

Nonaqueous electrolytes for wide-temperature-range operation of Li-ion cells

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Abstract

Nonaqueous electrolytes play a key role in extending the operating temperature range of Li-ion batteries. In developing electrolytes for wide temperature operations, we adopted an approach of starting with thermally stable lithium tetrafluoroborate (LiBF₄) and lithium bis(oxalato)borate (LiB(C₂O₄)₂, or LiBOB) salts. We have demonstrated that the capacity of Li-ion cells fades much slower in electrolytes using LiBF₄ or LiBOB than in electrolytes using LiPF₆. For low temperatures applications, suitable solvent systems for LiBF₄ and LiBOB were explored. We found that the charge transfer resistance (R_{ct}) is smaller in Li-ion cells in electrolytes based on LiBF₄ in selected solvent systems than that based on LiPF₆ and results in better capacity utilization at low temperatures. We also found that the electrolytes based on LiBOB in PC-based solvent system would allow Li-ion cells with graphite anode to be cycled. By comparing the properties of LiBF₄ and LiPF₆ in the propylene carbonate and diethyl carbonate (PC–DEC) solvent system, we found that it is possible to formulate proper solvent mixtures for enhanced conductivity for LiBF₄ and LiBOB salts at low temperatures. It is concluded that nonaqueous electrolytes for wide-temperature-range operations of Li-ion cells are achievable.

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Keywords: Nonaqueous electrolytes; Lithium salts; Li-ion batteries; High temperature; Low temperature; Solid electrolyte interface (SEI); Conductivity; Glass transition temperature

1. Introduction

Advancements in electrolyte are needed to extend the use of the present commercially available Li-ion cells to applications that demand high power and long cycle life and long calendar life in a wide-temperature-range (e.g. from –40 to 70 °C). Current Li-ion cells, employing electrolytes such as LiPF₆ salt dissolved in mixtures of cyclic and linear esters, have limited success in meeting the above demand. The cyclic esters include, for example, ethylene carbonate (EC, $T_m = 36.4$ °C), propylene carbonate (PC, $T_m = -54.8$ °C), and γ -butyrolactone (γ BL, $T_m = -43.5$ °C). The linear esters usually with low viscosity and low melting point include dimethyl carbonate (DMC, $T_m = -4.6$ °C), diethyl carbonate (DEC, $T_m = -74.3$ °C) [1], ethylmethyl carbonate (EMC, $T_m = -53$ °C), ethyl acetate (EA, $T_m = -83$ °C), methyl butyrate (MB, $T_m = -84$ °C), and ethyl butyrate (EB, $T_m = -93$ °C).

For low temperature applications, the approach of employing linear esters as the major solvent components in electrolytes, for the purpose of lowering the liquid freezing temperature and the viscosity of the electrolyte, was commonly taken. As reported recently, nonaqueous electrolytes of LiPF₆ in solvent systems formulated in such ways such as EC–DMC–EMC (1:1:1, volume ratio) [2], EC–DEC–DMC (1:1:1, volume ratio) [3], EC–DMC–MB [4], EC–DMC–EA [4], EC–DEC–DMC–EB (1:1:1:1, volume ratio) [5] were developed. Li-ion cells using these electrolytes have achieved significant improvements in discharge capacity at temperatures below –20 °C [2–6].

While the performance of Li-ion cells using these volatile electrolytes at temperatures above 55 °C is not available in literature, it is generally recognized that, at elevated temperatures, the Li-ion cell capacity fades gradually with cycling and decreases with storage time. The fading rate increases with increasing temperature due to the reactions between electrolyte solvents and electrodes in their highly charged-state [7]. To enhance Li-ion battery stability at high temperatures, without affecting performance at low temperatures, the most effective approaches reported

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include the use of additives or functional electrolytes to improve the properties of solid electrolyte interface and to stabilize the electrolytes [4,8,9].

We believe that, among many factors, the low thermal stability [10] and susceptibility to hydrolysis of the LiPF_6 salt are key factors affecting the high temperature performance and life of Li-ion batteries. To develop Li-ion batteries for both high temperature and low temperature applications, our approach was to start with thermally stable salts. In this work, we focus our attention to LiBF_4 and $\text{LiB}(\text{C}_2\text{O}_4)_2$ (or LiBOB) [11–13]. Other thermally stable salts were not considered because of their inability to passivate aluminum, for example $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (lithium imide) [12] and $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ (lithium methide) [2], or because of their high molecular weight or large anion size, for example $\text{LiPF}_3(\text{C}_2\text{F}_5)_3$ (lithium fluoroalkylphosphate) [14]. We believed this strategy would at least minimize the problems of Li-ion batteries at the high temperatures. The low temperature performance could then be improved through the identification of suitable solvent system for these salts.

We have already demonstrated in our recent publications [12,15] that Li-ion cells achieved better high temperature performance with electrolytes using either LiBF_4 or LiBOB salt in EC–EMC solvent system than those with LiPF_6 counterparts. The salt effects are shown not only in the conductivity of electrolyte, but also in the nature of SEI layer on the surface of both graphite anode and cathode. We also found that the solvent systems that work for LiPF_6 might not be optimal for LiBF_4 or LiBOB , owing to issues such as the nature of the SEI layer and salt solubility.

In this paper, our recent results on the use of LiBF_4 and LiBOB in some selected solvent systems, at both low and high temperatures, will be reviewed and discussed. The impact of salt on conductivity will also be discussed by comparing electrolytes of LiBF_4 in PC–DEC and PC–EC solvent systems with that of LiPF_6 in the same solvent systems, as an example.

2. Experimental

LiBF_4 and LiPF_6 from Stella Chemifa Co. were used as received. $\text{LiB}(\text{C}_2\text{O}_4)_2$ was made in our laboratory through an aqueous approach as described by Lischka et al. [13]. All solvents were from EM Sciences and dried over neutral alumina until the moisture level was below 10 ppm. All electrolyte solutions were prepared in argon atmosphere glove box. All solvent ratios indicated in this paper are in weight ratios. Solvent ratios indicated in volume percent will be specified. Salt concentration is expressed in molality (mole of salt in kg of solvents).

Measurements of dielectric constants, glass transition temperatures, and conductivities of either solvent mixtures or electrolytes were reported previously [16,17].

The 2335 button cells with double crimp seals were used as test vehicles for all electrolytes. Graphite based anode

(designated as Gr.) and lithium nickel based mixed oxide cathode films, provided by SAFT America Inc., were used for constructing half-cells with Li anode or Li-ion full cells. The anode and cathode were cut into disks of 1.27 and 0.97 cm^2 , respectively. The capacity of cells was measured between 2.5 and 4.1 V. Charging voltages will be specified when it is different from 4.1 V. Cycling tests on cells were conducted using a Maccor Battery Tester Series 4000. A Tenney Engineering Environmental Chamber, was used to control the temperature of cells during testing.

3. Results and discussion

3.1. Nonaqueous electrolytes with LiBF_4 as an electrolyte salt

The electrolyte of 1 m LiBF_4 in EC–DMC–DEC (1:1:1) behaves differently from that of LiPF_6 in the same solvent system [18]. In addition to lower conductivity, precipitation of LiBF_4 or EC was observed at temperatures below -20°C from the electrolyte while this is not observed in LiPF_6 electrolyte. However, what is notable is that a 15% more discharge capacity is achieved for Li-ion cells using LiBF_4 compared with LiPF_6 in the same solvents at -20°C [18]. We attributed this to a lower charge transfer resistance (R_{ct}) for the electrolyte using LiBF_4 salt [18] despite its lower conductivity.

In our recent studies [19], we found that the addition of PC to LiPF_6 in EC–EMC electrolyte slows down the increase of resistance of solid-state electrolyte interface (SEI) layer observed when the cells are cooled below -20°C . For example, we found that the SEI resistance (R_{SEI}) increases more slowly as the temperature is dropped below -20°C in LiPF_6 in PC–EC–EMC (2:2:6) than in the EC–EMC (3:7) electrolyte. With a slightly lower conductivity of 1 m LiPF_6 in PC–EC–EMC (2:2:6) than that of 1 m LiPF_6 in EC–EMC (3:7), we believe that the lower R_{SEI} in PC containing solvent system is due to the chemical nature of the SEI formed in the presence of PC.

We further examined the impact of LiBF_4 , in the PC containing electrolytes, on the performance of Li-ion cells by comparing the cell performances in 1 m LiBF_4 in PC–EC–EMC (1:1:3) and in 1 m LiPF_6 in PC–EC–EMC (1:1:3) [20]. To reduce the irreversibility of the first cycle, 1 wt.% of vinylene carbonate (VC) [4] was added to the respective electrolytes. We found that the capacity of the cell with LiBF_4 salt achieved 86% of the room temperature capacity even at -30°C , while the cell with LiPF_6 salt achieved only 72% of its room temperature capacity.

Judging from the fact that the conductivity of 1 m LiBF_4 in PC–EC–EMC (1:1:3) is about half of that of 1 m LiPF_6 in PC–EC–EMC (1:1:3), the lower R_{ct} in electrolyte with LiBF_4 salt is indeed associated with the LiBF_4 salt and/or the LiBF_4 salt and solvent combination. This result leads us to believe it is the R_{ct} , rather than the electrolyte conductivity,

Table 1
Capacity retention of Li-ion cells in 1 m LiBF₄ and 1 m LiPF₆ in EC–EMC– γ BL (1:1:1 weight ratio), respectively, at lower temperatures

	20 °C	–20 °C	–30 °C
Percent of capacity at 20 °C for electrolyte with LiBF ₄	100	89	74
Percent of capacity at 20 °C for electrolyte with LiPF ₆	100	76	62

that controls the low temperature performance of Li-ion cells.

The better performance of Li-ion cells resulting from the use of LiBF₄ instead of LiPF₆ at low temperatures is further demonstrated in the EC–EMC– γ BL (1:1:1) solvent system. As shown in Table 1, the Li-ion cells achieved higher capacity in 1 m LiBF₄ in EC–EMC– γ BL (1:1:1) than that in LiPF₆ in EC–EMC– γ BL (1:1:1) at –20 and –30 °C. Our results are also consistent with a recent report [21] on the superior performance of Li-ion cells using LiBF₄ based electrolytes.

The cell performance, as shown in solvent systems EC–DMC–DEC (1:1:1), PC–EC–EMC (1:1:3), and EC–EMC– γ BL (1:1:1) using LiBF₄ salt, demonstrates that the salt plays a key role in controlling the electrochemical reactivity between the graphite anode and the electrolyte notably at low temperatures. The results also suggest it is promising to formulate better low temperature electrolytes through the use of LiBF₄ salt in place of LiPF₆.

3.2. Nonaqueous electrolytes with LiBOB as an electrolyte salt

LiBOB was recently discovered independently by Lischka et al. [13] and Xu et al. [11]. Differing from LiBF₄ salt, LiBOB is halogen-free. Nonetheless, the electrolyte made of this salt in EC–EMC can be more effective than that made of LiPF₆ in EC–EMC to passivate Al [12].

We recently demonstrated that the capacity of Li-ion cells fades much more slowly in electrolyte using LiBOB salt than that using LiPF₆ salt [9] at elevated temperatures. The capacity of the Li-ion cells cycled between 2.5 and 3.9 V using 1 m of LiBOB in EC–EMC (1:1) electrolyte retains 97% of the capacity after 77 cycles at 60 °C, as versus the 56% capacity retention after 77 cycles at 50 °C for the Li-ion cells using 1 m of LiPF₆ in the same solvent mixture. We also noted that the irreversible capacity is lower in LiBOB in EC–EMC electrolyte than in LiPF₆ in EC–EMC electrolyte.

However, at low temperatures, cell performance with LiBOB in EC–EMC (1:1) electrolyte is not as good as when LiPF₆ is used in the same solvent system. As shown in Fig. 1, the cell only retains 19% of the room temperature capacity in LiBOB in EC–EMC at –20 °C versus 74% of the room temperature capacity in LiPF₆ in EC–EMC at the same temperature.

By changing the solvent system to PC–EC–EMC (1:1:3), the capacities of the cell with the LiBOB electrolyte increase

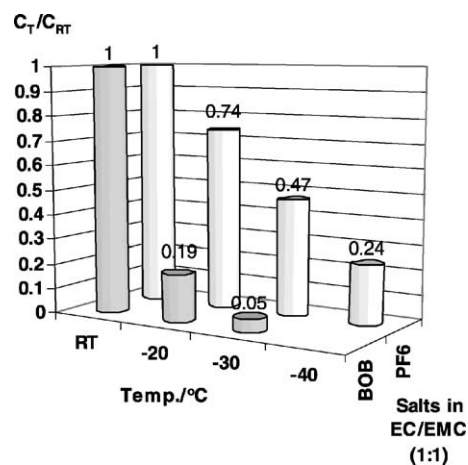


Fig. 1. Capacities of Li-ion cells in electrolytes of 1 m LiPF₆ in EC–EMC (1:1) and 1 m LiBOB in EC–EMC (1:1), respectively, at 20, 0, –20, –30, and –40 °C.

to 75 and 64% of the room temperature capacity at –20 and –30 °C, respectively (see Fig. 2). These capacities were still lower than those for the cells in LiPF₆ electrolyte at the same low temperatures, although improved much over the EC-rich solvent system. More notably, the cells could cycle in PC-rich electrolyte of a composition of PC–EC–EMC (3:3:4) with LiBOB salt, with an observed 18% of irreversible capacity during the first cycle and nearly 100% C efficiency in the subsequent cycles. Conversely, the cell could not even cycle in LiPF₆ in PC–EC–EMC (3:3:4) electrolyte. At 70 °C, as we reported recently, the cells using LiBOB in PC–EC–EMC (1:1:3) or in PC–EC–EMC (3:3:4) cycled for over 100 times with little capacity fade [22].

With LiBOB as a salt in electrolyte, the capacity utilization is quite different from cells using electrolyte containing LiPF₆ salt. The fact that the graphite anode can cycle in PC-rich electrolyte containing LiBOB also adds flexibility

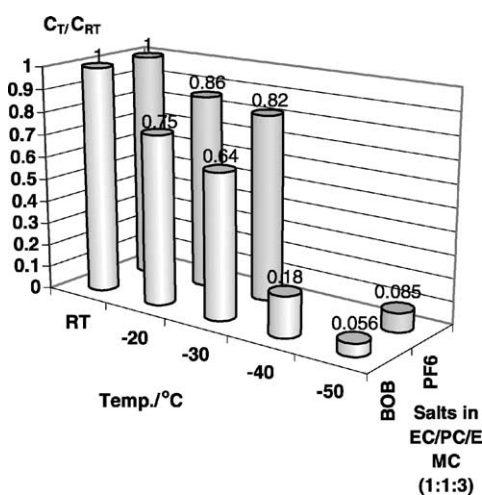


Fig. 2. Capacities of Li-ion cells in electrolytes of 1 m LiPF₆ in PC–EC–EMC (1:1:1) and 1 m LiBOB in PC–EC–EMC (1:1:1), respectively, at 20, 0, –20, –30, and –40 °C.

Table 2
Properties of PC and DEC

Solvent	MW	T_m (°C)	T_b (°C)	η (cP) at 25 °C	ϵ	d (g cm ⁻³) at 25 °C
PC	102.09	-48.8	242	2.53	64.92	1.200
DEC	118.14	-74.3	126	0.75	2.805	0.969

MW: molecular weight; T_m : melting point; T_b : boiling point; η : viscosity; ϵ : dielectric constant; d : density.

in formulating solvent mixtures for wide temperature operations. By formulating proper solvent mixtures for LiBOB, we believe we can also achieve high utilization and high rate at low temperature.

3.3. Conductivity of LiBF_4 in PC–DEC in comparison with LiPF_6 in PC–DEC

To seek clues on how to further improve the electrolytes while capitalizing on the unusual advantages of LiBF_4 and LiBOB salts, we selected the PC–DEC solvent system as an example to examine how the salt impacts on the electrolyte properties, especially the conductivity.

PC–DEC system is selected because both PC and DEC have wide liquid range and can form mixtures with selectable

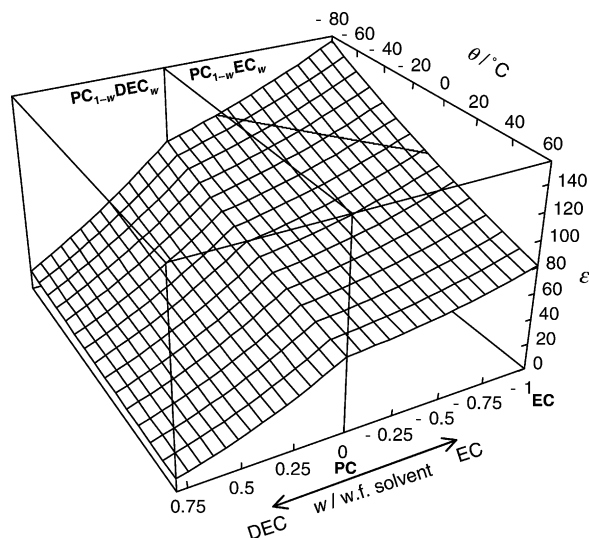


Fig. 3. Dielectric constants of PC–DEC and PC–EC with increasing DEC and EC content in PC, respectively, as a function of temperature from -80 to 60 °C.

ranges for liquid range [1], dielectric constant, and viscosity. The physical properties of PC and DEC are listed in Table 2 for reference. The smaller anion size of BF_4^- than PF_6^- may also shed light on the impact of salt on electrolyte properties.

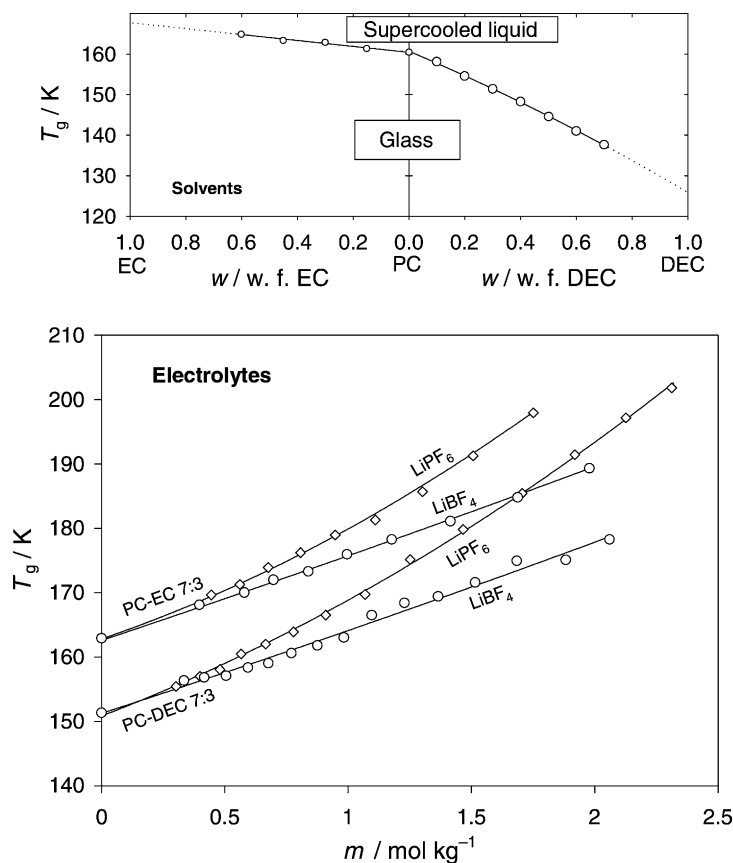


Fig. 4. Upper graph: glass transition temperatures of PC–DEC and PC–EC as a function of DEC and EC content in PC, respectively. Lower graph: glass transition temperatures of LiBF_4 in PC–DEC (7:3) and PC–EC (7:3) and LiPF_6 in the same solvent mixture as a function of respective salt concentration.

The dielectric constant, ϵ , of PC, PC–DEC with increasing DEC content from 0 to 0.8 weight fraction, and PC–EC with increasing EC content from 0 to 1 wt. fraction as a function of temperature is shown in Fig. 3. We note that ϵ increases with decreasing temperature and with increasing EC content. As expected, ϵ decreases with increasing DEC content. The dielectric constant is a measure of the ability of the solvent system in dissociating the salt and separating the ions. On the other hand, the viscosity of the solvent system

in general increases with decreasing temperature. Higher viscosity will result in lower ion mobility.

Because viscosity relates to glass transition temperature of the electrolyte solution [17], we measure the glass transition temperature, T_g , of PC–DEC, PC–EC, LiPF₆ in PC–DEC (7:3) and in PC–EC (7:3) and LiBF₄ in PC–DEC (7:3) and in PC–EC (7:3) as a function of salt concentration, m . A measure of T_g gives us an indication of how fast ions can move in the electrolytes. As expected from DEC's low

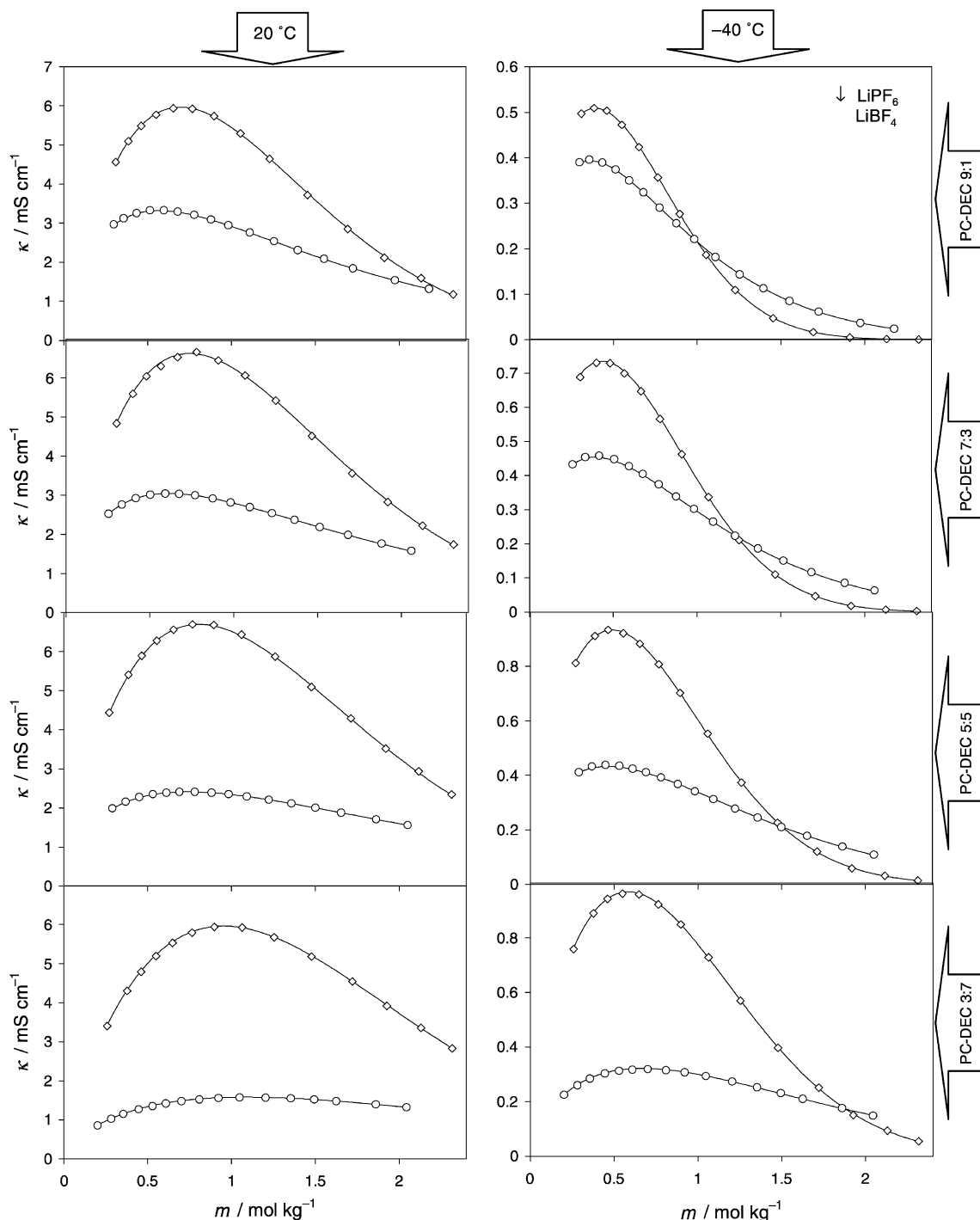


Fig. 5. Comparisons of conductivity of LiBF₄ and LiPF₆ in PC–DEC as a function of salt concentration in different PC–DEC weight ratios.

viscosity, T_g of PC–DEC decreases with increasing DEC content as shown in the upper graph in Fig. 4. T_g of the electrolytes in PC–DEC (7:3) and in PC–EC (7:3) for both LiBF_4 and LiPF_6 as a function of salt concentration are plotted in the lower graph in Fig. 4. We found that T_g of LiPF_6 containing electrolytes increases much faster with increasing salt concentration than that of LiBF_4 . The result suggests that the viscosity of LiBF_4 in either PC–DEC (7:3) or PC–EC (7:3) is lower than that of LiPF_6 in the corresponding solvent system. This is consistent with the smaller anion mass of BF_4^- relative to PF_6^- , i.e. electrolyte viscosity is proportional to anion size.

Comparisons of the conductivity of LiPF_6 in PC–DEC with that of LiBF_4 in PC–DEC in different solvent ratios as a function of salt concentration at 20 and at -40°C are shown in Fig. 5. In solutions of higher dielectric constant and at lower temperatures, the advantages of LiPF_6 over LiBF_4 in terms of conductivity are narrowing. This can be explained by the smaller anion size of BF_4^- , which requires higher dielectric constant solution to separate it from Li^+ . By balancing the dielectric constant and the viscosity of the solution, we believe that it is possible to formulate solvent mixtures using LiBF_4 for enhanced conductivity at low temperatures. We believe that the same methodology would be applicable to the development of LiBOB based electrolytes for use at low temperature.

4. Conclusion

The use of thermally stable LiBF_4 and LiBOB salts provided improved high temperature performance of Li-ion cells over that of state-of-the-art cells using LiPF_6 salt. The lower R_{ct} value observed at temperatures below -20°C for Li-ion cells using electrolytes with LiBF_4 salt suggests that it is possible to develop superior electrolytes for low temperature applications based on LiBF_4 . The electrolytes based on LiBOB for low temperature application might be challenging. The fact that the low temperature capacity utilization was improved by the addition of PC in EC–EMC electrolyte with LiBOB salt and the fact the graphite could be cycled in PC based electrolyte using LiBOB salt suggests that it is also possible to improve low temperature performance based on LiBOB salt. The conductivity studies of LiBF_4 in PC–DEC system suggests that, by balancing the dielectric constant and viscosity of the selected solvent mixtures, electrolytes

for wide-temperature-range applications based on LiBF_4 and LiBOB can be developed.

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