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Effect of propylene carbonate on the low temperature performance of Li-ion cells

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Abstract

The effect of propylene carbonate (PC) on the low temperature performance of Li-ion cells was studied by comparing two electrolytes of 1 m $LiPF_6$ 3:7 ethylene carbonate (EC):ethylmethyl carbonate (EMC) and 1 m $LiPF_6$ 1:1:3 PC:EC:EMC. We found that addition of PC to the electrolytes can significantly improve the low temperature performance of Li-ion cells. However, use of PC will cause a slight decrease in the ionic conductivity of the electrolytes owing to its high viscosity, especially at low temperatures. This result suggests that ionic conductivity of the electrolytes would not be the main limitation to the low temperature operation of the Li-ion cells. Analysis of the impedance spectra of fully charged Li-ion cells shows that at 20 °C these two cells without and with PC, respectively, have solid electrolyte interface (SEI) of similar resistance, however, the presence of PC can substantially decrease its dependence on the temperature. Therefore, the improved low temperature performance using PC can be ascribed to the relatively higher conductivity of the SEI film on the interfaces between electrolyte and electrodes. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Li-ion cell; Propylene carbonate; Low temperature; Electrolyte; Ionic conductivity

1. Introduction

Many recent papers have discussed the problem of poor low temperature performance of Li-ion cells [1–10]. In general, discharge capacity of the Li-ion cells is substantially reduced as the temperature falls below −10 °C. At −40 °C, for example, a commercial 18650 Li-ion cell loses most of its power and energy [7]. More importantly, the delivered capacity of Li-ion cells at low temperatures (less than −10 °C) greatly depends on the temperature at which the cells are charged [3]. That is, the cells can be effectively charged up only when the temperature is above −10 °C. It has been reported that the main limitation to the low temperature operation of Li-ion cells is the graphite anode instead of the lithium transition metal oxide cathode [3,6]. Two different hypotheses have been proposed to explain the poor performance of graphite electrodes at low temperatures. One is based on the low ionic conductivity of the electrolyte and solid electrolyte interface (SEI) film formed on the graphite surface [2,5] and the other one on the low diffusivity of lithium ion within graphite [3] and the related polarization of the graphite electrode [6]. Our study has shown that each of the above two hypotheses are true only under certain conditions, which depend on the source of the graphite as well as the type of salt and solvent in the electrolyte. It is because the solvent not only affects liquid temperature range of the electrolytes but also directly participates in the formation of the SEI film that attempts to improve low temperature performance of the Li-ion cells concentrated on the selection of new electrolyte solvents [2,4,5,8,9]. This approach is very useful in the development of a liquid electrolyte, which has low freezing temperature and is capable of forming a better SEI film with the graphite electrode.

It is known that propylene carbonate (PC) can effectively suppress ethylene carbonate (EC) crystallization. Therefore, PC is often used to formulate low temperature liquid electrolytes. In this work, we will study the effect of PC on the low temperature performance of the Li-ion cells and discuss the improvements related to the use of PC.

2. Experimental

Two electrolytes with composition of 1 m (mole solute per kilogram solvent) $LiPF_6$ 3:7 (wt.) EC: ethylmethyl carbonate (EMC) and 1 m $LiPF_6$ 1:1:3 (wt.) PC:EC:EMC,

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respectively, were prepared in an argon-filled glove box with both oxygen and water contents <20 ppm. Water content of the electrolytes thus prepared, determined by Karl–Fischer titration, was 10–15 ppm. Graphite anode and cathode films, provided by SAFT America Inc., were punched into disks with an area of 1.27 and 0.97 cm^2, respectively, and dried at 110 °C under vacuum for 16 h before use. The cathode active material was a lithium nickel-based mixed oxide. Using the above materials, BR2335-type Li-ion button cells were assembled and filled with 150 μl of electrolyte. The cells were galvanostatically cycled using a Maccor Series 4000 tester at a current density of 0.5 mA/cm^2 between 2.7 and 4.2 V unless specified otherwise. A Tenney Environmental Oven Series 942 was used to provide a constant temperature environment for the low temperature cycling tests, in which the cells were charged at 20 °C and discharged at various low temperatures.

Solartron SI 1287 electrochemical interface and SI 1260 impedance/gain-phase analyzer, controlled by a personal computer using Zplot software, were employed to determine the ionic conductivity of the electrolytes and to measure the electrochemical impedance of the cells. The ac impedance of the cells was potentiostatically recorded by applying a dc bias with its value equal to the open circuit voltage (OCV) of the cells and an ac oscillation of 10 mV over the frequencies from 100 kHz to 0.01 Hz. The obtained impedance spectra were analyzed by using ZView software (Scribner and Associates Inc.).

3. Results and discussion

3.1. Ionic conductivity of the electrolytes

It is known that EC is an essential component in the Li-ion cell electrolytes since it helps graphite electrode to form a desirable SEI film, which is critical to ensure the reversible cycling of the Li-ion cells. However, due to its high melting point (36.4 °C) and poor miscibility with linear carbonate solvents, EC will crystallize out in the electrolyte solutions at low temperatures. This leads to a decrease in the ionic conductivity of the electrolyte and in the cycling performance of Li-ion cells. For this reason, PC is often added to suppress the crystallization of EC at low temperatures since it not only has very good miscibility with EC, but also has a low melting point (−48.8 °C). Fig. 1 compares the ionic conductivities of 1 m $LiPF_6$ 3:7 EC:EMC and 1 m $LiPF_6$ 1:1:3 PC:EC:EMC electrolytes at various temperatures. Above 20 °C, these two electrolytes have very similar ionic conductivity. In the studied temperature range, no electrolyte freezing is observed from both electrolytes even when the temperature falls to −40 °C. However, ionic conductivity of the PC-based electrolyte declines faster when the temperature is lower than 0 °C. This phenomenon can be ascribed to the higher viscosity of the PC-based electrolyte, which is caused by the presence of highly viscous PC co-solvent. Thus, PC can be used to lower the freezing temperature of the electrolytes at a small expense in the ionic conductivity.

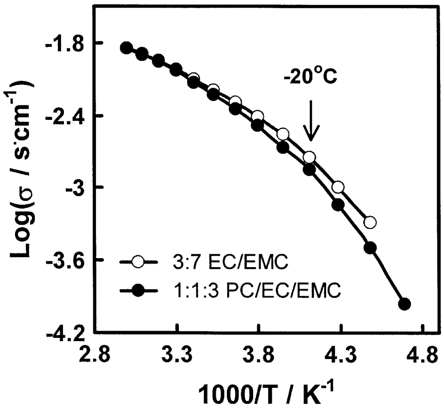

Fig. 1. Arrhenius plots of the ionic conductivities for the electrolytes with 1 m $LiPF_6$ dissolved in different mixed solvents.

3.2. Effect of PC on cycling behavior of Li-ion cells

Fig. 2 plots differential capacities versus the cell voltage for the initial two forming cycles of two Li-ion cells using

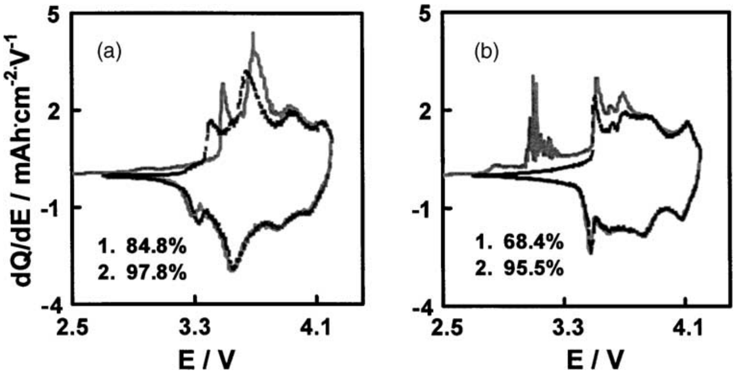

Fig. 2. Differential capacities versus voltage of the Li-ion cells with different electrolytes, which were obtained from the initial two cycles at 0.1 mA/cm^2. Note that a solid line represents the first cycle and a dotted line the second cycle. The numbers in the plots show cycle number and Coulombic efficiency, respectively: (a) 1 m $LiPF_6$ 3:7 EC/EMC; (b) 1 m $LiPF_6$ 1:1:3 PC:EC:EMC.

3:7 EC:EMC and 1:1:3 PC:EC:EMC electrolytes, respectively. We see that both cells have more than 15% irreversible capacity in the first cycle and the Coulombic efficiencies increase to higher than 95% in the following cycle. Our recent studies have shown that the irreversible capacities formed during the initial few cycles of Li-ion cells mostly arise from electrochemical decomposition of the electrolyte solvents on the surface of the graphite anode [11] and the cathode [12], which results in the formation of SEI film on both electrodes. In particular, the resultant SEI is essential for the reversible operation of graphite anode. Comparison of Fig. 2a and b indicates that the cell with PC-based electrolyte has an additional irreversible capacity peak at 3.0–3.3 V in the first charge process and this peak disappears in the second cycle. Such a peak does not appear in the cell with EC/EMC electrolyte (Fig. 2a). Therefore, we consider that this irreversible differential capacity peak is associated with PC decomposition since PC cointercalates along with Li^+ ion into the graphite and subsequently decomposes and exfoliates graphite [13]. It is because PC decomposition occurs that the cell with PC-based electrolyte shows relatively low Coulombic efficiency (68.4%) in the first cycle.

Fig. 3 compares the impact of electrolyte solvents on cycling performance of the Li-ion cells. It can be seen that both cells show similar cycling performance. However, the cell with PC-based electrolyte delivers lower capacity. This is because the cell has been designed to be cathode controlled and PC decomposition in the first cycle consumes a higher amount of lithium ions at the cathode. In a practical Li-ion cell, this drawback of PC can be overcome by many approaches such as: (1) using electrolyte additives, which can suppress PC decomposition and facilitate SEI formation [14,15]; (2) replacing $LiPF_6$ with a new lithium salt such as lithium bis (oxalato) borate (LiBOB), which can form a stable SEI with graphite in the presence of PC [10]; (3) modifying the graphite surface [16,17] or selecting another graphite as an anode material, for example, natural graphite LF-18A distributed by International Technology Exchange Society works with PC contents up to 30% [18]; (4) increasing cathode/anode mass ratio in the electrode coating processes. Therefore, we consider that the capacity loss associated with PC decomposition would not limit the use of PC in development of low temperature electrolytes.

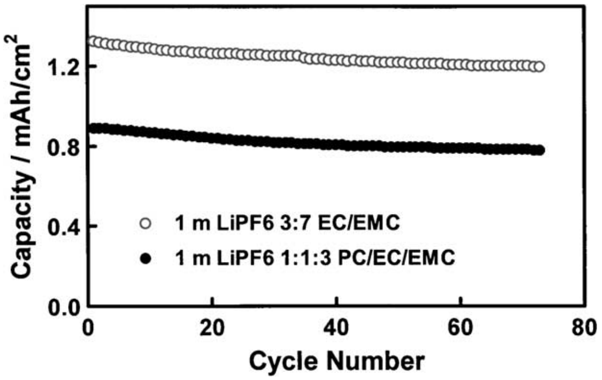

Fig. 3. Cycling performance of the Li-ion cells with two different electrolytes.

3.3. Galvanostatic cycling at low temperatures

The effect of PC on low temperature performance can be evaluated by comparing the voltage-capacity curves of the Li-ion cells. For this purpose, we have plotted cell voltage at various temperatures, as a function of the relative capacity for these cells without and with PC in Fig. 4a and b, respectively. It is shown that, with decreasing temperature, the cells not only suffer a lower operating voltage but also lose capacity. That is, both the power and energy density of the Li-ion cells are significantly reduced at the low temperatures. The decreased operating voltage at the low temperatures could be ascribed to the polarization caused by an increase in the cell resistance (including the electrolyte, electrodes, and SEI between them) and by a slowdown of the cell electrochemical reaction. When the temperature is decreased to −30 °C, the operating voltage and capacity of both cells become extremely low.

Comparing Fig. 4a and b, we find that the cell with PC-based electrode shows an improved capacity at the low temperatures. For example, at −20 °C such a cell retained 83% of relative capacity, while the one with 3:7 EC:EMC

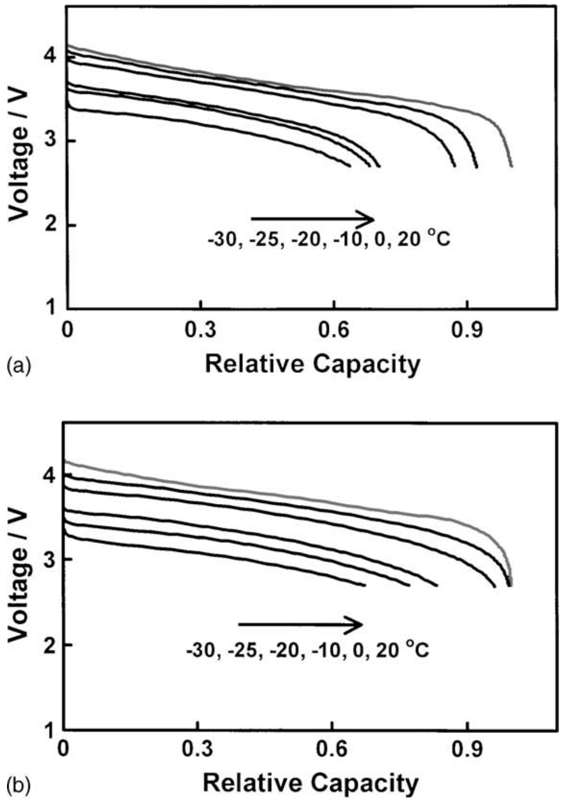

Fig. 4. Voltage-relative capacity curves of the Li-ion cells at various temperatures, in which the relative capacity is taken as the ratio of the capacity at a certain temperature to the one obtained at 20 °C: (a) 1 m $LiPF_6$ 3:7 EC:EMC; (b) 1 m $LiPF_6$ 1:1:3 PC:EC:EMC.

electrolyte fell to 70%. More interestingly, it is shown in Fig. 4b that at 0 °C the former delivers almost the same capacity as that obtained at 20 °C except for a slight decrease in the operating voltage caused by electrical polarization of the cell. It appears that the above observations cannot be explained in terms of the ionic conductivity of the electrolytes because at temperatures below 0 °C, the PC-based electrolyte has lower ionic conductivity (Fig. 1). Another interesting phenomenon is that from −10 to −20 °C there exists a noticeable decrease in the capacity for both cells (Fig. 4a and b), while the conductivity decrease is continuous (Fig. 1). Similar observations have been reported elsewhere [6]. The reason for this behavior of the Li-ion cells can be ascribed to a significant decrease in the diffusivity of lithium ions within the graphite anode, which occurs in the same temperature range [19].

3.4. Impedance analysis

To understand the origin of the improved low temperature performance by PC, we analyzed the impedance spectra of two Li-ion cells with different electrolytes at various temperatures. It was found that the impedance spectra greatly depends on the state-of-charge (SOC) of the cells. Therefore, we selected fully charged and discharged states, respectively, to analyze the effect of PC on the low temperature performance. Fig. 5 plots a typical impedance spectrum from a fully charged cell at −20 °C and an equivalent circuit used for fitting the resultant impedance spectra. The impedance spectrum is generally composed of three partially overlapping semicircles in high, medium and low frequency regions, and a straight sloping line in low frequency regions (note that the straight sloping line is not present in Fig. 5a because its appearance depends on the temperature). From high to low frequencies, these three semicircles can be respectively assigned to the spectra of the cell bulk impedance, SEI film impedance, and charge-transfer process [11,12,20,21]. Each spectrum can be fitted by an electric circuit consisting of a resistor and a parallel capacitor (Fig. 5b). In Fig. 5b, Z_e, which is indicated by the sum of R_1 and R_2 as shown in inset of Fig. 5a, represents the total impedance contributed by the resistance of the electrolyte and porous electrodes as well as their related geometric (double layer) capacitance; R_f and C_f are the resistance and capacitance of the SEI film; R_{ct} and C_{dl} are the charge-transfer resistance and the double-layer capacitance; W is the Warburg impedance related to the diffusion of lithium ions in the electrodes. Among these electrical components, the geometric capacitance of the cells is strongly affected by the ambient temperature and electrode structure (such as, particle size, porosity and surface area). Therefore, Z_e varies with the temperature. At low temperatures, it is a semicircle with its high frequency end intersecting the real axis, as indicated in the inset of Fig. 5a, while at room temperature, it merges into an intercept on the real axis, which is characterized by R_1 alone.

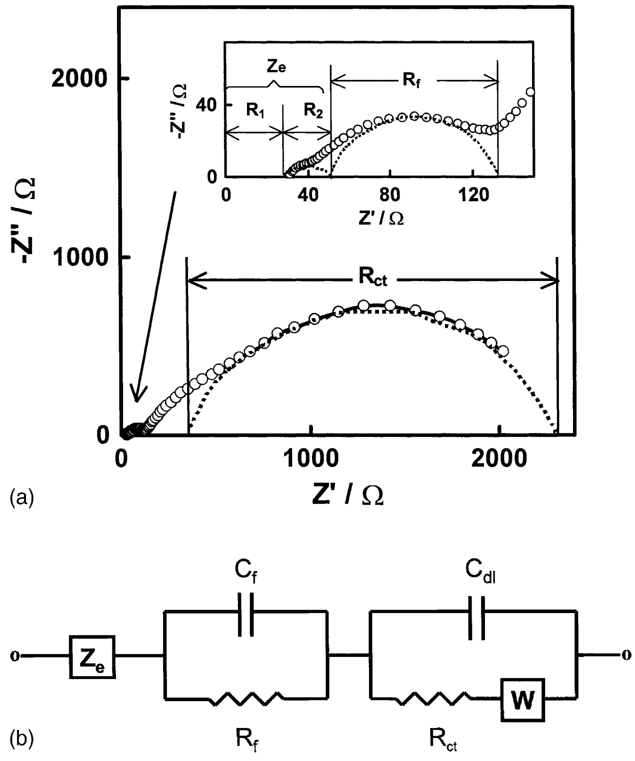

Fig. 5. (a) Impedance spectrum of a fully charged Li-ion cell at −20 °C and (b) equivalent circuit used for analysis of the impedance spectra.

Fig. 6 compares the impedance spectra of the cell in the fully charged and discharged states. We found that these two semicircles at high and medium frequency regions, respectively, as shown in inset of Fig. 6, are almost the same for both charged and discharged states. However, the one at the low frequency end, which reflects R_{ct} and its related C_{dl}, substantially changes with the SOC. In the discharged state,

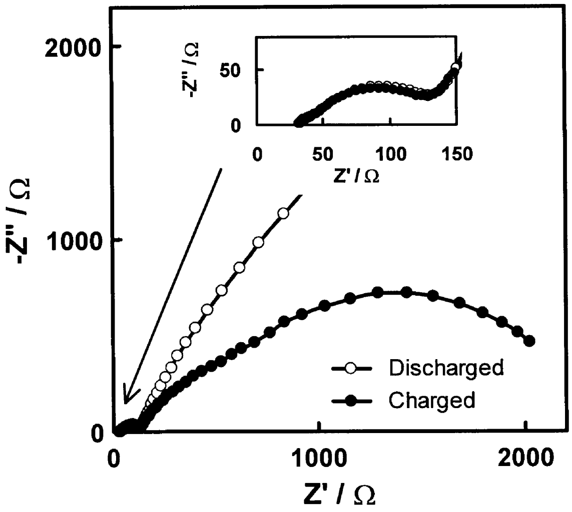

Fig. 6. Impedance spectra for the Li-ion cell using 1 m $LiPF_6$ 1:1:3 PC:EC:EMC electrolyte at charged (solid circle) and discharged (hollow circle) states, respectively.

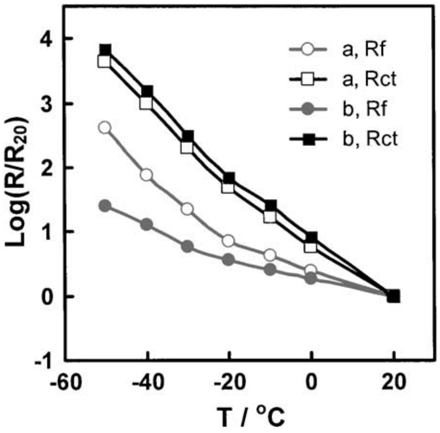

Fig. 7. Comparison for the temperature dependence of relative resistance (R/R_{20}) of the Li-ion cells using 1 m $LiPF_6$ 3:7 EC:EMC (a, hollow symbol) and 1 m $LiPF_6$ 1:1:3 PC:EC:EMC (b, solid symbol), respectively. R is the resistance at a certain temperature and R_{20} the resistance measured at 20 °C.

the R_{ct} is very high and its corresponding impedance spectrum changes into a straight sloping line (essentially a semicircle with very large diameter). As a result, R_{ct} in the discharged state is too large to be measured. For this reason, we use the impedance data measured in the charged state to evaluate the effect of PC on the low temperature performance of the Li-ion cells.

Fig. 7 plots the relative resistance of the SEI film and charge-transfer process as a function of the temperature for these two cells with different electrolytes. We have found that the R_{ct} is closely associated with the kinetics of a cell electrochemical reaction. Therefore, we may roughly use the R_{ct} change to evaluate the cycling performance of the cells. As Fig. 7 shows, the relative R_{ct} of both cells is significantly increased on decreasing the temperature. This result appears to reasonably explain the poor low temperature performance of the Li-ion cells. A difference in the temperature dependence, which is related to the electrolyte, can be noticed from the relative R_f. As the temperature decreases, the relative R_f of the cell using 1 m $LiPF_6$ 1:1:3 PC:EC:EMC electrolyte is increased at a much lower rate. This result reveals that the improved low temperature performance by PC can be ascribed to the reduced temperature dependence of the SEI resistance since at 20 °C these two cells have similar R_f and Z_e values. Therefore, we conclude that the higher conductivity of the SEI film formed with a PC-based electrolyte leads to an improved low temperature performance of the Li-ion cells.

Figs. 5a and 7 reveal more about the poor low temperature performance of the Li-ion cells. Firstly, the R_{ct} at −20 °C has a much higher value, which appears to dominate the total impedance of the cell. Secondly, R_{ct} increases faster than R_f with decreasing temperature (Fig. 7). Therefore, we consider that the low temperature performance of the Li-ion cells is likely limited by the slow kinetics of the cell reaction. Changing solvents can improve the ionic conductivity of the electrolyte and SEI film, but it cannot facilitate the cell electrochemical reactions. On the other hand, the substantially higher R_{ct} in the discharged state than in the charged state (at −20 °C, Fig. 6) suggests that the cell reaction in the discharged state is much slower. This explains the well-known fact that charging of the Li-ion cells from a discharged state is very difficult when the temperature is below −10 °C.

4. Conclusion

From this work, we may conclude that an improved low temperature performance of Li-ion cells can be obtained using PC as a co-solvent in the electrolyte for a slight loss in the ionic conductivity. This conclusion suggests that, for the low temperature operation of Li-ion cells, the ionic conductivity of the electrolyte is not as important as expected. Another negative impact of PC is that it increases irreversibility in the initial forming cycles due to PC decomposition on the graphite surface. Impedance analysis shows that at low temperatures, the SEI film formed with PC-based electrolyte has higher conductivity. Therefore, the improved low temperature performance of the Li-ion cells can be ascribed to a less resistive SEI film on the interfaces between the electrolyte and electrodes.

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