Optimization of the forming conditions of the solid-state interface in the Li-ion batteries

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Abstract

We optimized the forming conditions of Li-ion batteries from the standpoint of the stability of the solid-state interface (SEI) on the surface of graphite. The optimization processes were focused on the initial two cycles of the Li/graphite half-cell in terms of the current density and the temperature. We evaluated the stability of the SEI from two aspects: (1) self-delithiation at 60 °C of the lithium intercalation compound, which reflects storage stability of the SEI and (2) cycling performance of the Li/graphite cell, which reflects cycling stability of the SEI. It was observed that the low current density and the low temperature favored increasing effectiveness of the SEI formation, and resulted in formation of a stable SEI. However, the SEI formed under such conditions had relatively high impedance. That is, there was a contradictory relationship between the ionic conductivity and the stability of the SEI. Based on the graphite and electrolyte used in this work, we found that the optimum conditions for the formation of the SEI were at the current densities of 10–20 mA/g and at the temperatures of 20–35 °C.
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1. Introduction

Success of Li-ion batteries is based on the formation of a so-called solid-state interface (SEI) on the surface of the graphite anode. The SEI is a layer that allows ions to move freely but isolates flow of the electrons. It has been identified that the SEI is mainly composed of the insoluble solid products of solvent reduction, which is completed in the initial few cycles [1–5]. The composition of the SEI usually is a variety of molecular moieties of the electrolytic salt and solvents such as LiF, Li_2CO_3, RCO_2Li, and lithium semi-carbonates since $LiPF_6$ and carbonates are the main components of the electrolytes of the Li-ion batteries. The most important function of the SEI is to block co-intercalation of the electrolytic solvents into the graphite plane layers so that both solvent reduction and graphite exfoliation are minimized or entirely eliminated. It has been known that Li^+ ions are able to intercalate and de-intercalate with the graphite only when a stable SEI is successfully formed. Furthermore, capacity retention and storage life of

the Li-ion batteries directly depend on the stability of the SEI [6]. Therefore, the formation of the SEI has been recognized to be an essential process in the manufacture of Li-ion batteries. Due to the above reasons, work has been conducted to understand and to improve the formation of the SEI [7–20]. From the standpoint of the materials, nearly all factors relating to the graphite and the electrolyte have been found to affect the properties of the SEI, such as, the morphology [7,8] and surface chemistry [9–11] of the graphite, as well as the solvent [12–15], salt [16–18] and additive [19,20] of the electrolyte. However, little detailed work has been published concerning the optimization of the forming conditions of the SEI.

The desired SEI must meet two requirements: highly ionic conductivity and good thermal stability. These two properties are closely associated with the morphology of the SEI, which is certainly affected by the depositing kinetics of the SEI components. Because the SEI is a layer accumulated by the insoluble solid products of solvent reduction, its morphology must be influenced by the forming conditions in the initial few cycles. Therefore, in this work we used Li/graphite half-cell to optimize the forming conditions of the SEI and studied the relationship between the forming conditions and the SEI properties.

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2. Experimental

A solution of 1.0 m LiPF$_6$ dissolved in a 3:7 (by weight) mixture of ethylene carbonate and ethylmethyl carbonate, whose properties were described elsewhere [21], was used as the electrolyte. A graphite electrode film composed of 95 wt.% natural graphite (99.9%, Alfa) and 5 wt.% poly(acrylonitrile-methyl methacrylate) (AN/MMA = 94 : 6, MW = 100, 000, Polysciences Inc.) with a copper foil as the current collector was used to assemble Li/graphite half-cells [22]. Before use, the graphite electrode was punched into small disks with an electrode area of 1.27 cm^2 and dried at 110 °C for 16 h under vacuum. In an argon-filled glove box with both water and oxygen contents of less than 20 ppm, BR2335-type Li/graphite button cells were assembled and filled with 100 μl of the liquid electrolyte.

A Tenney Environmental Oven Series 942 was used to provide the constant temperature environment for the forming and storage tests. A Solartron SI 1287 Electrochemical Interface and a SI 1260 Impedance/Gain-Phase Analyzer were used to measure the impedance of the cells with an ac oscillation of 10 mV amplitude over the frequencies from 100 kHz to 0.01 Hz. A Maccor Series 4000 tester was used to perform cycling tests and to record open-circuit voltage (OCV) of the cells. The testing conditions were described either in the text or in the figure captions.

3. Results and discussion

3.1. Effect of the current density

It is known that formation of the SEI on the surface of graphite must be completed during the initial few cycles. In most of cases, Coulomb efficiency (CE) of the cycling of the Li$^+$ ions with graphite often approaches 100% in the second cycle unless a stable SEI cannot be formed. Therefore, in this work we used the CE of the second cycle to evaluate degree of the formation of the SEI. Typical voltage curves of the initial two cycles for the Li/graphite cells are displayed in Fig. 1. It is shown that reversible cycling of the
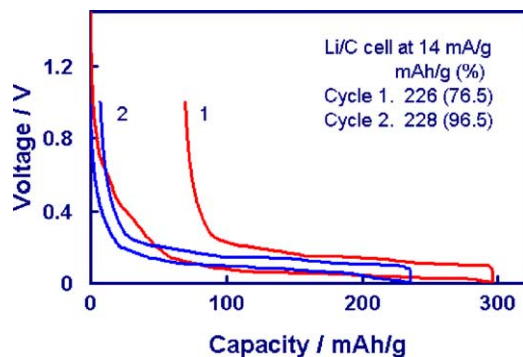

Fig. 1. Typical voltage curves of the initial two cycles for the Li/graphite cell, which were recorded at 14 mA/g.
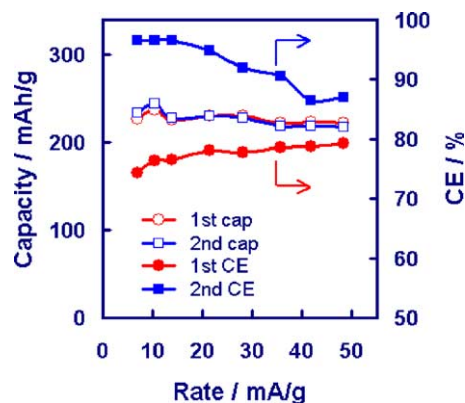

Fig. 2. Effect of the current density on the Coulomb efficiency and reversible capacity of the initial two cycles for the Li/graphite cells. Current density was 14 mA/g.

intercalation and de-intercalation of Li$^+$ ions takes place between 0 and 0.3 V, and that the graphite has a specific capacity of 225–230 mAh/g. The CE of the cycling was 76.5% in the first cycle and increased to 96.5% in the second cycle. The much lower CE in the first cycle is due to the irreversible reduction of the electrolytic solvents, which would be most significantly affected by the catalytic effect of the fresh surface of the graphite. A substantial increase of the CE in the second cycle is probably because the catalytic effect of the graphite was invalided as a result of the insoluble products covering the catalytic sites during the first cycle, which suppresses solvent co-intercalation and graphite exfoliation.

Fig. 2 exhibits the effect of current density on the CE and reversible capacity of the initial two cycles for the Li/graphite cells. It is shown that the current density has little impact on the capacity while it significantly affects the CE. The CEs of the first and second cycles are changed with the current density in a reverse trend. With an increase in the current density, the CE of the first cycle is slowly increased while that of the second is dramatically decreased. We observed that the SEI could be effectively formed only when the current density was not higher than 15 mA/g, as indicated by the CE of near 100% in the second cycle. This observation can be ascribed to the effect of the current density on the morphology of the SEI. The formation of the SEI is involved in both the processes of nucleation and growth. A high nucleation rate, which corresponds to a high current density, results in the SEI with loose texture and poor adhesion to the surface of graphite. Such an SEI cannot well protect the electrolytic solvents from the further reduction. On the other hand, the formation of the SEI was accompanied by two reverse processes of the growth and the dissolution back to the electrolytic solution. When the current density was low, the dissolution process became obvious since the preliminarily formed SEI has a longer time to expose itself to the electrolytic solution. Therefore, the CE of the first cycle was gradually decreased with a decrease in the current density.
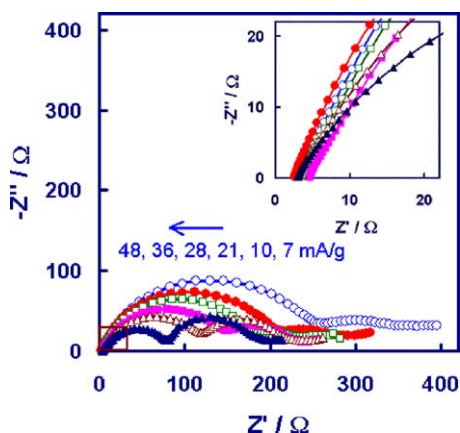
Fig. 3. Nyquist plots of the Li/graphite cells at the fully lithiated state, in which the inset shows an enlarged part of the plots at high frequency end. Before the impedance measurement, all cells were cycled 10 times to ensure a complete formation of the SEI.

Fig. 4. Self-delithiation at 60 °C of the Li/graphite cells, which were formed at different current densities.

Fig. 3 compares impedance spectra of the Li/graphite cells, which were measured at the fully lithiated state after the cells were cycled 10 times. As discussed previously [5], the semi-circle at high frequency regions reflects the impedance of the SEI. We might see from Fig. 3 that the resistance of the SEI was regularly decreased with increasing of the current density. Again, this observation can be explained in terms of the morphology of the SEI. As stated in the introduction, the SEI is composed of the insoluble solid products of the solvent reduction. Such a solid layer by itself is non-conductive. Its ionic conductivity must be incorporated by the liquid electrolyte, which is distributed throughout the pores of the SEI. It is the distributed liquid electrolyte that provides the source of ionic conductivity for the SEI. When a high current density was applied, the resulting SEI was more loose (or porous) and less adhesive, which allows more liquid electrolyte to be incorporated. Therefore, the SEI such-formed has relatively higher ionic conductivity.

Storage stability of the SEI can be determined by recording the open-circuit voltage change of a fully lithiated Li/graphite cell. In order to achieve the same state-of-lithiation, we held all the cells at 0.002 V for 5 h then started to record their OCV as a function of the storage time. Fig. 4 compares the storage performance at 60 °C of the fully lithiated Li/graphite cells, which were formed at different current densities. In the testing period (100 days), we observed that the OCV slowly increased with the storage time roughly through two voltage plateaus, in which the second plateau still kept extending as the pre-scheduled testing program ended the experiment. In previous works [23,24], we have found that the above-described increase in the OCV corresponds to a self-delithiation process of the lithium intercalation compound, which directly reflects the storage stability of the SEI. Results of Fig. 4 suggest that after 100-day storage at 60 °C all the cells still retained charge at the second stage (i.e., $LiC_{12} \Leftrightarrow LiC_{18}$), showing excellent stability of the SEI. From the standpoint of the

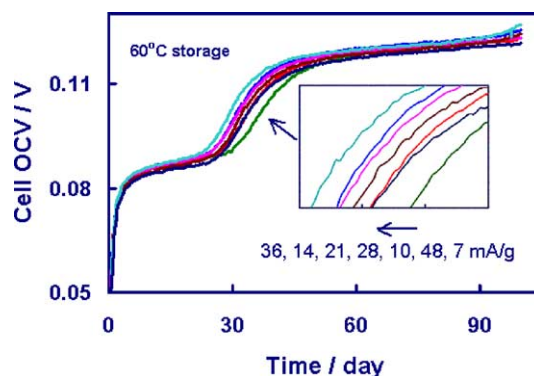OCV change, we considered that the current density of the forming process has no visible impact on the storage stability of the SEI.

After 100-day storage testing at 60 °C, all the cells were delithiated by charging them to 1.5 V at a constant current density of 14 mA/g. Fig. 5 records voltage curves of the immediate delithiation process for these cells. Setting the curve at 48 mA/g aside, we find that the low current density favored increasing capacity retention. This observation roughly accords with the result in Fig. 2, which indicates that the low current density favors increasing effectiveness of the SEI. After the above tests, the cells were further cycled between 0.002 and 1.0 V at a constant current density of 55 mA/g. Fig. 6 plots delithiating capacities of these cells as a function of the cycling number. It is obvious that the delithiating capacity is increased with a decrease in the current density for the formation of the SEI although all these cells remained at constant capacity (250–270 mAh/g, respectively) for 200 cycles. Summarizing the results of Figs. 2–6, we may conclude that the optimized current density for the formation of the SEI should be 10–20 mA/g. The low current density produced a more resistive SEI (Fig. 3) and needed a longer forming time. While the high current density resulted in insufficient formation, as indicated by the decreased CE of the
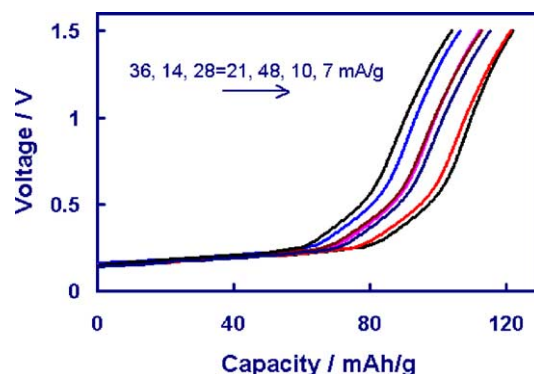

Fig. 5. Retained capacity of the Li/graphite cells after 100-day storage at 60 °C, which was measured at 14 mA/g.
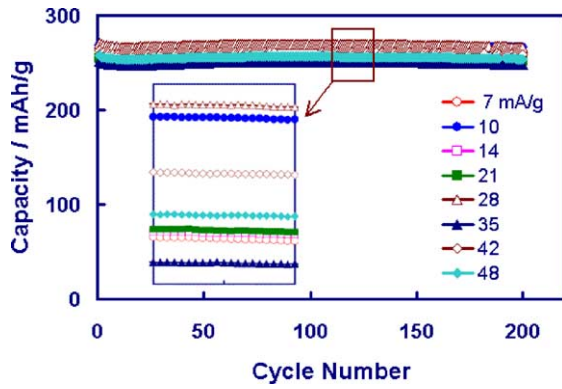
Fig. 6. Delithiating capacities of the Li/graphite cells formed at different current densities as a function of the cycling number. Current density was 55 mA/g.

second cycle in Fig. 2, and resulted in relatively low capacity (Fig. 6).

3.2. Effect of the temperature

Using the same approaches as described in Section 3.1, we evaluated the effect of the forming temperature on the CE and reversible capacity of the Li/graphite cells. It is shown in Fig. 7 that the CEs of both the first and second cycles were decreased with an increase in the temperature. Especially, the ones of the first cycle were more sensitive to the temperature. However, it appears that the temperature has little impact on the reversible capacities. The above phenomena can be explained as the effect of the temperature on the dissolution of the preliminarily formed SEI. As discussed in Section 3.1, the formation of the SEI is accompanied by two reverse processes: increased growth and decreased dissolution. The growth relates to a process of electrochemical-induced reduction of the electrolytic solvents, which is less sensitive to the temperature. In contrast, an increase in the temperature greatly accelerates dissolution of the preliminarily formed SEI into the electrolytic

Fig. 8. Nyquit plots of the Li/graphite cells at the fully lithiated state, in which the inset shows an enlarged part of the plots at high frequency end. Before the impedance measurement, all cells were cycled 10 times to ensure a complete formation of the SEI.

solution. It is judged from Fig. 7 that the suitable temperature range for the formation of the SEI should be between 20 and 35 °C. Lower temperature (<20 °C) may increase the initial CE, however, it would result in a direct deposit of the metal lithium due to the high electric polarization [25].

There is a close relationship between the SEI impedance and the forming temperature (Fig. 8). A general rule is that the impedance of the SEI is decreased with an increase in the forming temperature. This is probably because the SEI formed at high temperatures is more porous, which likely is associated with the increased dissolution of the preliminarily formed SEI. In such a case, the ionic conductivity of the SEI is mainly contributed by the absorbed liquid electrolyte. Unfortunately, the highly conductive SEI does not result in good performance, as described in the next text.

Figs. 9 and 10 show the impact of the forming temperature on the storage performance of the Li/graphite cells. It is clearly indicated that the storage performance of the Li/graphite cells was increased in the order of 60 < 45 < 20 < 35 °C. The cell formed at 60 °C suffered the fastest self-delithiation although its corresponding SEI exhibited
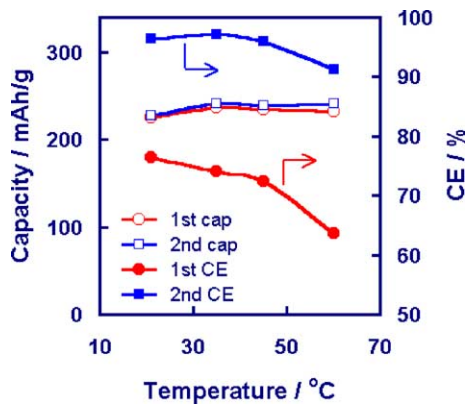

Fig. 7. Effect of the forming temperature on the Coulomb efficiency and reversible capacity of the initial two cycles for the Li/graphite cells. Current density was 14 mA/g.
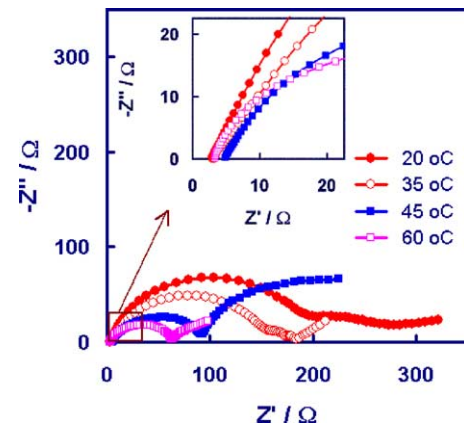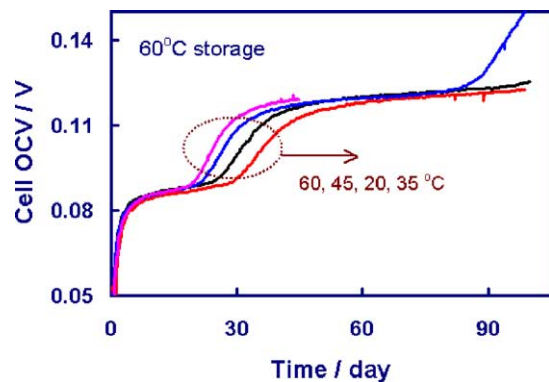

Fig. 9. Self-delithiation at 60 °C of the Li/graphite cells, which were formed at different temperatures.
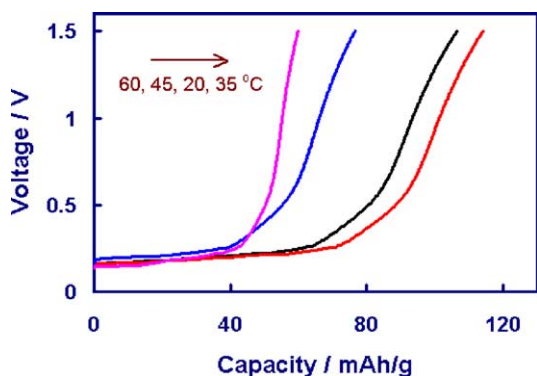
Fig. 10. Retained capacity of the Li/graphite cells after 100-day storage at 60 °C, which was measured at 14 mA/g.
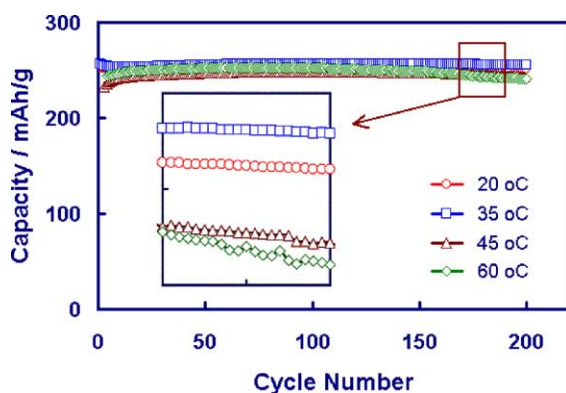

Fig. 11. Delithiating capacities of the Li/graphite cells formed at the different temperatures as a function of the cycling number. Current density was 55 mA/g.

the highest ionic conductivity (Fig. 8). That is, there is a contradictory relationship between the ionic conductivity and the stability of the SEI. Summarizing the results of Figs. 8–10, we found that the optimized SEI could be formed at 35 °C. Such an SEI not only had satisfactorily ionic conductivity (Fig. 8) but also had good stability (Figs. 9 and 10).

Stability of the SEI was further evaluated by galvanostatic cycling test (Fig. 11). In the beginning, we did not find any difference caused by the forming temperature. Starting from ~150th cycle, however, the capacity of the cells formed at 45 and 60 °C, respectively, started accelerated fading. This observation is consistent with the results of the storage testing, as shown in Figs. 9 and 10.

4. Conclusions

In this work, the forming conditions of the SEI on the surface of graphite were optimized in terms of the current density and the temperature. We found that the forming conditions vastly affected the Coulomb efficiency, ionic conductivity and storage stability of the SEI. However,

there was not a direct relationship between the above three parameters. In general, the high current density and high temperature favored increasing the ionic conductivity of the SEI. However, such conditions resulted in low effectiveness of formation, i.e., more cycles are needed for the formation of the necessary SEI. There was a contradictory relationship between the ionic conductivity and the stability of the SEI. From the standpoint of the storage life and cycling stability of the graphite electrode, the optimized forming conditions would be in a current density range of 10–20 mA/g and a temperature range of 20–35 °C. It should be noted that the optimized conditions might vary with many factors, such as the type of graphite and electrolyte, as well as the electrode loading, battery design and so forth.

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