

Short Communication

Cycling Stability of Li-ion Batteries at Elevated Temperature

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Cycling stability of commercial Li-ion batteries (LIBs) at elevated temperature is investigated in the present study. Galvanostatic discharge/charge cycling demonstrates that LIB shows a much faster capacity fading at 60 °C with a low capacity retention rate of 47% after 100 cycles, in contrast to the value of 97% at 25 °C. Electrochemical impedance spectroscopy indicates that the internal resistance shows a much faster increase at 60 °C than at 25 °C. Further scanning electron microscopy observation suggests that the increase of resistance is mainly originated from the thickening of the solid electrolyte interface on the anode surface. These results indicate that temperature has a significant effect on the performance of LIBs, and operation of LIBs at elevated temperature should be prevented.

Keywords: Li-ion batteries; cycling stability; temperature; impedance; scanning electron microscopy

1. INTRODUCTION

Pressing worries about energy crisis and environmental problems have led to an urgent demand for high-performance energy storage batteries [1]. Currently, Li-ion batteries (LIBs) attract a remarkable attention as energy sources for electric vehicles (EVs) [2–5]. Because of the outstanding performance including high energy densities, high power densities, and long cycle life for LIBs, the design, manufacturing, and application of LIB-based EVs are under a comprehensive development all over the world, and LIBs are considered to be the most promising candidate to alleviate our reliance on nonrenewable fuels in the future.

Besides the above-mentioned merits, one of the issues needs to be addressed for LIBs is the cycle life still calls for elongation. Such an issue is of great significance because long cycle life will be helpful for a more effective usage of LIB materials and favorable for the sustainable development of

our society. Presently, the LIBs used for EVs need to be changed after usage for a certain time. More importantly, depending on the usage conditions, the cycle life of LIBs varies significantly, which leads to uneven phenomena and causes even serious capacity fading. Therefore, it is of great significance to investigate the fading mechanism and find out the dominant factor which affects the cycle life of LIBs.

Among the various factors affecting the LIB performance, temperature plays an important role, as manifested in previous reports about coin-type Li half or full cells [6–11]. However, studies on the performance at different temperatures for commercial LIBs used for EVs are quite limited. As the EV-used LIBs have a totally different size with the coin-type cells, it is thus necessary to conduct an investigation to elucidate the effects of temperature on the performance of EV-used LIBs. In the present study, the electrochemical performance of LIBs is investigated by galvanostatic charge/discharge cycling and electrochemical impedance spectroscopy (EIS) at different temperatures. The detailed electrode surface morphology is further observed by scanning electron microscopy (SEM).

2. EXPERIMENTAL

The LIBs used for the test are commercial products (Citic Guoan MGL Co., Ltd.) with a capacity of 500 mAh, using LiFePO_4 cathode and artificial graphite anode. The electrolyte is mainly composed of LiPF_6 as conducting salt and ethylene-carbonate/ethyl-methyl-carbonate (3:7, v/v) as solvent. The galvanostatic discharge/charge cycling was performed with the voltage interval of 2.75–3.6 V at a current of 0.2C using a charge-discharge apparatus (Maccor, S4000). The temperature of LIBs was controlled with an oven (DHG-9003) and set as 25 or 60 °C. EIS spectra were recorded using Autolab PGSTAT302N workstation at cycles of 1, 50, and 100, with 50% charged state and an acoscillation voltage of 10 mV over the frequencies from 10^2 to 10^7 Hz. After 100 cycles, the LIBs were dismantled in the fully discharged state in a glove box filled with argon (Mikrouna, super, H_2O and $\text{O}_2 < 0.1$ ppm). The electrodes were rinsed with dimethyl carbonate, and then dried under vacuum at room temperature for 12 hours (DZF-6050) for the following SEM observation.

3. RESULTS AND DISCUSSION

Fig. 1 shows the cycling performance of the LIBs at 25 and 60 °C. It is observed that LIB shows a good cyclability at 25 °C, with a capacity retention rate of 97% after 100 cycles at 0.2 C. However, at a higher temperature of 60 °C, the capacity faded dramatically. The capacity retention rate is only 47% after 100 cycles. As illustrated in Table 1, the results herein is comparable with reported data [12]. The results above clearly indicate that temperature has a significant influence on the cyclability of LIBs.

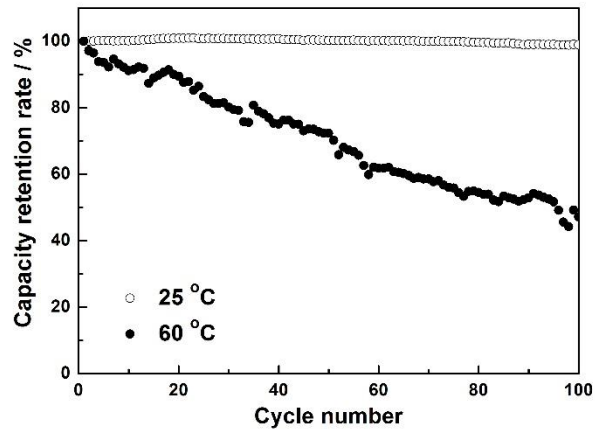


Figure 1. Cycling performance of LIBs at 25 and 60 °C.

Table 1. Comparison of capacity retention rate with reported data [12].

Cycle	This work	Reported data [12]
25	81%	84%
50	72%	76%
75	58%	63%
100	47%	55%

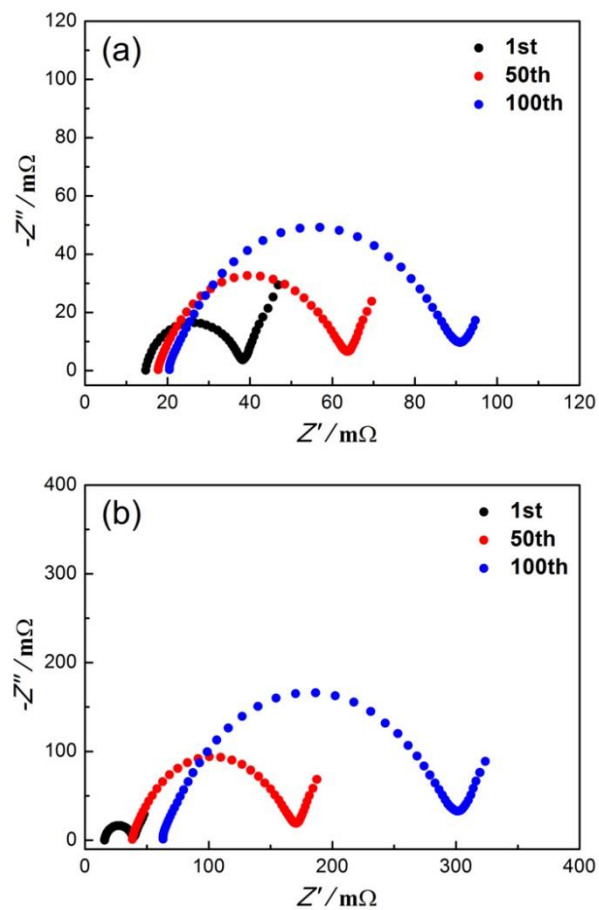


Figure 2. EIS spectra at different cycles of LIBs cycled at (a) 25 and (b) 60 °C.

To further investigate the effects of temperature, EIS spectra were recorded for the LIBs after cycled at 25 and 60 °C. Fig. 2 shows the typical EIS spectra measured at 25 and 60 °C for the LIBs at 1st, 50th, and 100th cycles. The spectrum is composed of a semicircle and a straight sloping line at low frequency end. Generally, this type of EIS spectra could be fitted with the equivalent circuit depicted in Fig. 3a [4,13]. In Fig. 3a, R_b is the ohmic resistance, which is determined by the intersection point of the semicircle at high frequency. C_{dl} and R_{ct} correspond to the semicircle, and are the double-layer capacitance and charge-transfer resistance, respectively. W , the Warburg impedance, appears as a sloping line at low frequency region, and corresponds to the solid state diffusion of Li^+ ions in the electrode.

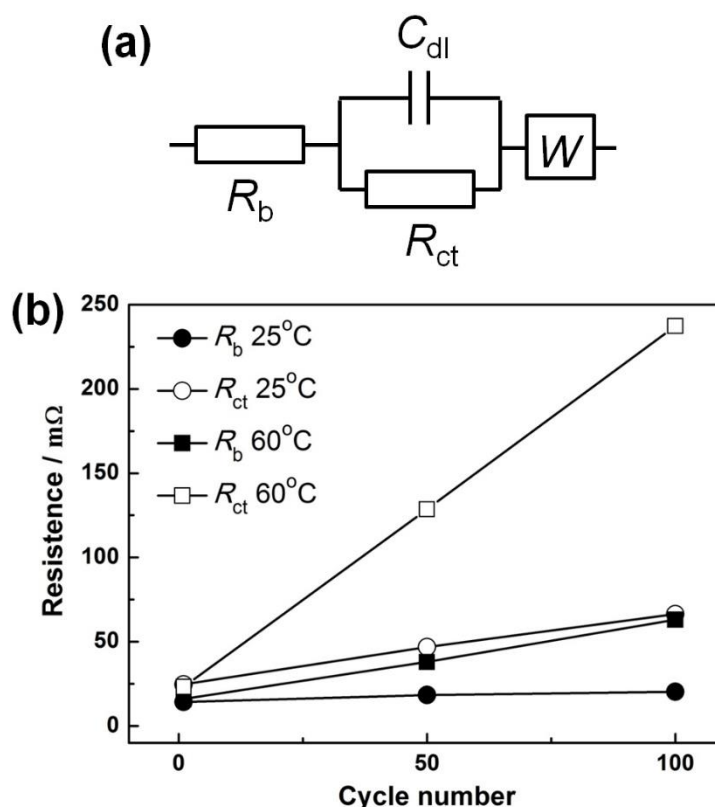


Figure 3. (a) Equivalent circuit for EIS spectra and (b) the best-fitting values of R_b and R_{ct} .

Fig. 3b shows the values of R_b and R_{ct} obtained at 25 and 60 °C. The optimum parameters were calculated by nonlinear least square fitting method for the equivalent circuit. As seen in Fig. 3b, the values of R_b at 25 °C is almost constant during the cycling, indicating there is no increase in ohmic resistances. However, the values of R_{ct} at 25 °C increase as the cycling proceeds, which could be explained by the thickening of the solid electrolyte interface (SEI) and the morphology change of the electrode. This is caused by the decomposition of the electrolyte components on the electrode surface during the cycling [14,15]. On the other hand, for the values for R_b and R_{ct} at 60 °C, a much faster increase is observed, indicating the thickening of SEI is much more serious at elevated temperature. These results are in good accordance with the cycling performance, and suggest that higher

temperature will lead to a faster increase of the resistance, and thus result in a worse cycling performance for the LIBs.

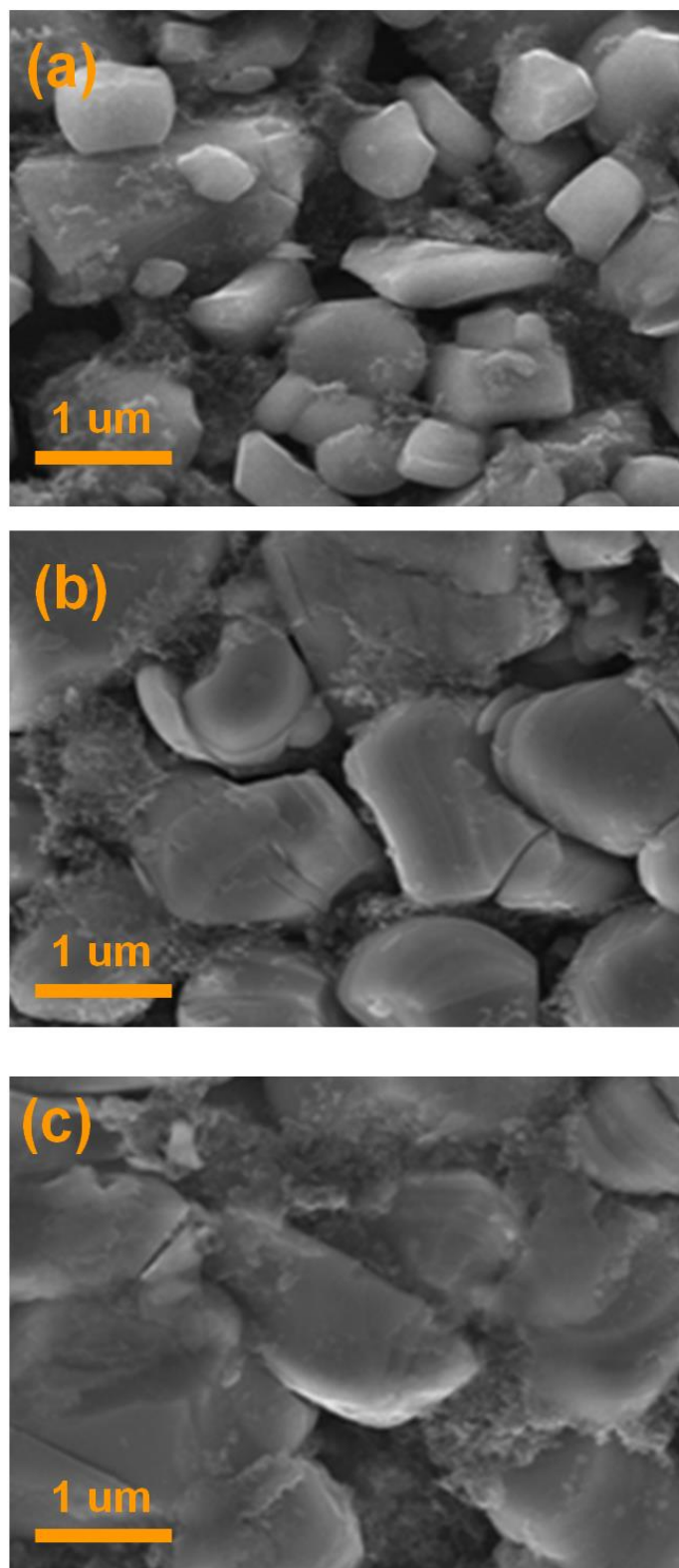


Figure 4. SEM images of cathode in the (a) fresh state, (b) at 100th cycle at 25 °C, and (c) at 100th cycle at 60 °C.

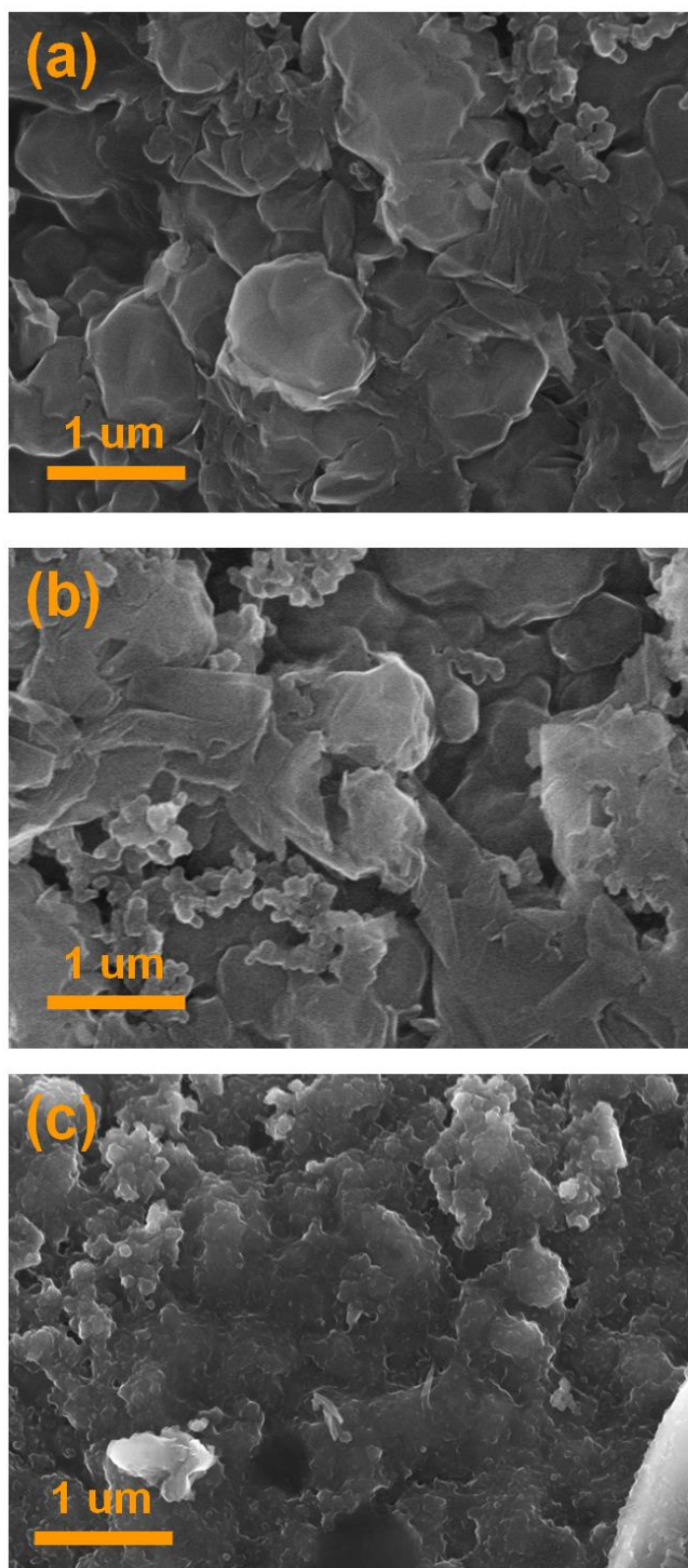


Figure 5. SEM images of anode in the (a) fresh state, (b) at 100th cycle at 25 °C, and (c) at 100th cycle at 60 °C.

SEM observation was also conducted to confirm the morphology change of the electrode after

cycling at 25 and 60 °C, and the results are shown in Figs. 4 and 5. As seen in Fig. 4a, the fresh cathode is characterized as aggregated particles with diameter of about 1.0 μm . It is found that the cathode is very stable during the cycling, and the morphology did not change obviously after 100 cycles at either 25 (Fig. 4b) or 60 °C (Fig. 4c). This is reasonable as the carbonate-based electrolyte is stable at high potential and hardly decomposes on the surface of cathode [6,7]. On the hand, the effects of temperature on the morphology change are much more obvious for the anode. As shown in Fig. 5a, the fresh graphite anode is characterized as aggregated platelets with the size of about 1.0 μm . After 100 cycles at 25 °C (Fig. 5b), the surface of the anode became vague, which is ascribed to the reductive decomposition of the carbonate-based electrolyte on the anode surface and the formation of SEI. Furthermore, after 100 cycles at a higher temperature of 60 °C (Fig. 5c), the change of the anode surface is even more obvious, indicating a more serious thickening of SEI. Based on a comprehensive investigation of EIS and SEM, it can be thus revealed that the increase of resistance is mainly due to the thickening of SEI on the anode surface, which becomes serious at high temperature and leads to a faster performance fading for the LIBs. According to some very recent reports, using anode protective layers or adding functional electrolyte additives could be effective method to extend the cycling life of LIBs at elevated temperatures [16,17].

4. CONCLUSIONS

In summary, the performance of commercial 500 mAh LIBs is investigated at 25 and 60 °C. Galvanostatic discharge/charge cycling demonstrates that LIB shows a much faster capacity fading at 60 °C with low capacity retention of 47% after 100 cycles. EIS spectra indicate that at 60 °C, the R_b and R_{ct} values show a much faster increase, indicating a more serious thickening of SEI. Further SEM observation suggests that the increase of resistance is mainly originated from the anode surface. These results indicate a high temperature will lead to a fast fading of the performance for LIBs.

ACKNOWLEDGEMENTS

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