A new approach toward improved low temperature performance of Li-ion battery

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Abstract

We report a new approach toward formulating an electrolyte for low temperature operation of Li-ion batteries. The core of this new approach is to use $LiBF_4$ salt instead of $LiPF_6$, which is the chosen solute in the state-of-the-art Li-ion electrolytes. We found that although $LiBF_4$-based electrolyte has lower ionic conductivity than the $LiPF_6$ analogue, it provides improved low temperature performance. In particular, at -30 °C, a Li-ion cell with 1 m (mol/kg solvent) $LiBF_4$ dissolved in 1:1:3 (wt.) propylene carbonate (PC)/ethylene carbonate (EC)/ethylmethyl carbonate (EMC) mixed solvent delivers as high as 86% of capacity, in comparison to that obtained at 20 °C. Whereas the counterpart one, using $LiPF_6$, only retains 72%. Furthermore, the cell with $LiBF_4$-based electrolyte shows lower polarization at -30 °C. The above results suggest that the ionic conductivity of the electrolyte is not the only limitation to the low temperature operation of Li-ion batteries. Analysis of cell impedance reveals that the improved low temperature performance by $LiBF_4$ arises from a reduced charge-transfer resistance.
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1. Introduction

A number of papers have addressed the problem of poor low temperature performance of Li-ion batteries [1–11]. In general, both energy (discharge capacity) and power (operating voltage) of Li-ion batteries are substantially reduced as the temperature falls below -10 °C. Recent work has shown that the main limitation to the low temperature operation of Li-ion batteries arises from the graphite anode instead of the lithium transition metal oxide cathode [3,6]. The speculated origins of poor low temperature performance include (i) reduced ionic conductivity of the electrolyte and solid electrolyte interface (SEI) formed on the graphite surface [2,5,10], (ii) limited diffusivity of lithium ion within graphite [3], and (iii) high polarization of the graphite anode, which is associated with the former two factors [6,11]. Because

the solvent not only affects liquid temperature range and viscosity of the electrolyte but also directly participates in the formation of SEI, the previous approaches toward improving the low temperature performance of Li-ion batteries were mainly focused on the optimization of electrolyte solvent systems [2,4,5,8–10]. It has been proven that this approach is very effective to formulate an electrolyte, which has low freezing temperature and is capable of forming a better SEI with graphite anode.

We recently studied the effect of solvents on the cell impedance by comparing two electrolytes of 1 m $LiPF_6$ dissolved in 3:7 (wt.) EC/EMC and 1:1:3 PC/EC/EMC mixed solvents [12]. We observed that the resistance of both SEI and charge-transfer process of the Li-ion cell is substantially increased as the temperature falls below -20 °C. However, SEI resistance of the cell with PC-based electrolyte is increased much more slowly with decreasing of the temperature. At temperatures below 0 °C, a PC-based electrolyte has lower ionic conductivity, but provides higher capacity. In another work [13], we used 1:1:1 EC/dimethyl carbonate (DMC)/diethyl carbonate (DEC) mixed solvent to evaluate the effect of

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lithium salt on the low temperature performance. We discovered that, between 0 and −20 °C, use of $LiBF_4$ in the Li-ion electrolyte led to a much lower charge-transfer resistance and hence provided an improved performance although the ionic conductivity of such an electrolyte is lower. Unfortunately, this electrolyte freezes as the temperature falls below −20 °C, which causes a dramatic drop in the cycling performance. On the other hand, for the high temperature operation of Li-ion cell, we found [14] that the cell with $LiBF_4$-based electrolyte is of improved high temperature performance and is less moisture sensitive.

Based on our above results [12–14], we infer that it is possible to use $LiBF_4$ and 1:1:3 PC/EC/EMC ternary mixed solvent to formulate an electrolyte that is able to provide an improved performance over a wide temperature range (−40–60 °C). In this paper, we will discuss the effect of $LiBF_4$ on low temperature performance of the Li-ion cell.

2. Experimental

In an argon-filled glove box with both oxygen and water contents less than 20 ppm, two electrolytes with a composition of 1 m $LiPF_6$ or 1 m $LiBF_4$ dissolved in 1:1:3 PC/EC/EMC mixed solvent were prepared. For cell assembly, an additional 1.0 wt.% of vinylene carbonate (VC, 97%, Aldrich) was added into the resultant electrolytes so as to improve the cycling performance of graphite anode. Both graphite anode and cathode films, provided by SAFT America, Inc. were dried at 110 °C under vacuum for 16 h before use. The cathode active material was a lithium nickel-based mixed oxide. Li-ion button cells with an anode and cathode area of 1.27 and 0.97 cm^2, respectively, were assembled and filled with 150 μl of electrolyte.

A Tenney Environmental Oven Series 942 was used to provide a constant temperature environment for the tests at various low temperatures. For discharge capacity measurement, the cells were always charged at 20 °C before lowering the cell temperature to a specific temperature. In order to reach equilibrium of the cell temperature and the oven pre-set temperature, the cells were kept at the specified temperature for at least 6 h. Using a Maccor Series 4000 tester, the cells were first charged to 4.2 V with a time limit of 3 h at 20 °C, and then discharged to 2.5 V at a specified low temperature. Current density for both charge and discharge processes was 0.5 mA/cm^2 (∼0.5 C rate). We hereby used "relative capacity", which is defined as a ratio of the capacity at a specified temperature to the capacity measured at 20 °C, to describe low temperature performance.

Solartron SI 1287 Electrochemical Interface and SI 1260 Impedance/Gain-Phase Analyzer were employed to determine ionic conductivity of the electrolytes and to measure electrochemical impedance spectroscopy (EIS) of the cells. AC impedance of the cells was potentiostatically measured by applying a DC bias with its value equal to open circuit voltage (OCV) of the cell and an AC oscillation of 10 mV over the frequencies from 100 kHz to 0.01 Hz. The obtained EISs were fitted by using ZView software (Scribner and Associates).

3. Results and discussion

3.1. Ionic conductivity

Fig. 1 compares ionic conductivity of two electrolytes composed of 1 m $LiPF_6$ and 1 m $LiBF_4$, respectively, dissolved in a 1:1:3 PC/EC/EMC mixed solvent. In most of the temperature range, $LiPF_6$ provides higher ionic conductivity, especially at elevated temperatures where viscosity of the solution is relatively low. Similar result was also observed from 3:7 EC/EMC binary mixed solvent [14]. This observation can be ascribed to the larger anion of $LiPF_6$, which not only helps to delocalize negative charge of the anion but also favors to weaken the ion pairing between lithium ion and the anion. As a result, $LiPF_6$ can be more effectively dissociated and the solution with it exhibits higher ionic conductivity. With the temperature falling, viscosity of the solution is increased and gradually becomes the dominant factor to the ionic conductivity. Therefore, at very low temperatures such as −60 °C, conductivity of these two electrolytes tends to converge. It should be noted that, during the measurement of ionic conductivity, we did not observe any freezing phenomenon from both $LiPF_6$ and $LiBF_4$-based electrolytes. This fact reveals that 1:1:3 PC/EC/EMC ternary mixed solvent is suitable for formulation of an electrolyte with low freezing temperature.
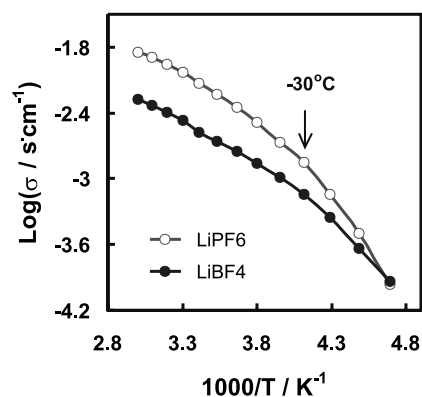

Fig. 1. Arrhenius plots of the ionic conductivities for the electrolytes composed of 1 m lithium salt dissolved in 1:1:3 PC/EC/EMC mixed solvent.

3.2. Galvanostatic cycling

As observed and discussed in our previous work [12], addition of PC into the electrolyte increases irreversible capacity of the first cycle of Li-ion cell. According to the literature [9,15], we added 1.0 wt.% of VC into the electrolytes to reduce this irreversibility resulting from the use of PC. Before the cycling test at the low temperatures, the cells were first cycled 10 times at a rate of 0.5 mA/cm^2 to allow a complete formation of SEI on both graphite and cathode surfaces. Fig. 2 plots voltage–capacity curves for the discharge of these two cells using LiPF$_6$ and LiBF$_4$, respectively, at various temperatures. At 20 °C where the value of "relative capacity" is defined as 1.0, discharge capacities of these two cells are 1.13 mAh/cm^2 (LiPF$_6$) and 1.05 mAh/cm^2 (LiBF$_4$), respectively. Slightly lower capacity of the LiBF$_4$ cell is due to its slightly higher irreversible capacity in the first cycle, which consumes parts of the limited lithium ions in the cathode. It can be seen that, with decreasing of the temperature, the cells not only suffer a lower operating voltage (power) but also lose capacity (energy). The decreased operating voltage at the low temperatures can be ascribed to the polarization caused by an increase of the cell electric resistance (including electrolyte, electrodes, and SEI) and by a slowdown of the cell electrochemical reaction. When the temperature is above −10 °C, the relative capacities of both cells are close to

unity. In these cases, decreasing of the temperature is mainly reflected by an increase in the cell polarization with a negligible change in the discharge capacity.

Comparing Figs. 2(a) and (b), one may find that the cell with LiBF$_4$ shows an improved low temperature capacity. For example, such a cell retained 86% of relative capacity at −30 °C and about 20% at −50 °C, while the LiPF$_6$ counterpart fell to 72% at −30 °C and completely failed at −50 °C. [1] This result is hard to explain in terms of electrolyte conductivity since at −30 °C LiBF$_4$-based electrolyte has only half the ionic conductivity of the LiPF$_6$-based one (also see Fig. 1). Therefore, we may conclude, under the condition that solvent freezing and salt precipitation does not occur, that ionic conductivity of the electrolytes would not be the only limitation to the low temperature performance of Li-ion cell.

3.3. Effect of ionic conductivity

Fig. 3 compares cell polarization caused by use of different salts. We notice that at 20 °C these two cells using LiPF$_6$ and LiBF$_4$, respectively, have very similar voltage–capacity correlation, showing a negligible merit of the higher conductivity of LiPF$_6$-based electrolyte. This may be due to the fact that the tested current rate (0.5 mA/cm^2, ~0.5 C) is not high enough to reflect the difference in the ionic conductivity of the electrolytes. More interestingly, at −30 °C the cell with LiBF$_4$ not only shows lower polarization but also delivers higher capacity in spite of the relatively lower conductivity of LiBF$_4$-based electrolyte (see curves 3 and 4). The above results reveal that LiBF$_4$ may play a critical role in improving low temperature performance of Li-ion cell.

3.4. Impedance analysis

To understand the fact that LiBF$_4$ improves low temperature performance, we studied the effect of salt on the impedance of a Li-ion cell. We have found [12,13] that the impedance spectrum of a Li-ion cell depends greatly on the state-of-charge (SOC). For a fair comparison, in this work we selected a fully charged cell (at 100% SOC) to observe the effect of salt. Fig. 4 plots impedance spectra of two fully charged Li-ion cells, which were recorded at −30 °C. According to our early work [12], impedance spectrum of a Li-ion cell is composed of three partially overlapped semicircles in high, medium and low frequency regions, and a straight sloping line at the low frequency end. Depending on the cell's structure such as geometric configuration and electrode porosity, the semicircle at the high frequency
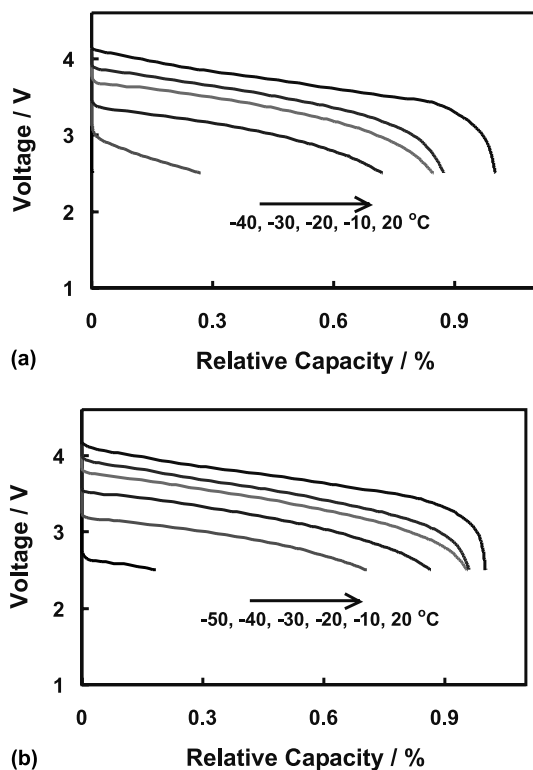
Fig. 2. Voltage–capacity plots of Li-ion cell at various temperatures, in which relative capacity is a ratio of the capacity at a specified temperature to the one obtained at 20 °C. (a) LiPF$_6$ and (b) LiBF$_4$.

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[1] Relative capacities of a specified cell at low temperatures are highly dependent on cycling conditions such as cut-off voltages, specially the low cut-off voltage, and current density. The present data were obtained at 0.5 mA/cm^2 (~0.5 C) between 4.2 and 2.5 V.
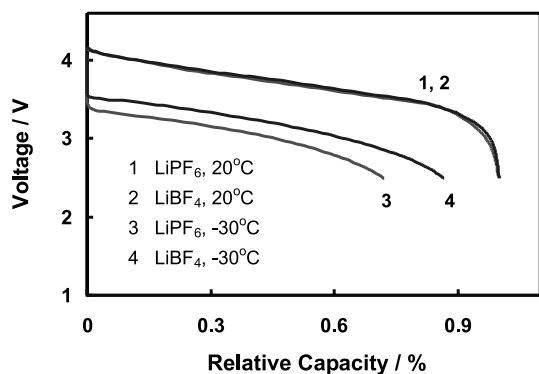
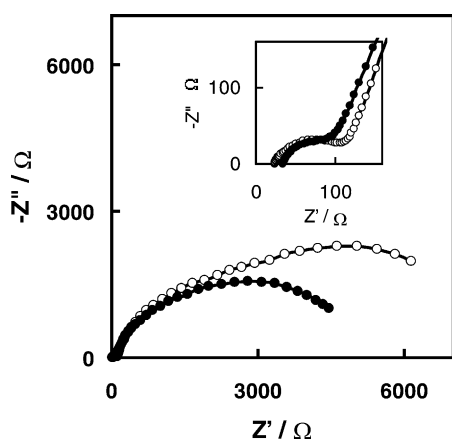Fig. 3. Effect of salts on the discharge voltage and capacity of Li-ion cell at 0.5 mA/cm^2.

Fig. 4. Impedance spectra of the fully charged Li-ion cells at −30 °C, in which inset shows the parts at high frequency end. (1) LiPF$_6$ (hollow circle) and (2) LiBF$_4$ (solid circle).

end, which reflects the impedance of two porous electrodes, may merge with electrolyte resistance to form an intercept with the real impedance axis, being an indication of the cell bulk resistance (R_b). The straight sloping line at the low frequency end is related to a combination of the diffusional effects of lithium ion in bulk of the active material particles and electrolyte. In the present case, the impedance spectra are composed of two overlapped semicircles, which reflect the impedance of SEI (R_{SEI}) and charge-transfer process (R_{ct}), respectively, without the slopping straight line at the low frequency end. This is because, at −30 °C, the low frequency limit (0.01 Hz) of the impedance measurement is too high to observe the diffusion process of lithium ion, or alternatively that it is masked by the large R_{ct}.

As discussed above, total impedance of a Li-ion battery is composed of R_b, R_{SEI}, and R_{ct}, of which only the R_b is directly related to the ionic conductivity of the electrolytes. Therefore, it is important to identify which resistance dominates the impedance of the cell because cycling performance of the battery is affected by total impedance other than by the R_b alone. We can see from

inset and Fig. 4 that, at −30 °C, the cell with LiBF$_4$-based electrolyte has slightly larger R_b but lower R_{SEI} and R_{ct}. Among these three resistances, the R_{ct} obviously dominates the impedance of Li-ion cell. In other words, at low temperatures, impact of the R_b and R_{SEI} on cycling performance of the cell is rather small as compared to that of the R_{ct}. Similar results might be observed from the whole cycling process (including charge and discharge). In particular, at a fully discharged state the R_{ct} became extremely high, while both the R_b and R_{SEI} changed little [12]. The substantially high R_{ct} of the fully discharged state led to a sharp drop in the discharge voltage of the cell, which usually is a symbol showing the end of discharge. When the Li-ion battery is charged right after the end of discharge, the substantially high R_{ct} of the fully discharged state causes a considerable polarization so that the cell voltage is immediately jumped to the pre-set upper voltage limit for the charge process. Therefore, Li-ion batteries are minimally charged up at the low temperatures (<−10 °C), otherwise, direct deposition of metal lithium on the graphite anode readily occurs as a result of the high polarization. For this reason, we performed all charging processes near room temperature (20 °C) to avoid the above problems and to ensure the same initial conditions for a fair comparison of the discharge curves. This is also the reason that we focused our attention on the impedance of a fully charged cell, especially on the reduced R_{ct}, which we believe to be relative to the use of LiBF$_4$. One may find from Fig. 4 that the improved low temperature performance by the use of LiBF$_4$ arises from the reduced R_{ct}.

To explain the low temperature behavior of Li-ion cells, we plot the R_b and R_{ct} of the cells as a function of the ambient temperature in Fig. 5, in which the resistances are illustrated in a logarithm scale due to their large difference caused by the temperature change. We see that the R_{ct} is much more sensitive to the temperature than the R_b. As a result, at low temperatures, the R_{ct}
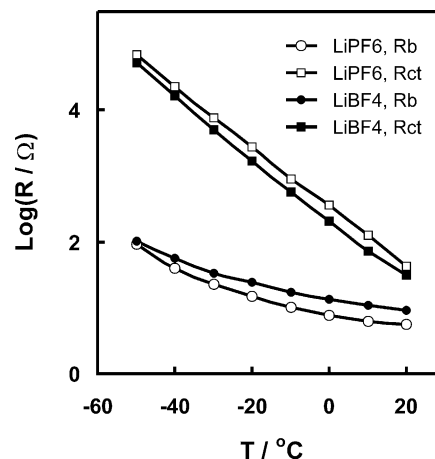

Fig. 5. Temperature dependence of R_b and R_{ct} of the Li-ion cells with different salts.

could become a predominant limitation to the operation of Li-ion cell. Therefore, we may conclude that the poor low temperature performance of Li-ion cell originates from the substantially high R_{ct} and that the improved performance by the use of $LiBF_4$ salt directly arises from its reduced R_{ct}.

4. Conclusions

From this work, we conclude that ionic conductivity of the electrolyte would not be a predominant limitation to the low temperature performance of Li-ion cell unless either solvent freezing or salt precipitation occurs. In comparison to $LiPF_6$-based electrolyte, the electrolyte made of $LiBF_4$ salt has lower conductivity, but it provides an improved low temperature performance. This behavior can be ascribed to a reduced charge-transfer resistance as the result of using $LiBF_4$ salt. Combining our previous work [13,14], we speculate that $LiBF_4$ can be used to formulate an electrolyte that can enable Li-ion cell to operate in a wide temperature range (-40–60 °C).

Acknowledgements

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