. [16], Saito et al. [15] and Ota et al. [18] and industrial practice. Basic solvent mixture and lithium salt concentrations were based on own research. The following electrolytes were employed as a result: 0.31 mol kg^{-1} LiTDI in EC:DMC (1:2 weight ratio) and 0.63 mol kg^{-1} LiTDI in EC:DMC (1:2 weight ratio). In order to shorten the notation, these mixtures are hereafter referred to by their short names: 0.31 M LiTDI and 0.63 M LiTDI, respectively. Solvent mixture description (EC:DMC, 1:2 weight ratio) is generally omitted, as it is the one and only used throughout the results in the present paper. To both electrolytes FEC and VC additives were added. FEC was incorporated in 1–10% additional weight range and VC in 1–5% additional weight range. Finally, both additives were added at once at 1:5 (VC to FEC) ratio, namely: +1% VC +5% FEC and +2% VC +10% FEC.

Samples of electrolytes were prepared in an argon-filled MBraun glovebox with less than 1 ppm of moisture content. 1 mol kg^{-1} sample of LiPF$_6$ in EC:DMC (1:2 weight ratio) was also made for comparison (as an industrial standard).

Ionic conductivity measurements were performed using electrochemical impedance spectroscopy (EIS) in the temperature range from −10 to 40 °C. Electrolyte samples were put into a micro conductivity cell with cell constant values of 0.3–0.7 cm^{-1} calibrated with precision of 0.3%. Cells were then placed in a cryostat-thermostat system (Haake K75 with a DC50 temperature controller). All impedance measurements were carried out on the

computer-interfaced multichannel potentiostat with frequency response analyzer option Bio-Logic Science Instruments VMP3 within 500 kHz–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 higher consistency. Samples for conductivity measurements were prepared in an argon-filled glovebox with less than 1 ppm of moisture content.

VC viscosity measurement was performed with Physica MCR301 Anton Paar Rheometer with CP40 cone tip and thermoelectric heat pump base for thermostating. 0.4 ml volume (excess) of the VC was used, thermostated with precision of 0.1 °C at each temperature and measured in shearing rate range of 10–1000 s^{-1}.

Lithium cation transference numbers (t_{Li+}) were calculated using the D.C. polarization method combined with the A.C. impedance method introduced by Bruce and Vincent [19]. Details of the method were described elsewhere [20]. The t_+ experiment for each measured composition was performed on at least three samples for a higher consistency of data. Samples were handled in an argon-filled glovebox with less than 1 ppm of moisture content, then sealed and measured.

Cyclic voltammetry used Li | electrolyte | Pt cell with lithium metal as a reference. Bio-logic Science Instruments VMP3 was used for measurements and the speed rate was equal to 1 mV s^{-1}.

Charge-discharge cycling used Li | electrolyte | Si-C half-cell system with silicon-carbon nano-structured composite thin-film anode obtained through use of in-house method of microwave plasma assisted chemical vapor deposition (MPCVD). Triethoxy (phenyl)silane was used here as the precursor. Details of the MPCVD method for nano-structured composite electrodes manufacturing are described elsewhere [1]. Carbon content was ca. 43% and silicon content was ca. 57% (EDX analysis) and 90% of grains were in size range of 15–20 nm (SEM and TEM analysis). Swagelok-type cell was assembled and sandwiched between stainless blocking electrodes. Cycling voltage was set in 0.05–1.4 V (half-cell containing Si-C) range. Current was chosen every time in such a way that both discharge and charge would take one hour (1C current). Astrol Electronic Bat-Small battery cycler was used for cycling experiment. Experiments were carried out for not less than 3 samples.

3. Results and discussion

The first step of the investigation was to determine the range of additive concentrations at which ionic conductivity of the basic electrolyte was not compromised. Fig. 1 shows the ionic conductivity's dependence on temperature with 0.31 M LiTDI (Fig. 1a) and 0.63 M LiTDI (Fig. 1b) electrolytes, with varied content of fluoroethylene carbonate (FEC). On the one hand, the exhibited ionic conductivities clearly showed no effect, or a negligibly small negative effect, upon FEC addition to 0.31 M LiTDI. On the other hand, FEC addition to 0.63 M LiTDI was advantageous, with all compositions showing proportional conductivity increasing with additive concentration. Thus, in the case of 0.31 M LiTDI, in terms of ionic conductivity it is preferable to keep a low FEC content. However, in the case of 0.63 M LiTDI electrolyte, a higher content of FEC is better.

Both effects can be explained using lithium salt concentrations and FEC's properties. Aside from the choice of anion, the lithium cation solvation layer's composition is the most important contributor towards electrolyte properties, such as conductivity. A solvation layer is needed to separate the anion from the cation and enable cation conductivity. However, the TDI anion more readily undergoes isolation by solvent molecules, due to its weak coordination properties [20]. In a plain electrolyte, statistically the most polar solvent tends to form the solvation layer, as has been
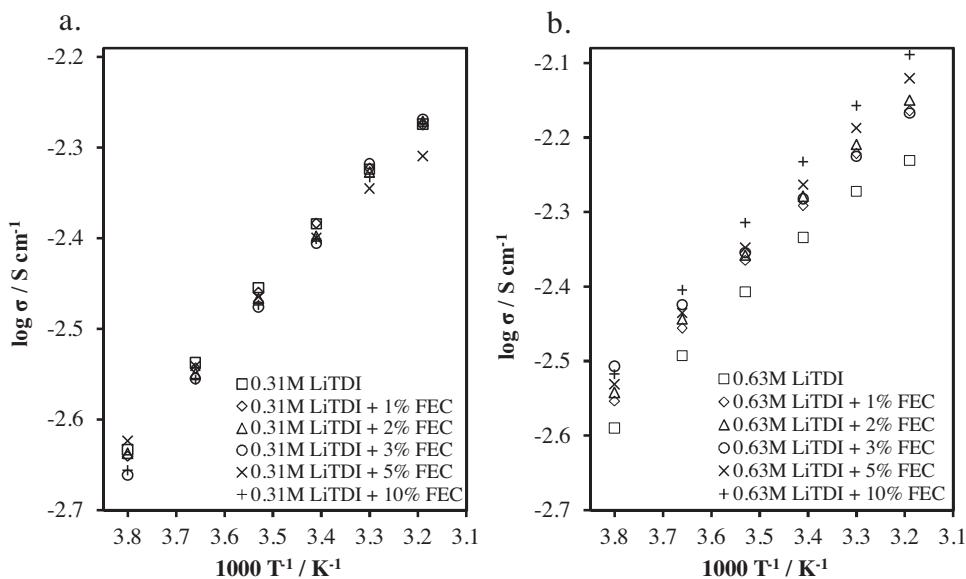
Fig. 1. Ionic conductivity dependence of fluoroethylene carbonate content in −10 to 40 °C temperature range in EC:DMC (1:2 weight ratio) solution of: a. 0.31 mol kg^{-1} LiTDI; b. 0.63 mol kg^{-1} LiTDI.

previously proven by our group [9]. In case of a deficiency of the most polar solvent, other solvents are used to fill in the solvation layer. Here, in a kilogram of EC:DMC (1:2 weight ratio) there are 3.78 mol of EC. The lithium coordination number is equal to 4 (or even 4.5 considering recent measurements [21]). As our previous measurements have established, about 50% of the EC content for a 0.3–0.8 mol kg^{-1} lithium salt concentration range is incorporated into the lithium cation solvation layer. Thus, the EC to Li ratio has to be at least 8:1, in order to fill whole lithium solvation layer with EC molecules. In the case of 0.31 mol kg^{-1} lithium salt content this ratio is above 12:1. In case of 0.63 mol kg^{-1} LiTDI concentration, it is only 6:1. In the latter case, there is space for other molecules in the solvation layer. FEC would be the second choice for filling this gap, as it has a slightly higher dielectric constant (relative permittivity) than EC (107 vs. 90 at 40 °C [22,23]), but a much smaller donor number (9.1 vs. 16.4 [22,24]). Thus, its smaller donor number

restricts FEC from frequent incorporation into the lithium cation solvation layer at low salt concentrations. In the case of EC deficiency, as in the higher salt concentration case, FEC substitutes for EC. As it has a higher polarity, its incorporation causes an increase in conductivity. However, in the case of low salt concentration, FEC addition, as a solvent component not taking part in solvation layer formation, contributes only towards solvent mixture viscosity. As FEC has a very high viscosity in comparison with EC or DMC (FEC: 4.1 mPa s @ 40 °C, EC: 1.93 mPa s @ 40 °C, DMC: 0.59 mPa s @ 20 °C [23,25]), it contributes to a higher overall solvent mixture viscosity, especially when it is present in high amounts (5 or 10%). However, its high polarity and statistically-possible trace interaction with the lithium cation solvation layer probably mitigates this effect to some extent. Thus, all these different effects might explain the slightly negative ionic conductivity effect of FEC addition at low LiTDI concentration.
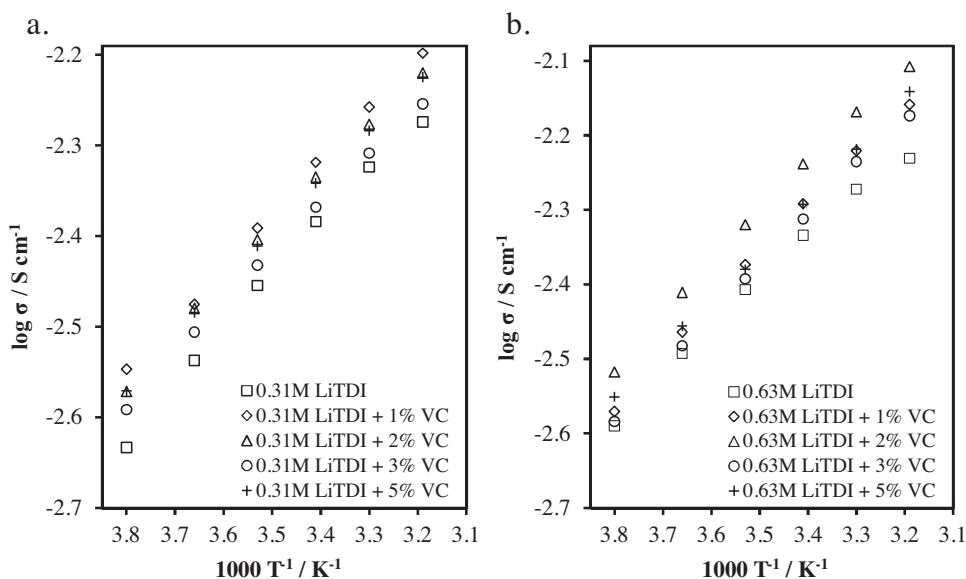

Fig. 2. Ionic conductivity dependence of vinylene carbonate content in −10 to 40 °C temperature range in EC:DMC (1:2 weight ratio) solution of: a. 0.31 mol kg^{-1} LiTDI; b. 0.63 mol kg^{-1} LiTDI.

Fig. 2 presents the ionic conductivity's dependence on temperature with 0.31 M LiTDI (Fig. 2a) and 0.63 M LiTDI (Fig. 2b) electrolytes, with varied additions of vinylene carbonate (VC). In both cases it was clear that there was an optimum concentration of VC in the electrolyte for the given lithium salt concentration, above and below which the properties of the electrolyte were worse. Generally, any addition of VC seemed to be advantageous (in the investigated range) in comparison with the plain electrolyte. However, VC contents of 1% in the case of 0.31 M LiTDI and 2% in the case of 0.63 M LiTDI were the most preferable. 5% VC content (the highest investigated) was more beneficial than 3% addition, although to a lesser extent than 1% in both electrolytes. The conductivity gain upon a 1% VC addition to 0.31 M LiTDI over pure electrolyte was 16% (at 20 °C), while a 2% VC content in 0.63 M LiTDI gained as much as 25% of the conductivity value. In case of a 1% VC addition into the higher lithium salt concentration (0.63 M) there was also gain (10% ionic conductivity gain), although less than half of that seen with the 2% VC addition. As the optimal VC content seemed to be relative to the lithium salt, it was decided to compare molar concentrations. It turned out that the VC content translated into molar concentration was 1%–0.11 mol kg^{-1} and 2%–0.22 mol kg^{-1} and so on. It meant that the optimal concentration of VC was a 1:3 ratio with the lithium salt. Also, a ratio above 1:1 (over 5% VC) seemed to also benefit conductivity to a lesser extent. VC has a dielectric constant much higher than EC or even FEC ($\varepsilon = 126$ [26]). On the other hand, it is less viscous than EC and FEC, but more so than DMC (VC viscosity: 1.63 mPa s @ 20 °C, 1.17 mPa s @ 40 °C). As a result, it would statistically have priority with regard to taking its place in the solvation layer around the lithium cation. As a more polar solvent, VC would give rise to greater ionic conductivity. However, the higher value of viscosity inputs negatively to overall conductivity. Thus, these two effects balance, depending on the fraction of the VC interacting with the lithium cation, causing nonlinear VC-conductivity dependence.

To look for the synergic effect of both additives, electrolyte compositions were made with combined FEC and VC addition. The measured ionic conductivities are shown in Fig. 3. In the case of 0.31 M LiTDI electrolyte, +2% VC +10% FEC addition did not change conductivity (or there were negligible differences). On the other hand, +1% VC +5% FEC improved ionic conductivity significantly, by approximately 30%. This result is counter-intuitive, as the 5% FEC addition was the least favorable (or even slightly negative) addition

with regard to 0.31 M LiTDI conductivity gain. A 10% FEC addition had a moderately positive effect towards conductivity in the context of other samples. As for the VC, the 1% addition was indeed the most advantageous VC content in the case of the 0.31 M LiTDI electrolyte, however the 2% addition was similarly effective. The explanation may be due to the low concentration of lithium salt, which in combination with a sufficient amount of EC (EC:Li ratio over 8:1) fills up the solvation layer solely with EC molecules. In such situations, FEC and VC contribute to the electrolyte parameters mostly with their viscosity, which is higher than that of EC (FEC, which is in higher concentration) or DMC (both FEC and VC). In the case of 0.63 M LiTDI, both combinations (+1% VC +5% FEC and +2% VC +10% FEC) exhibited very similar positive effects on conductivity, with negligible differences. However, the extent of the change depended on temperature, with a larger conductivity gain at higher temperatures (ca. 3% gain at −10 °C, ca. 30% at 40 °C).

The last combination's dependence on temperature demanded more insight into the conductivity activation energy. Activation energies were calculated using the Arrhenius fit, $\sigma = A \exp^{-Ea/(RT)}$). Results are shown in Table 1. It turned out that while most of the measured electrolytes both with and without additives had activation energies in the range of 10.5–12.5 kJ mol^{-1}, a few samples clearly stood out. These were 0.63 M LiTDI with +5% FEC and all the VC additions, which exhibited activation energies of ca. 13 kJ mol^{-1} ($\pm$0.1 kJ mol^{-1}). A few samples had even higher activation energy, namely (all based on 0.63 M LiTDI): +10% FEC, +2% VC + 10% FEC, and +1% VC +5% FEC. In comparison, both basic electrolytes (without additives) exhibited 11.4 kJ mol^{-1} conductivity activation energy. Generally speaking, additives in the case of 0.31 M LiTDI gave rise to negligible changes or a slight decrease of activation energy upon addition. In the case of 0.63 M LiTDI, the additives' presence generally noticeably increased the conductivity activation energy. This means that in the case of 0.31 M LiTDI there was a visibly smaller change to the conductivity mechanism in comparison to electrolytes based on 0.63 M LiTDI. That would support an earlier claim that there should be a greater change in the lithium coordination sphere in the case of higher lithium salt concentrations, due to insufficient EC content. In the case of 0.63 M LiTDI, the highest activation energies were found for the highest additive content, which is in line with earlier considerations.

For a few of the better conducting electrolytes, lithium cation transference numbers were measured. The results are shown in Table 2. The additives did not compromise the lithium cation
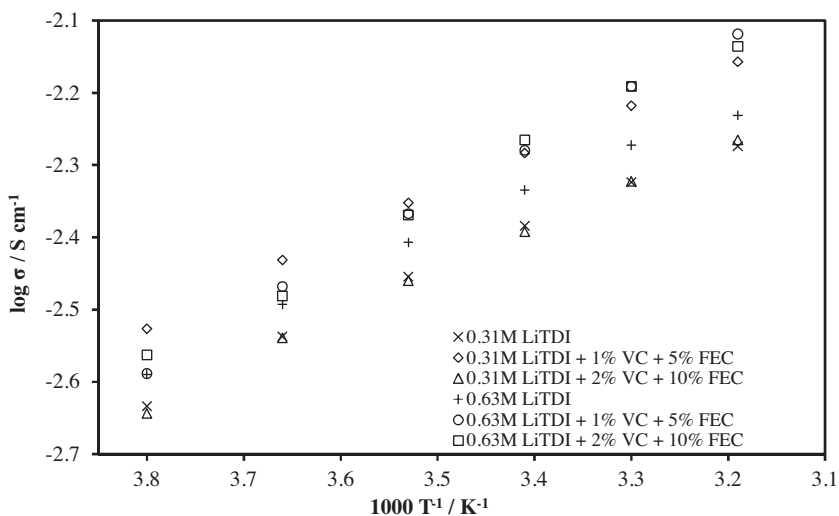

Fig. 3. Ionic conductivity dependence of vinylene carbonate and fluoroethylene carbonate content in −10 to 40 °C temperature range in EC:DMC (1:2 weight ratio) solution of various concentrations of LiTDI.

Table 1
Conductivity activation energies of LiTDI electrolytes with and without additives.

0.31 mol kg⁻¹ LiTDI in EC:DMC (1:2 weight ratio)		0.63 mol kg⁻¹ LiTDI in EC:DMC (1:2 weight ratio)	
additive	Ea/kJ mol⁻¹	additive	Ea/kJ mol⁻¹
w/o additives	11.4	w/o additives	11.5
+1% FEC	11.6	+1% FEC	12.3
+2% FEC	11.6	+2% FEC	12.4
+3% FEC	12.4	+3% FEC	10.7
+5% FEC	10.1	+5% FEC	13.0
+10% FEC	12.0	+10% FEC	13.4
+1% VC	11.1	+1% VC	13.0
+2% VC	11.0	+2% VC	12.9
+3% VC	10.6	+3% VC	13.0
+5% VC	10.9	+5% VC	12.8
+1% VC +5% FEC	11.6	+1% VC +5% FEC	14.8
+2% VC +10% FEC	11.8	+2% VC +10% FEC	14.0

Table 2
Lithium cation transference numbers measured and calculated for various LiTDI-based compositions and one LiPF₆-based composition for comparison.
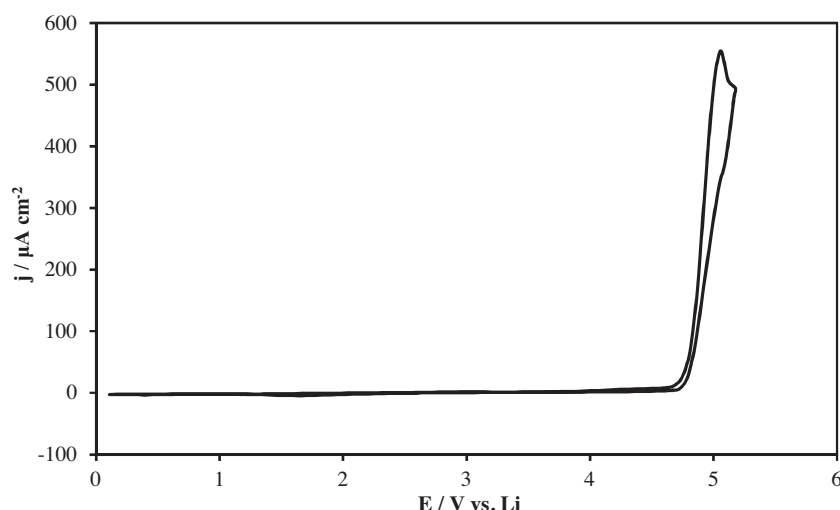
EC:DMC (1:2 weight ratio) compositions	$t_{Li+/-}$	
0.31 M LiTDI	0.62	±0.01
0.31 M LiTDI +1% VC +5% FEC	0.41	±0.04
0.63 M LiTDI	0.55	±0.05
0.63 M LiTDI +5% VC	0.55	±0.01
0.63 M LiTDI +1% VC +5% FEC	0.53	±0.04
0.63 M LiTDI +2% VC +10% FEC	0.51	±0.06
1 M LiPF₆	0.35	±0.05

transference number in the case of 0.63 M LiTDI (apart from negligible differences), but there was a visible decrease upon addition of both additives to 0.31 M LiTDI. It is worth mentioning, though, that all of the measured transference numbers were still higher than that of LiPF₆ in the same solvent mixture. Values for LiPF₆ are noted for comparison.

Finally, the electrolytes were tested in half-cells. Before that, to test the basic electrolyte's stability, cyclic voltammetry of the 0.31 M LiTDI electrolyte was performed in the Li | electrolyte | Pt system. It turns out that the electrolyte was stable in the range of 0.05–4.7 V vs the lithium metal anode. A cyclic voltammetry plot of the first cycle is shown in Fig. 4. With such a wide electrochemical stability window, most electrode materials used in the battery industry can now be used with this electrolyte.

Li | electrolyte | Si/C composite half-cells were assembled using the most promising electrolytes. Charge-discharge cycling with a 1C rate was performed for at least 100 cycles, and if there was no or very little capacity fade, cycling was continued. The results of the 0.31 M LiTDI and 0.31 M LiTDI with +1% VC +5% FEC additives cycling are shown in Fig. 5a. Although the anodic capacities were very high for both electrolyte compositions, a noticeable capacity fade took place. Even upon addition of VC and FEC, there was a capacity drop of almost 50%.

The case was different for 0.63 M LiTDI-based compositions (Fig. 5b). All electrolytes with the higher lithium salt concentration exhibited stable anodic capacity, even at the high cycling rate (1C). The anode capacity cycled with the electrolyte without additives stabilized at ca. 870 mAh g⁻¹, which was clearly higher than its initial value, 807 mAh g⁻¹. Application of the electrolyte with 5% VC addition stabilized cycling and exhibited 90% anodic capacity retention after 100 cycles (504–454 mAh g⁻¹ decrease). However, this composition showed much lower capacity than the electrolyte without additives. Addition of both additives at their lower concentration (1% VC and 5% FEC) resulted in a similar anodic capacity as in the case of 5% VC addition. In that case, however, the initial formation of SEI was observable, as after an initial capacity increase in the first 4 cycles, there was a decrease and capacity stabilization from the 6th cycle on. This electrolyte gave 82% anodic capacity retention, but if compared to the 6th cycle, after the irreversible capacity loss, it was higher than 95%. Finally, the

Fig. 4. Cyclic voltammetry at 1 mV s⁻¹ rate of 0.31 mol kg⁻¹ LiTDI-EC:DMC (1:2 weight ratio) electrolyte against lithium metal anode.
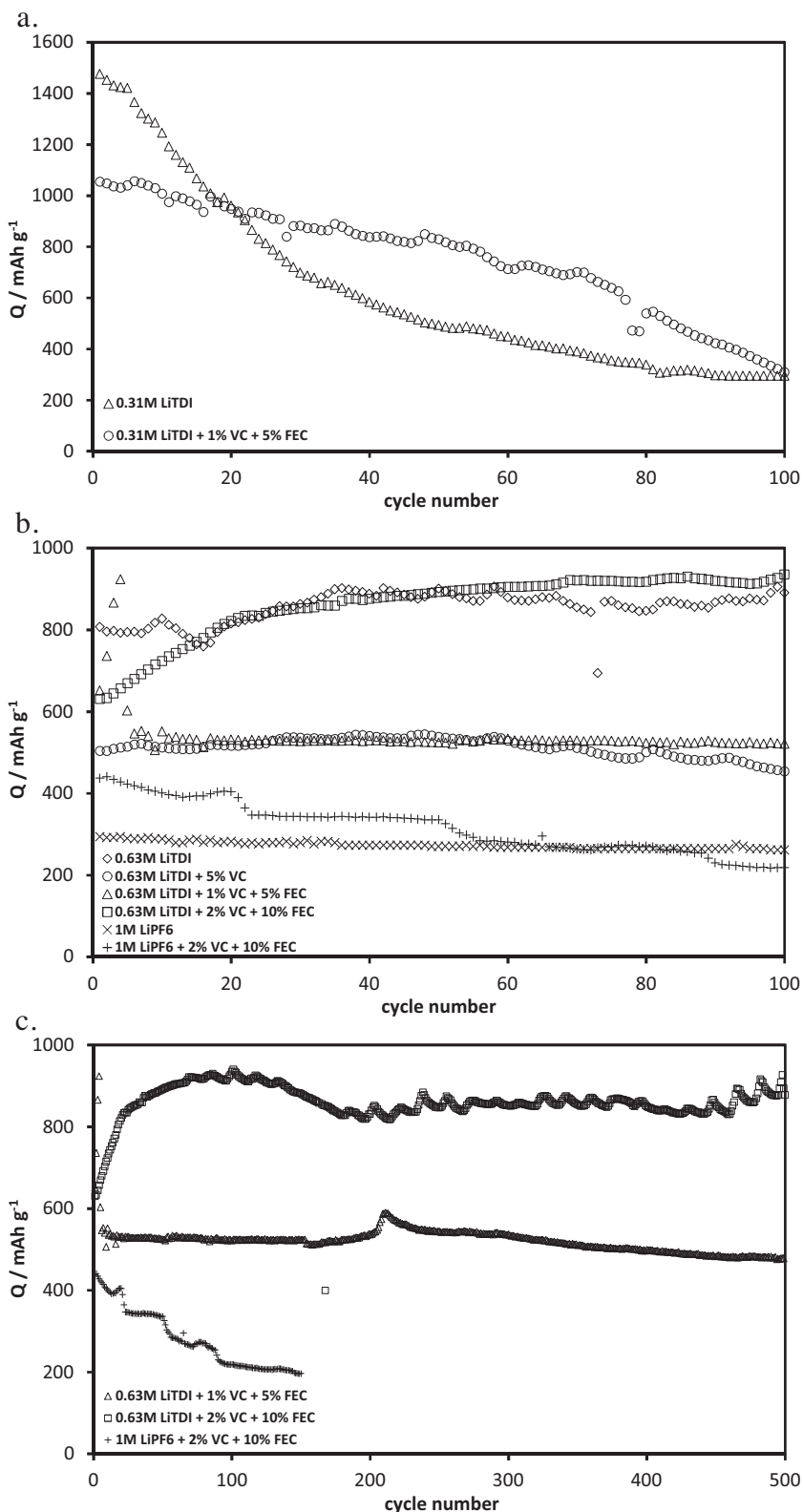
Fig. 5. Discharge capacity during cycling of (Si/C | LiTDI-solvent mixture | Li) half-cell for different electrolyte compositions in EC:DMC (1:2 weight ratio) solvent mixture: a. electrolyte compositions based on 0.31 mol kg^{-1} LiTDI concentration; b. electrolyte compositions based on 0.63 mol kg^{-1} LiTDI concentration and based on 1 mol kg^{-1} LiPF$_6$ concentration for comparison – 100 charge-discharge cycles; c. the best electrolyte compositions based on 0.63 mol kg^{-1} LiTDI concentration and 1 mol kg^{-1} LiPF$_6$ concentration for comparison cycled for 500 charge-discharge cycles (LiPF$_6$ for 150 cycles).

electrolyte composition with both additives at their higher concentration was tested in the half-cell, showing a fast initial anodic capacity increase for the first 20 cycles (from the 630 mAh g^{-1} in the first cycle) and then a steady increase up to ca. 940 mAh g^{-1}. Use of the commercially available salt resulted in only 89% capacity retention after 100 cycles in the case of LiPF$_6$

without additives, but the anodic capacity in the cell stabilized around 260 mAh g^{-1}. When LiPF$_6$ was tested with the same additives (in the same amounts) as LiTDI, the initial anodic capacity increased to 437 mAh g^{-1}, but it was still lower than any of the LiTDI-based compositions. Also, capacity retention was much lower.

An expanded view of the two most successful compositions' cycling is shown in Fig. 5c. Fluctuations resulted from the lack of air conditioning in the lab. Use of 0.63 M LiTDI electrolyte with +1% VC +5% FEC additives resulted in stable cycling for 500 cycles with an 87% capacity retention. It was clear that for 0.63 M LiTDI +2% VC +10% FEC the electrolyte capacity retention was over 100% compared to the first cycle, and did not change (apart from minor fluctuations) from the 50th (893 mAh g^{-1}) to the 500th cycle (894 mAh g^{-1}). It was a great success in terms of both capacity value and high retention in comparison with the commercially available salt-based electrolyte with additives, LiPF$_6$ in EC:DMC (1:2 weight ratio) +2% VC +10% FEC. Use of the commercially available salt resulted in only 45% capacity retention after 150 cycles. Anodic capacity in the cell with the LiPF$_6$-based electrolyte stabilized around 200 mAh g^{-1}, which was more than four times lower than in the case of LiTDI (both with and without additives). However, the LiPF$_6$-based electrolyte without any additives, even though it had a much lower initial anodic capacity (294 mAh g^{-1}), had a much better capacity retention − 89%. However, it was still worse than LiTDI-based electrolytes, and the LiPF$_6$-based electrolyte's anodic capacity was more than three times lower than that for LiTDI.

4. Conclusions

LiTDI salt was used to form electrolytes based on an ethylene carbonate and dimethyl carbonate solvent mixture (1:2 weight ratio). Popular, commercially available additives (namely vinylene carbonate and fluoroethylene carbonate) were used in various concentrations to obtain electrolytes of differing compositions. The aim was to make electrolytes more stable during cycling with silicon composite anodes, without compromising other electrochemical parameters. Optimal additive concentrations were found based on conductivity gain, lithium cation transference number, and cycling behavior. The highest conductivities were achieved for 2% VC in 0.63 M LiTDI-EC:2DMC electrolyte and 10% FEC in 0.63 M LiTDI-EC:2DMC. To find the most favorable composition with the synergistic effect of both additives, their optimal concentrations were mixed. +2% VC +10% FEC in 0.63 M LiTDI-EC:2DMC electrolyte exhibited a very high lithium cation transference number of 0.51 (compared to 0.35 for LiPF$_6$-based electrolytes) and a wide electrochemical stability range up to 4.7 V vs. Li. Finally, the optimal composition was tested in half-cells with silicon composite anodes, achieving a high capacity of ca. 890 mAh g^{-1}. Cells containing the LiTDI-based electrolyte showed 100% capacity retention (no capacity loss) after 500 cycles in comparison to the 50th cycle and a large capacity gain in comparison to the first cycle. The LiPF$_6$-based electrolyte in the same system and conditions exhibited a capacity of ca. 200 mAh g^{-1} and 45% capacity retention. Thus, it is possible to obtain an electrolyte based on LiTDI that is superior to the commercial electrolyte, exhibiting much better cyclic performance with state-of-the-art electrode materials. The LiTDI electrolyte does not sacrifice electrolyte parameters and still makes major materials' savings by using a 0.63 mol kg^{-1} LiTDI concentration, in comparison to the industrial standard of a 1 mol kg^{-1} concentration of lithium salt.

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