

Short communication

# The low temperature performance of Li-ion batteries

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## Abstract

A symmetric cell was adopted to analyze low temperature performance of Li-ion battery. Results showed that impedances of both Li-ion and symmetric cells are mainly composed of bulk resistance ( $R_b$ ), surface layer resistance ( $R_{sl}$ ) and charge-transfer resistance ( $R_{ct}$ ). Among these three components, the  $R_{ct}$  is most significantly increased and becomes predominant as the temperature falls to below  $-10^\circ\text{C}$ . Therefore, we may ascribe the poor low temperature performance of Li-ion battery to the substantially high  $R_{ct}$  of the graphite and cathode. Comparing impedance spectra of the symmetric cells, we found that at  $-30^\circ\text{C}$  the delithiated graphite and lithiated cathode, both of which correspond to a discharged state in a Li-ion battery, have a much higher  $R_{ct}$  than when charged. This means that the Li-ion battery in the discharged state suffers a higher polarization. This result explains the phenomenon that at low temperatures, charging of a discharged Li-ion battery is more difficult than discharging of a charged battery.

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## 1. Introduction

A number of papers have addressed the problem of the low temperature performance of Li-ion batteries [1–10]. Generally, both energy and power of the Li-ion batteries are substantially reduced as the temperature falls to below  $-10^\circ\text{C}$ . It has been reported that at  $-40^\circ\text{C}$  a commercial 18650 Li-ion battery only delivered 5% of energy density and 1.25% of power density, as compared to the values obtained at  $20^\circ\text{C}$  [6]. In addition, significant differences in the cycling performance has been observed. At low temperatures, a Li-ion battery can be normally discharged, while the reverse charging process is rather difficult [2,4,9]. Although the origin of low temperature phenomena are still under debate, they can be summarized as follows: (i) reduced ionic conductivity of the electrolyte and solid electrolyte interface (SEI) formed on the graphite surface [1,3,5], (ii) limited diffusivity of lithium ion within graphite [2,9], (iii) high polarization of the graphite anode, which is associated with the former two factors [4,7], and (iv) substantially increased charge-transfer resistance on the electrolyte–electrode interfaces [8,10]. It should be noted that all the above conclusions were obtained from either Li-ion or Li

half-cells, which may represent a combined effect of the electrodes in an asymmetric cell.

To reduce the complication of asymmetric cells, in this work we use symmetric cells with a configuration of graphite/graphite and cathode/cathode, respectively, to analyze the temperature dependence of the impedance of Li-ion electrodes. Using impedance data from the symmetric cells, we attempt to understand these two low temperature phenomena of Li-ion batteries: (1) poor cycling performance and (2) significant difference in the cycling performance between charging and discharging processes.

## 2. Experimental

The 1.0 m (mole solute/kg solvent)  $\text{LiPF}_6$  solution in 1:1:3 (wt.) propylene carbonate (PC)/ethylene carbonate (EC)/ethyl methyl carbonate (EMC) mixed solvent was used as an electrolyte. To achieve a better SEI film with graphite electrode, a 1.0 wt.% of vinylene carbonate (97%, Aldrich) was added into the electrolyte prior to assembly of the cells. Graphite and cathode films, provided by SAFT America Inc., were dried at  $110^\circ\text{C}$  under vacuum for 16 h before use. The cathode active material was a lithium nickel-based mixed oxide. Li-ion cells and Li half-cells with an electrode area of  $0.97\text{ cm}^2$  were assembled in an argon-filled glove-box.

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A Tenney Environmental Oven Series 942 was used to provide a constant temperature environment for the tests at various temperatures. Using a Maccor Series 4000 tester, discharge capacity was measured by first charging the cell to 4.2 V at 20 °C with a time limit of 3 h, and then discharging to 2.5 V at a specific temperature. Current density for both charge and discharge processes was 0.5 mA/cm<sup>2</sup> (~0.5 C rate). To describe low temperature performance, we defined the ratio of the capacity at a specific temperature to the capacity obtained at 20 °C as a “relative capacity”, and the ratio of the resistances as a “relative resistance”.

Solartron SI 1287 Electrochemical Interface and SI 1260 Impedance/Gain-Phase Analyzer were adapted to determine the ionic conductivity of the electrolyte and to measure electrochemical impedance spectroscopy (EIS) of the cells. Before the impedance measurement was made, all cells were cycled 10 times to ensure completion of SEI formation. To assemble a symmetric cell, the electrodes were first cycled 10 times and ended at a specific state-of-charge (SOC) in Li half-cells, followed by re-assembling them into a symmetric cell in the glove-box. To ensure an identical SOC of the electrodes, the resultant symmetric cell was further electrically shorted for 2 h before impedance measurements were done. The ac impedance of the cell was potentiostatically measured by applying a dc bias with its value equal to the 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 spectra were fitted using ZView software (Scribner and Associates Inc.).

### 3. Results and discussion

#### 3.1. Low temperature cycling performance

Fig. 1 compares discharge curves of a Li-ion cell at various temperatures. It is shown that with decreasing temperature, both the operating voltage and capacity are reduced. The decreased operating voltage can be ascribed to an increased electric polarization of the cell due to a decrease in the ionic conductivity of electrolyte and SEI

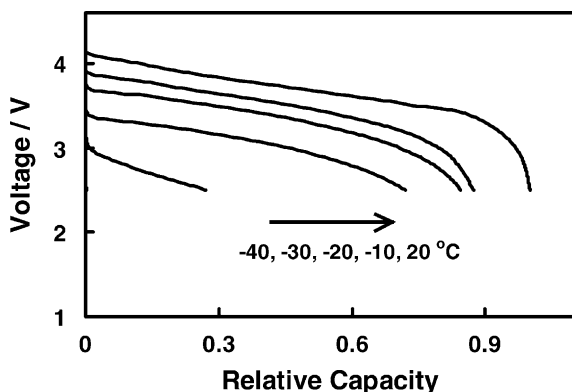


Fig. 1. Discharge curves of a Li-ion cell at various low temperatures.

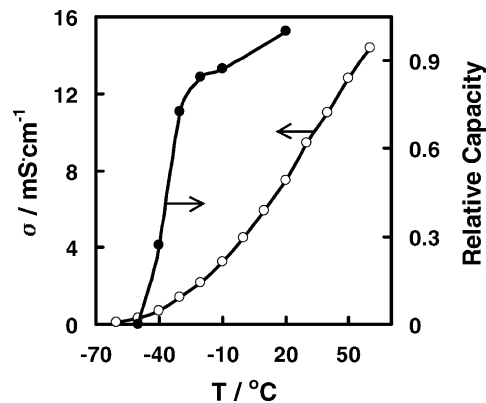


Fig. 2. Relative capacity of Li-ion cell and ionic conductivity of electrolyte as a function of temperature.

and to a slowdown of the cell electrochemical reactions. To observe the role of electrolytic conductivity in affecting cell performance, we plot electrolytic conductivity and relative capacity as a function of the temperature in Fig. 2. Due to participation of the highly compatible PC, we find that even at  $-60$  °C EC crystallization from the electrolytic solution has been suppressed. In the testing temperature range, electrolytic conductivity is changed in a continuous manner, as indicated by a smooth curve in the conductivity–temperature plot (Fig. 2). However, there exists a rapid decrease in the relative capacity as the temperature falls to below  $-10$  °C. Obviously, this rapid decrease in the relative capacity cannot be explained in terms of electrolytic conductivity. This fact reveals that electrolytic conductivity is not the only limitation in the low temperature performance of Li-ion batteries.

#### 3.2. Temperature dependence of impedances

Symmetric cells with a graphite/graphite and cathode/cathode configuration, respectively, are used to distinguish the contributions of the graphite anode and cathode to the total impedance of a Li-ion battery. Nyquist plots of Li-ion and symmetric cells at 20 °C are plotted in Fig. 3. It is apparent that the impedance spectra of the cells are composed of two semicircles and a straight sloping line, regardless of the cell configuration. Such a pattern in the impedance spectra can be simply explained by an equivalent circuit shown as an inset of Fig. 3. The  $R_b$  represents bulk resistance of the cell, which reflects electrical conductivity of the electrolyte, separator, and electrodes;  $R_{sl}$  and  $C_{sl}$  are resistance and capacitance of the surface layer, i.e. the SEI film formed on the surface of the electrodes, which corresponds to a semicircle at high frequencies;  $R_{ct}$  and  $C_{dl}$  are the Faradic charge-transfer resistance and its relative double-layer capacitance, which correspond to the semicircle at medium frequencies;  $W$  is the Warburg impedance related to a combination of the diffusional effects of lithium ion at the interface between the active material particles and electrolyte, which is generally indicated by a straight sloping line at

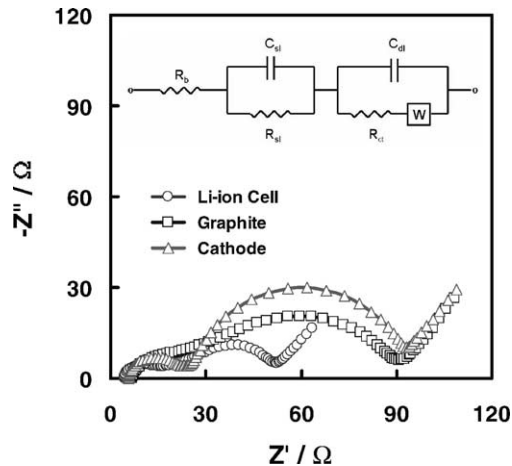
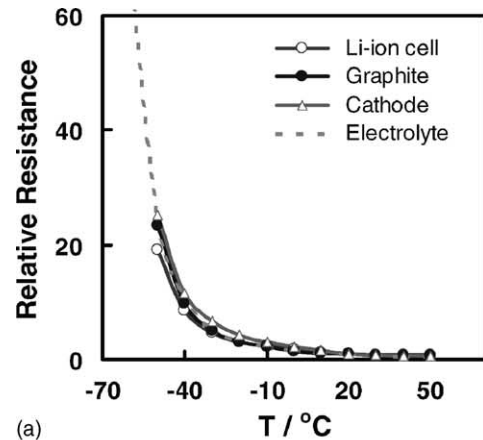


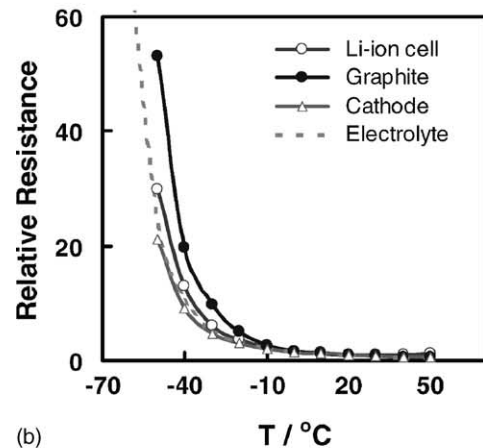
Fig. 3. Nyquist plots of charged Li-ion, lithiated graphite/graphite and delithiated cathode/cathode cells at 20 °C. Inset is an equivalent circuit used for analysis of the impedance spectra.

low frequencies. The combination of  $R_{ct}$  and  $W$  is called Faradic impedance, which reflects the kinetics of the cell reactions. Generally, the higher the  $R_{ct}$ , the slower the kinetics of the Faradic reaction. For example, as ionic diffusion of the electrode active materials becomes controlling step, the lower  $R_{ct}$  usually reflects a high apparent diffusivity of the Li ion [11]. In addition, the  $R_{ct}$  value also has been used as a kinetic parameter to compare the rate of metal corrosion [12].

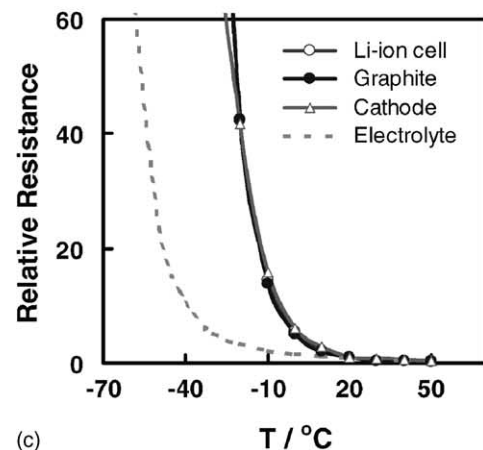
As Fig. 3 shows, the  $R_{ct}$  dominates the impedance of the cells, especially in the symmetric cells, which means that the cell impedance is mainly due to electrode reaction kinetics. Graphite and the cathode have a similar  $R_{ct}$  value, while the combined  $R_{ct}$  in a Li-ion cell is less than either the graphite or cathode cell. It is shown in Fig. 3 that at 20 °C the impedances of three different cells are comparable. Therefore, we may adopt the term of “relative resistance”, by selecting the 20 °C value as a reference, to compare temperature dependence of the impedance components. Relative resistances of the  $R_b$ ,  $R_{sl}$ , and  $R_{ct}$  for Li-ion and symmetric cells are, respectively, plotted as a function of the temperature in Fig. 4a–c. For comparison, the relative resistance of the electrolyte is also plotted. It is observed from Fig. 4a and b, that temperature dependences of the  $R_b$  and  $R_{sl}$  are roughly consistent with that of the electrolytic resistance. A significant difference in the temperature dependence can be found in the  $R_{ct}$  (Fig. 4c). The relative  $R_{ct}$  is rapidly increased around  $-10$  °C, which is almost 30 °C higher than the temperature at which the relative resistance of the electrolyte starts to increase rapidly. Comparing the temperature dependence of the relative capacity (Fig. 2) and relative  $R_{ct}$  (Fig. 4c), one may find that low temperature performance of the Li-ion batteries is most likely affected by the  $R_{ct}$  rather than the  $R_b$  and  $R_{sl}$ . Although with decreasing of the temperature, the  $R_{sl}$  of graphite is increased faster than that of the cathode (Fig. 4b), the  $R_b$  and  $R_{sl}$  are still very small in comparison with the  $R_{ct}$  so that their



(a)



(b)



(c)

Fig. 4. Comparison for temperature dependence of the relative resistance of charged Li-ion, lithiated graphite/graphite and delithiated cathode/cathode cells. The dotted curve shows “relative resistance” of the electrolyte, which is taken as the ratio of electrolytic conductivity at a specific temperature to the conductivity at 20 °C. (a)  $R_b$ , (b)  $R_{sl}$  and (c)  $R_{ct}$ .

impact on the cell performance at low temperatures is not obvious. Thus, we may conclude that the poor performance of the Li-ion batteries at low temperature originates from the substantially higher  $R_{ct}$ , which can be further ascribed to the slow kinetics of the electrode reactions.

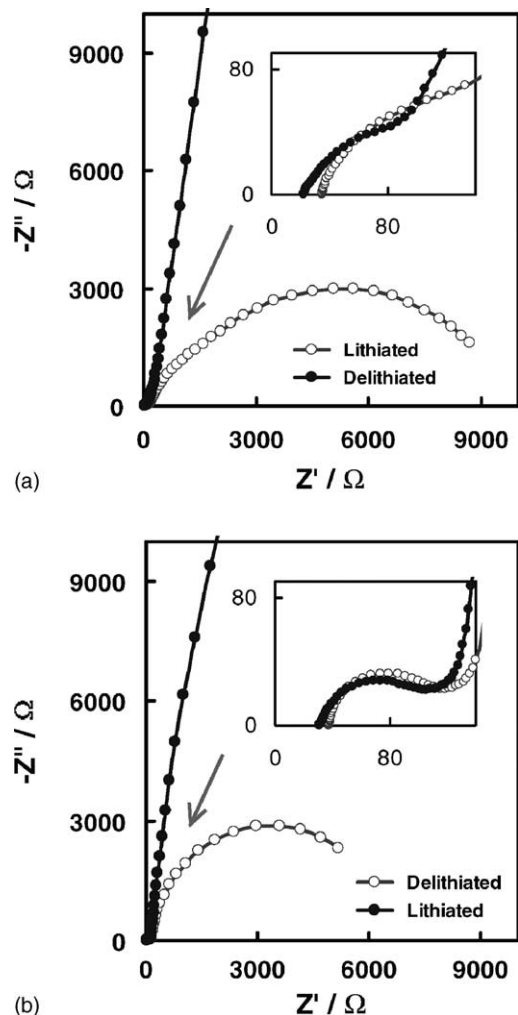


Fig. 5. Comparison for Nyquist plots of the symmetric cells with different SOC. (a) Graphite and (b) cathode.

### 3.3. Effect of SOC on impedance

Nyquist plots of the symmetric cells with different SOC are compared in Fig. 5, showing that the SOC of the electrodes greatly affects  $R_{ct}$  (Fig. 5) while having less impact on  $R_b$  and  $R_{sl}$  (see inset). In our earlier work [9,13], we found that the  $R_{ct}$ -SOC correlation is very similar to the pattern of cyclic voltammogram of the cell. That is, the minimum  $R_{ct}$  is observed in the potential regions where the current peaks appear in the cyclic voltammogram. In the cells of delithiated graphite and lithiated cathode, whose SOC corresponds to a discharged Li-ion battery, the  $R_{ct}$  is very high so that its semicircle is replaced with a straight sloping line, or a semicircle with very large diameter, at rather high frequencies (see solid symbols in Fig. 5a and b). We speculate that high sensitivity of the  $R_{ct}$  to the SOC of Li-ion battery is an origin for the performance difference between the charging and discharge processes at low temperatures. In the discharged state, the  $R_{ct}$  of Li-ion battery is substantially high, which consequently results in a high

polarization for the following charging process. As a result of the high polarization, the voltage of the cell is immediately raised to the pre-set voltage limit so that the charging fails. Therefore, at low temperatures Li-ion batteries can scarcely be charged although they can be discharged normally.

## 4. Conclusions

The cycling performance of a Li-ion battery is affected by the total impedance of the cell, which includes  $R_b$ ,  $R_{sl}$ , and  $R_{ct}$ . With decrease in temperature, the  $R_{ct}$  becomes significantly higher than  $R_b$  and  $R_{sl}$ . Therefore, at low temperatures  $R_{ct}$  is considered to be a predominant factor to influence the cycling performance of the Li-ion battery. As the  $R_{ct}$  reflects the charge-transfer process of the Faradic reactions taking place on the electrode–electrolyte interfaces, we believe that slow kinetics of the battery reactions is the major limitation to the low temperature performance of the Li-ion battery. In addition, the  $R_{ct}$  is greatly affected by SOC of the electrodes. The electrodes with their SOC corresponding to a discharged state of the Li-ion battery have a much higher  $R_{ct}$ . This would be the reason for the difference in the low temperature performance between charging and discharging process, i.e. the charging process is much more difficult than discharging.

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