Short communication

New low temperature electrolytes with thermal runaway inhibition for lithium-ion rechargeable batteries

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Abstract

This paper describes a low temperature electrolyte system for lithium-ion rechargeable batteries. The electrolyte exhibits high ionic conductivity, good electrochemical stability and no exothermic reaction in the presence of lithium metal. The system features a low lattice energy lithium salt in a specific mixture of carbonate solvents and a novel thermal runaway inhibitor.
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1. Introduction

Electrolyte systems for lithium-ion batteries consist of two components. *Organic solvent*: ethylene carbonate (EC) is the key solvent because of its low cost, good electrochemical stability, and high dielectric constant, which permits better ionic dissociation of the salt and improved ionic conductivity. Dimethyl carbonate (DMC), commonly known as thinning solvent, is also used with EC (typically, 1:1 ratio) to reduce viscosity and increase wettability of the electrolytes with cell components, such as electrodes and separator. *Lithium-ion source*: $LiPF_6$ has been the preferred salt because it dissolves readily in carbonates and its cost is lower than lithium salts of strong organic acids, e.g., CF_3SO_3Li and lithium bis(trifluoromethylsulfonyl)imide [LiTFSI, $(CF_3SO_2)_2NLi$]. A liquid electrolyte composed of EC, DMC, and $LiPF_6$ exhibits conductivity greater than $10^{-3}\,S\,cm^{-1}$ at room temperature [1–3]. A shortcoming of this system is the sharp reduction in conductivity at temperatures below about $-10\,°C$, due to freezing. This situation can be obviated to some degree by adding a variety of thinning solvents, but conductivity is markedly reduced, due primarily to lowering of the dielectric constant of the electrolyte.

Military and space applications often require operations over a broad temperature range, including those conducted at very low temperatures. Recent studies [4,5] reported improved low temperature performance of electrolyte in lithium-ion batteries and encouraged us to explore solvent electrolyte systems for the temperature range of -40 to $+70\,°C$. Our chief goal was the identification and development of electrochemically stable solvent electrolyte systems for lithium-ion rechargeable batteries which exhibit ionic conductivities better than $10^{-3}\,S\,cm^{-1}$ over the aforementioned temperature range, with a wide operating voltage window (0–5 V versus Li). A secondary objective was to improve flame retardancy in the best electrolyte systems by using diethyl(2,6-di-*tert*-butyl-4-methylphenyl)phosphate, a thermal runaway inhibitor (TRI) [6,7].

To accomplish these objectives, we have conducted a detailed series of experiments, including: (a) selection and screening of readily available potential solvents (e.g., carbonates and carbonate-like) for formulation of electrolytes. (b) Testing and evaluation of the best performing electrolytes. (c) Improvement of thermal stability by incorporating a thermal runaway inhibitor to mitigate exothermic reactions due to abuse or overcharge of batteries below $200\,°C$. (d) Comprehensive testing and cycling of the new electrolytes in half-cells and full cells.

2. Materials and measurements

Salts, solvents, electrodes, and LiPF$_6$ were obtained from Aldrich Chemical and LiTFSI (lithium imide) from the 3 M company, and were used as received. Ethylene carbonate (EC), dimethyl carbonate (DMC), and propylene carbonate (PC) were obtained from Aldrich and ethyl methyl carbonate (EMC) from Ferro Chemicals. All solvents were vacuum-distilled over argon and stored in a dry glove box. Electrode and cell components were purchased from several sources and used as received: lithium and aluminum foil (Alfa Chemicals); LiNiCoO$_2$ (Ferro Chemicals); Carbon (SLC-15, Superior Graphite). The TRI was prepared as described in a recently issued patent [6]. Details of the experimental procedures employed in this study are described elsewhere [7].

3. Optimization of solvent system

Using liquid/solid phase diagrams, we screened the solubilities and freezing characteristics of ternary mixtures of the common carbonates (EC, DMC, PC, DEC and EMC). We also examined the behavior of ternary mixtures of the carbonates with 25 "carbonate-like" thinning co-solvents, including esters, such as ethyl butyrate, as well as butyronitrile, 2-nitropropane, ethers, furans, pyrans, oxazolines, and siloxanes. After many experiments and thorough study of previous work [8], we have concluded that an EC–DMC–EMC ternary solvent system is best suited for low temperature applications. The presence of ethylene carbonate (EC) in the solvent system is essential, because its high dielectric constant assures the dissolution and complete dissociation of the salt and for its ability to form the solid electrolyte interface (SEI) layer on the electrodes. A solvent with low viscosity and low melting point, such as DMC or EMC, is necessary for good ionic conductivity and the low liquidus temperature of the mixture required for low temperature operation. A liquidus temperature of $-7.6\,^{\circ}$C for the EC–DMC binary system is not useful for such applications. Phase separation occurs in the EC–EMC binary mixture even with low concentrations of EC [8]. The DMC–EMC system has a low liquidus temperature, but because of the low dielectric constants of the components, it is not suitable as a solvent for Li-ion batteries. Therefore, we introduced EC–DMC in proportions corresponding to the eutectic point (DMC/EC = 2.42 molar ratio) with EMC as the solvent thinner, as shown along the line in Fig. 1. An electrolyte composed of 1 M LiPF$_6$ in EC, DMC and EMC (15:37:48 by weight) had a freezing point of $-41\,^{\circ}$C.
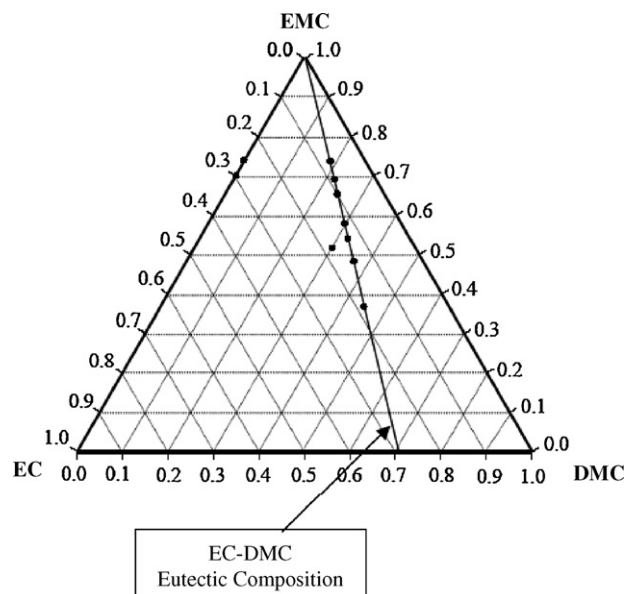

Fig. 1. EC–DMC–EMC ternary solvent system.

4. Formulation of electrolytes

Although LiPF$_6$ is the most commonly used lithium salt for rechargeable batteries, it possesses several drawbacks which are mitigated by use of a more stable lithium salt, such as LiTFSI. A comparison of certain characteristics of these salts is depicted in Table 1 and elaborated in the discussion that follows.

Our conductivity studies revealed a very large charge-transfer resistance for electrolytes with LiPF$_6$. Fig. 2 shows a Nyquist
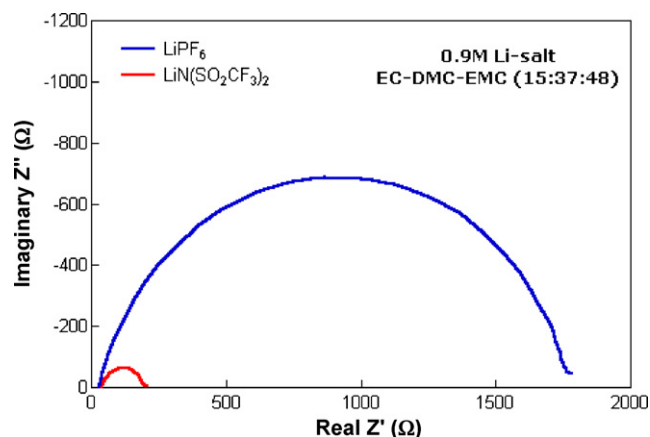

Fig. 2. Nyquist plot showing the lithium-electrolyte interfacial impedance for 0.9 M LiPF$_6$ and LiN(SO$_2$CF$_3$)$_2$ in EC, DMC and EMC (15:37:48) mixture.

Table 1
Comparison of LiPF$_6$ and LiTFSI

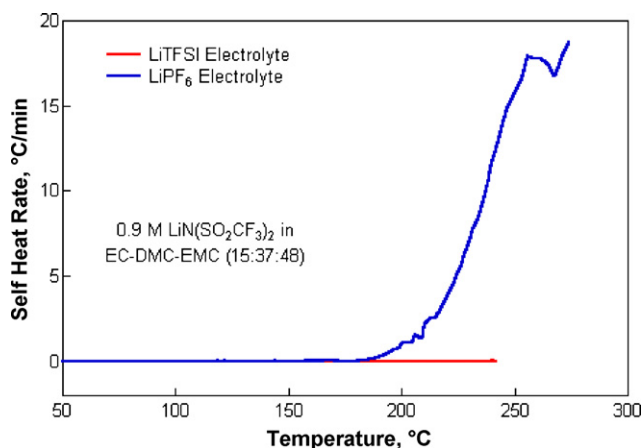| LiPF$_6$	LiTFSI
Slowly deteriorates on storage and begins to decompose above 100 $^{\circ}$C	Thermally stable on storage up to 375 $^{\circ}$C
Exothermic runaway of the electrolyte near 175 $^{\circ}$C (ARC)	Stable up to 250 $^{\circ}$C
Large lithium-electrolyte interfacial impedance	Much lower lithium-electrolyte interfacial impedance
Dissolution of Mn occurs when spinel-based cathode material LiMn$_2$O$_4$ is used in LiPF$_6$-based electrolytes	Stable under these conditions

Fig. 3. ARC studies showing the self-heating rate for 0.9 M LiPF$_6$ and 0.9 M LiTFSI in EC, DMC and EMC (15:37:48) mixture.

plot for 0.9 M LiPF$_6$ and 0.9 M LiTFSI in the EC, DMC and EMC (15:37:48) mixture, respectively. Conductivity measurements were performed with liquid samples between two lithium disks. Although the bulk resistance is similar in both electrolyte formulations at 30 °C, the charge-transfer resistance with the LiPF$_6$-based formulation is almost an order of magnitude higher than that with LiTFSI.

LiTFSI has been shown to be thermally stable up to 375 °C, while LiPF$_6$ decomposes at temperatures slightly above 100 °C. Results of accelerated rate calorimetry (ARC) experiments performed on LiPF$_6$ and LiTFSI electrolytes are presented in Fig. 3. There is a large exothermic runaway reaction for the LiPF$_6$ electrolyte around 200 °C. The LiTFSI electrolyte is stable up to 250 °C, without any exothermic reaction. This observation demonstrates that the electrolyte formulation (0.9 M LiTFSI in EC, DMC and EMC::15:37:48 by weight) is safer and more stable than the LiPF$_6$-based electrolyte.

LiTFSI is being used increasingly in Li-ion batteries because of its stability, high conductivity in any medium, its safety and lack of toxicity. Therefore, we have chosen LiTFSI as the preferred salt in our electrolyte formulations for low temperature application. The change in conductivity with LiTFSI content at various temperatures is presented in Fig. 4. The electrolyte with 0.9 M LiTFSI had the highest conductivity, 2 mS cm^{-1} at
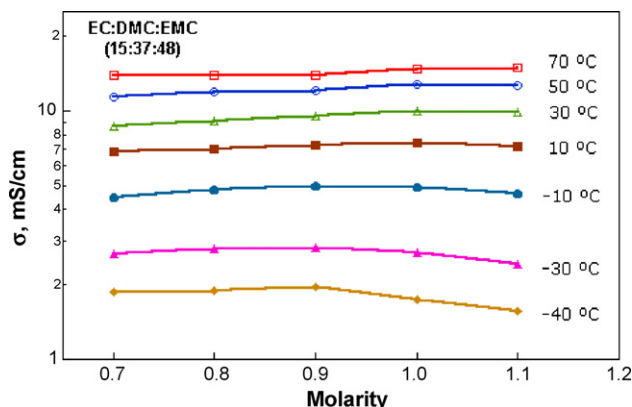

Fig. 4. Change of conductivity with LiTFSI content at different temperatures.

−40 °C, as well as at −30 °C. The optimized electrolyte formulation is 0.9 M LiTFSI in EC, DMC and EMC (15:37:48 by weight).

5. Characterization of electrolytes

5.1. Cyclic voltammetry

The electrochemical stability window for the LiTFSI optimized electrolyte with added 2 wt.% TRI was obtained by cyclic voltammetry. The experiment was carried out in an O-ring sealed glass cell, with a 0.07 cm^2 glassy carbon working electrode against lithium as reference electrode and platinum wire as counter electrode. To ensure reproducible conditions of the glassy carbon electrode, it was polished with 0.5 μm alumina powder and washed with deionized water and acetone before each experiment. The cell was cycled between 1.0 and 5.0 V (with reference to Li/Li$^+$) at a scan rate of 10.0 mV s^{-1} to establish the oxidation potentials of the electrolyte formulations. The experiment showed that the electrolyte formulation is stable up to 4.5 V versus Li/Li$^+$ potential. The conductivity of the electrolyte was not affected by the addition of 2 wt.% TRI.

5.2. Conductivity

The lithium ion conductivity of the electrolyte formulation [0.9 M LiTFSI in EC, DMC and EMC (15:37:48)] at different temperatures was determined by two different cell configurations. The specific conductivities of the electrolytes were measured by the AC impedance technique with a Solartron impedance/grain-phase analyzer (SI 1260) coupled with a Solartron electrochemical interface (SI 1287). A sealed two-electrode cell (HS test cell, Hohsen Corp.) with a pair of lithium foil electrodes was assembled inside a helium-filled glove box. An environmental chamber was used to maintain the desired temperature within ±1 °C for the cells.

In another set up, a dip-type conductivity cell, made of a Pyrex glass body and a pair of platinum electrodes, with a cell constant of about 0.18 cm^{-1}, calibrated with a standard KCl solution, was used. A glass tube with a ground-glass opening was connected on the cell body by which the electrolyte could be put into the cell and then sealed with a ground-glass stopper. Each measurement for a particular temperature was carried out after the cell had been kept at that temperature for 1 h to achieve thermal equilibrium. The impedance of the sample was scanned from 1 MHz to 0.1 Hz, from which a Nyquist plot was plotted. The conductivity was calculated from the bulk resistance of the electrolyte, i.e. high frequency intercept on the real axis. The temperature dependency of conductivity is shown in Fig. 5. No significant differences in the conductivity data at low temperatures was observed, although slight improvement in conductivity was observed at higher temperatures using a platinum cell.

5.3. Accelerated rate calorimetry (ARC)

The effect of addition of TRI on the thermal stability of Li-ion battery electrolytes with and without the presence of lithium
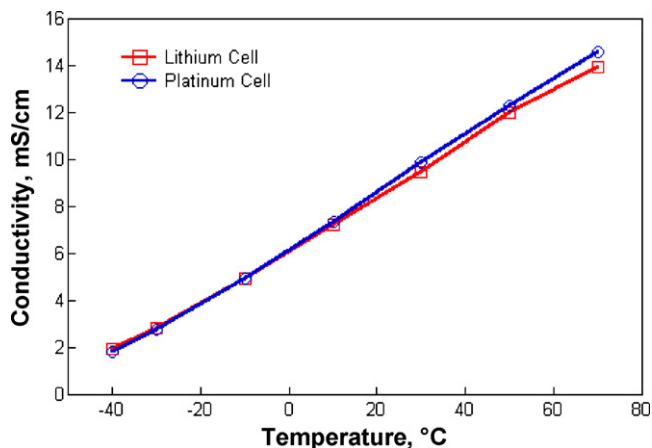
Fig. 5. The conductivities of TRI modified electrolyte with lithium and platinum conductivity cells.
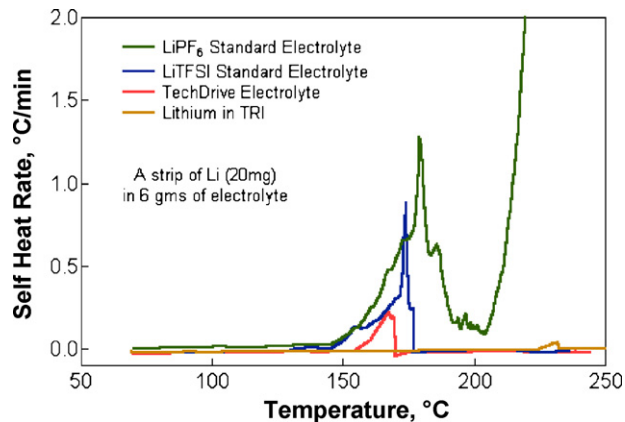

Fig. 6. The self-heating rate of the exothermic reaction of a strip of Li with electrolyte in the absence and presence of TRI. TechDrive electrolyte: 0.9 M LiTFSI in EC–DMC–EMC: 15:37:48.

metal was measured. The thermal stability was determined using an accelerating rate calorimeter over the temperature range of 70–275 °C. The ARC measures the self-generated heating rate of the sample material under adiabatic conditions while monitoring the pressure of the generated gases. The sample solutions were prepared in a 1-in. diameter titanium reaction vessel, which allows good thermal contact with the sample thermocouple while maintaining pressure integrity up to several 100 psi. The calorimeter measures the heating rate during a heat/wait/search mode of operation. The sample was heated in 5 °C increments. After a wait period of 20 min, the temperature of the sample bomb was monitored for another 20 min to determine the average heating rate. If the heating rate was below the threshold limit of 0.02 °C min^{-1}, the temperature was increased by another 5 °C and the process repeated. Once the heating rate exceeded the threshold limit, the ARC switched to an exotherm mode of operation where it closely matched the temperature of the sample bomb during its self-generated heating period, thus maintaining adiabatic conditions. The heating rate was then determined by the heat generation rate of the sample and the heat capacity of the sample and holder assembly.

Solutions were prepared in a He filled glove box by adding 2 wt.% TRI to each of the 0.9 M LiPF$_6$ and the new 0.9 M LiTFSI electrolyte. The sample bombs were filled with 6.0 g of solution and a Li-metal strip weighing 20 mg. The bomb was loaded into the ARC head and measured with Ar as cover gas. Another experiment was performed with the new electrolyte formulation and a Li-strip, but without TRI. The self-heating rates of these exothermic reactions are presented in Fig. 6. The onset of the exothermic reaction between lithium metal and the LiPF$_6$ and LiTFSI electrolytes without TRI additive occurred at 150 °C. The decomposition of LiPF$_6$ electrolyte was observed at about 200 °C. The LiTFSI electrolyte showed a lower self-heating rate than the LiPF$_6$ electrolyte, and no decomposition of electrolyte at 200 °C. With 2% TRI in LiTFSI electrolyte, the onset of the exothermic reaction was delayed to 160 °C. The maximum self-heating rate for electrolyte was substantially reduced by addition of TRI. Thus, with 2% TRI, the onset of exothermic reaction was delayed, and the reaction drastically suppressed. The ARC

experiment performed with lithium and TRI suggest that there was no exothermic reaction up to 230 °C. A small rise in self-heating rate was observed at 240 °C.

5.4. Differential scanning calorimetry

Differential scanning calorimetry studies were conducted to investigate the thermal stability of the fully charged LiNi$_{0.8}$Co$_{0.2}$O$_2$ cathode using a DSC 7, Perkin-Elmer instrument. The fully charged state was chosen since this state poses greater thermal hazards than any other state of charge. The cathode materials from the charged cells were recovered by opening in a dry glove box under an argon atmosphere. The recovered electrodes, including electrolyte, were sealed in a standard aluminum DSC pan. DSC scans were carried out at a heating rate of 5 °C min^{-1}, from 30 to 350 °C under nitrogen purging.

Fig. 7 shows the DSC behavior of fully charged cathodes from the cells containing TRI, compared with DSC behavior of a cell containing no additive. The maximum heat flow for the major exotherms is lowered with addition of TRI. The onset temperature for the exothermic reactions is shifted higher, indicating
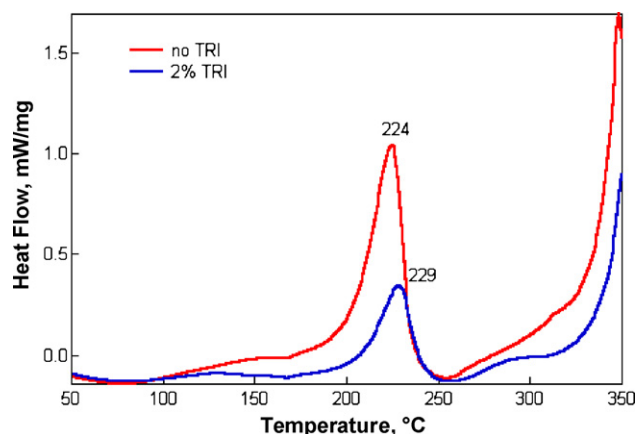

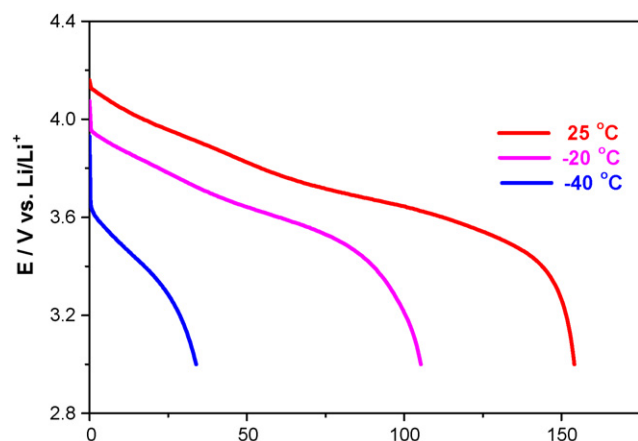Fig. 7. DSC curves for charged LiNi$_{0.8}$Co$_{0.2}$O$_2$ cathodes cycled with and without TRI.

Fig. 8. Typical discharge curves for Li/electrolyte/LiNiCoO$_2$ half-cell at a constant current of 1 mA at various temperatures. Electrolyte is 0.9 M LiTFSI in 15:37:48 EC–DMC–EMC.

improved thermal properties in the presence of the additive. The exothermic reaction at 224 °C is delayed by 5 °C.

5.5. Temperature dependence of half-cells at constant current

Measurements show that the new electrolyte has a relatively high ionic conductivity at very low temperature (~2 mS cm^{-1} at −40 °C). The performance of this new electrolyte in cells at different temperatures was evaluated in a Li/electrolyte/LiNi$_{0.8}$Co$_{0.2}$O$_2$ cell. The cells were initially subjected to three charge/discharge conditioning cycles at room temperature between 4.2 and 3.0 V at a constant current of 1 mA before temperature dependencies were studied. The cells were then discharged down to 3.0 V at constant current of 1 mA at a different temperature. Fig. 8 shows the discharged curves obtained at 25, −20, and −40 °C. It was observed that, at −40 °C, the lithium cell could deliver almost 20% of the capacity obtained at 25 °C, indicating that the cell with the new electrolyte could operate down to −40 °C.

5.6. Full cell studies

Li-ion cells were assembled as follows: graphite (SLC-15)/electrolyte/LiNi$_{0.8}$Co$_{0.2}$O$_2$. Starting with discharged state cells, the Li-ion cells were charged at constant current (i = 1 mA) to 4.2 V, then continued charging at constant potential (E = 4.2 V) to a current cutoff at 0.1 mA). The cells were then discharged at constant current of 1 mA to a cutoff voltage of 2.9 V. All tests were carried out at 25 °C in a Tenny environment chamber. The charge/discharge curves for the first 10 cycles are shown in Fig. 9. When the new LiTFSI electrolyte was used in the lithium-ion cell, the reversible capacity decreased from 2.76 mAh at the first cycle to 2.51 mAh at the eighth cycle. By contrast, the lithium-ion cell with commercial EM Industrial electrolyte exhibits very good capacity retention. This observation may be attributed to the poor cycling performance of LiNi$_{0.8}$Co$_{0.2}$O$_2$ in the new electrolyte system (see the cycling results of Li/LiNi$_{0.8}$Co$_{0.2}$O$_2$ half-cell).
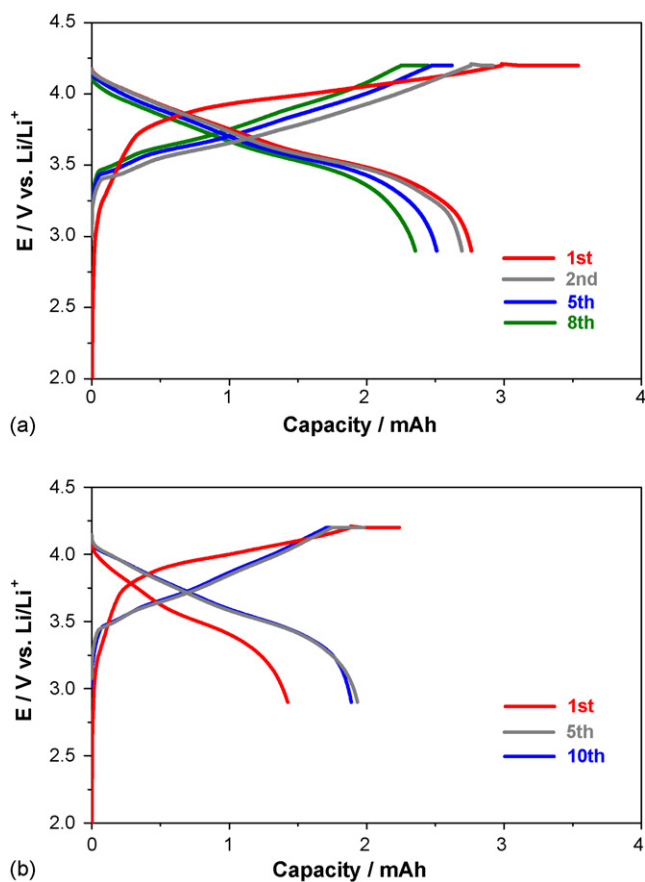

Fig. 9. Charge–discharge curves of the Li-ion cells cycled between 4.2 and 2.9 V. (a) 0.9 M LiTFSI–EC/DMC/EMC (15:37:48) electrolyte; (b) standard electrolyte (1:1 EC:DMC, 1 M LiPF$_6$).

6. Promising quaternary carbonate electrolyte system

While the new ternary solvent system is very effective at low temperatures, it is not as efficient as desired at ambient temperature. Therefore, we have developed a new quaternary solvent system including 10 wt.% propylene carbonate (PC), which performs quite well at low temperature and is clearly superior to the ternary system from 30 to 70 °C. The quaternary solvent electrolyte formulation of 0.9 M LiTFSI in EC–DMC–EMC–PC (15:37:38:10) was prepared. The conductivity data were compared with our best ternary formulation of 0.9 M LiTFSI in EC–DMC–EMC (15:37:48). The dependence of ionic conductivity of the electrolytes was assessed in the temperature range of −40 to 70 °C. The specific conductivities of the electrolytes were measured by the AC impedance technique with a Solartron impedance/grain-phase analyzer (SI 1260) coupled with a Solartron electrochemical interface (SI 1287), as described earlier.

The conductivity versus temperature plots are presented in Fig. 10. Although the addition of PC enhances conductivity at higher temperatures by virtue of its higher dielectric constant, at low temperatures the conductivity is lower (0.85 mS cm^{-1} at −40 °C and 2.12 mS cm^{-1} at −30 °C), perhaps because of phase separation of EC. These promising results suggest that additional studies may be fruitful.
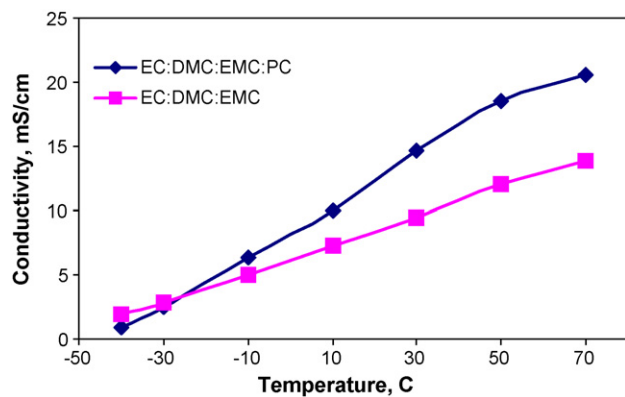
Fig. 10. The conductivity vs. temperature profile of electrolyte solutions 0.9 M LiTFSI in EC–DMC–EMC and EC–DMC–EMC–PC mixtures.

7. Conclusions

The electrolyte formulation, 0.9 M LiTFSI in EC, DMC and EMC (15:37:48), has provided the best conductivities with lithium and platinum conductivity cells over the temperature range −40 and +70 °C. At −40 °C, the conductivity is close to 2.0 mS cm^{-1}. The formulation of 0.9 M LiPF$_6$ in the same solvent mixture gave similar results. However, LiPF$_6$ possesses several drawbacks, as noted earlier, which are mitigated by use of the more stable LiTFSI. ARC studies confirmed that addition of 2 wt.% TRI prevents self-heating of lithium metal up to 230 °C. The thermal stability of a fully charged LiNi$_{0.8}$CO$_{0.2}$O$_2$ cathode is measurably enhanced by addition of 2 wt.% of TRI, as demonstrated by differential scanning calorimetry. A mixture of EC–DMC–EMC–PC (15:37:38:10) with 0.9 M LiTFSI shows considerable promise as an effective electrolyte over the temperature range −30 to +70 °C and merits further investigation.

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