Two-and three-electrode impedance spectroscopic studies of graphite electrode in the first lithiation

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Two- and three-electrode impedance spectroscopic studies of graphite electrode in the first lithiation

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The first lithiation of graphite electrode was investigated by electrochemical impedance spectroscopy (EIS) and scanning electron microscope (SEM) in a two-electrode button cell and a three-electrode glass cell. The results demonstrate that the study of the variation of EIS feature of the graphite electrode in the two-electrode button cell with electrode polarization potential decreasing in the first lithiation cannot be used to investigate the formation mechanism of the solid electrolyte interphase (SEI) film. However, the formation and growth process of the SEI film can be acquired by investigating the variation of EIS features of the graphite electrode in the three-electrode glass cell with the decrease of electrode polarization potential in the first lithiation. Moreover, the results also point out that the SEI film on graphite electrode is mainly formed between 1.0 and 0.6 V in the first lithiation.

lithium-ion batteries, graphite electrode, electrochemical impedance spectroscopy, solid electrolyte interphase

Electrochemical impedance spectroscopy (EIS) is one of the most important electrochemical techniques which can provide unique information about the nature of electrode processes relating to a wide time constant (demonstrated in terms of frequencies in EIS). It was widely applied, in the past 10 years, to the studies of electrochemical lithium intercalation into carbonaceous materials and transition metal oxides[1–5]. According to Aurbach and co-workers[6], lithium insertion involves several processes that occur in series: diffusion of lithium ion in solutions, charge transfer, migration of lithium ions through the surface films covering the graphite particles, charge transfer, solid state diffusion of lithium ions into the graphite often described as finite space or restricted diffusion. EIS can reflect all the above processes by their different time constants, and is therefore a suitable technique of investigations. The main problem remaining in the practical application of EIS is its ambiguity: many physically different procedures or separate stages of a complicated process show similar features in terms of impedance spectroscopy. A classical electrochemical system contains processes such as electron-transfer, dif-

fusion, and absorption of reacting species, and to discern these processes may be easy if all absorption sites have the same energy, i.e. the electrode surface is energetically homogeneous. However, the processes occurring in practical ion-insertion electrodes are much more complicated compared to the classical systems. The practical ion-insertion electrodes are composite materials, in which the active mass particles are bound to a copper current collector with a polymeric binder such as poly-vinylidene difluoride (PVdF). In addition, the composite electrodes have to contain a conductive additive, usually carbon black. The electrodes are usually prepared from slurry of the particles and the binder in an organic solvent, which is spread on the current collector, followed by drying. The final shape of the electrode is obtained by applying some pressure to the electrode. So the shape and value of the resistance in the impedance spectrum should be affected by the amount of conductive additive

in the composite materials, the contact between the electrode film and the current collector, the solvent, particle size, thickness of electrode, and stack pressure[7,8]. Without systematic and integrated comparison of EIS spectra of these processes, incorrect interpretation may arise. In this work, therefore, impedance studies have been carried out in both two-electrode and three-electrode Li-C systems, and the variation of impedance with the decrease of the electrode polarization potential in the first lithiation has been analyzed.

1 Experimental

All electrochemical experiments were conducted in either a two-electrode button cell or a three-electrode glass cell with Li foils as both auxiliary and reference electrodes. The graphite electrode used in this study was prepared by spreading a mixture of 90% mesophase-pitch-based carbon fibers (Petoca, Japan) and 10% polyvinylidene fluoride (Kynar FLEX 2801, Elf-atochem, USA) binder dissolved in N-methyl pyrrolidone (Fluka Inc.) onto a Cu foil (thick: 20 μm) current collector. The electrolyte consists of 1 mol·L^{-1} LiPF$_6$ in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (1:1:1, volume ratio, Guotaihuarong Co., Zhangjiagang, China).

The morphology of graphite electrode was investigated by scanning electron microscope (LEO 1530 Field Emission Scanning Electron Microscope (SEM, Oxford Instrument). EIS measurements were carried out with an electrochemical work station (CHI 660B, Chenhua Co, Shanghai, China). The amplitude of ac perturbation signal was 5 mV and the frequency range varied from 10^5 to 10^{-2} Hz. The electrode was equilibrated for 1 h before the EIS measurements, in order to attain steady state conditions.

2 Results and discussion

## 2.1 SEM analysis of graphite electrode

Figures 1 and 2 show SEM images of the graphite electrode before and after the electrode has been subjected to charge-discharge cycles. As shown in Figure 1(a) and (b), smooth surfaces of the graphitie electrode are observed, which imply that no SEI film is formed before the charge-discharge cycles. After the charge-discharge cycles, granular solids on the surfaces of the graphte electrode subjected to charge-discharge cycles were clearly observed, as illustrated in Figure 2. Apparently, the insoluble granules arise from the decomposition of EC. The enlarged SEM image (Figure 2(b)) further indicates that the decomposition product of EC deposited on the surface of the graphite electrode was sheet-like.

2.2 EIS analysis of the electrodes during the first lithiation in different cells

Nyquist plots of graphite electrode during the first lithiation at various potentials (3.0−1.0 V) in 1 mol·L^{-1} LiPF$_6$-EC:DEC:DMC electrolyte are shown in Figure 3. It can be seen from Figure 3(a) that the Nyquist plots of graphite electrode in the two-electrode button cell at open circuit potential (3.0 V) show an arc in the high-frequency (HF) range and a slightly inclined line in the low-frequency (LF) region which represents the blocking character of the nonlithiated electrode at equilibrium potential. These observations are in accordance with the results reported by Holzapfel et al[9]. obtained in a three-electrode button cell, indicating that without using an additional lithium foil as reference electrode in the button cell does not affect significantly the EIS features. With the decrease of the electrode polarization potential, the diameter of the HF arc increases by above 1.5 V, and
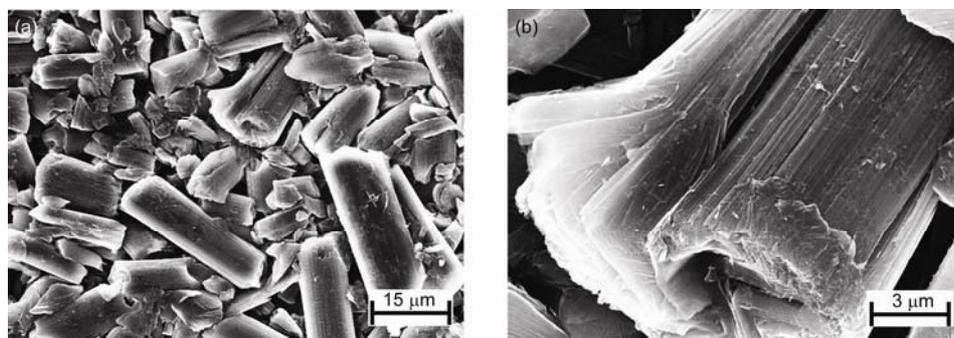
Figure 1   SEM images of the graphite electrode magnified by 1000 (a) and 5000 (b) times before charge-discharge cycles.
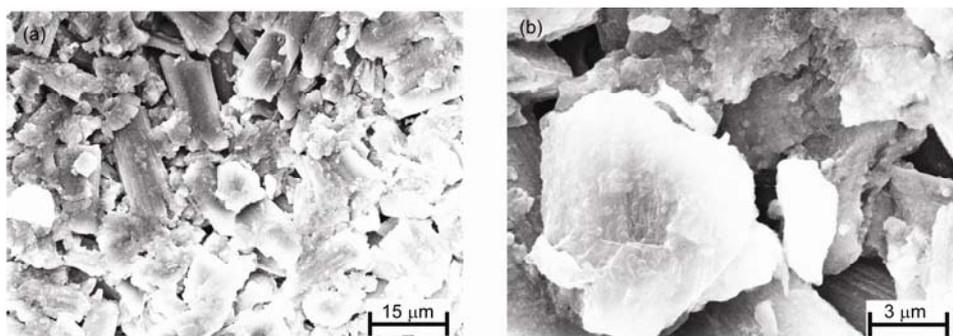
Figure 2 SEM images of the graphite electrode magnified by 1000 (a) and 5000 (b) times after charge-discharge cycles.

remains invariant between 1.5 and 1.1 V. According to Aurbach and co-workers [6,10–12], the HF arc is related to SEI film (the resistance of SEI film coupled with SEI film capacitance). If we presume that the HF arc in the Nyquist plots recorded with the two-electrode button cell in this study is mainly related to the SEI film, at least two important aspects can not be interpreted properly: (1) As illustrated by the SEM results, no SEI film is formed on the surface of graphite electrode before electrochemical scan cycles, thus there should be no HF arc in the Nyquist plots at open circuit potential. (2) According to the cyclic voltammetry results reported by our group in early studies[13], the SEI film is mainly formed between 1.0 and 0.5 V. However, it is observed that the diameter of the HF arc in the Nyquist plots of graphite electrode in the two-electrode button cell increases rapidly with the decrease of electrode polarization potential between 3.0 and 1.5 V. As a result, the HF arc in the Nyquist plots of graphite electrode in the two-electrode button cell could not be attributed to the SEI film, but it should be related to contact problem reported in literature [9,14,15]. The increase in diameter of the HF arc in the Nyquist plots of graphite electrode in the two-elec-

trode button cell may be related with the increase of storage time of graphite electrode in electrolyte solution or due to the reduction of the contaminant of the electrolyte solutions, such as water, which results in the increase of the contact resistance.

As can be seen from Figure 3(b), the Nyquist plots of graphite electrode in the three-electrode glass cell during the first lithiation at open circuit potential (3.0 V) are different from those in the two-electrode button cell, i.e. no arc can be observed in the high-frequency region, which corresponds to the SEM result that there is no initial SEI film on the graphite electrode before lithiation. With the decrease of the electrode polarization potential, the sloping line bends toward the real axis and forms a semicircle at 2.0 V, and the Nyquist plots at 1.5 and 1.0 V are similar, which include an arc in the high frequency region and an inclined straight line in the low-frequency region. However, there is no HF arc appearing in Nyquist plots of graphite electrode in the three-electrode glass cell above 1.0 V. The above results illustrate that the formation and growth of the SEI film due to electrolyte reduction decomposition do not happen to the gra-
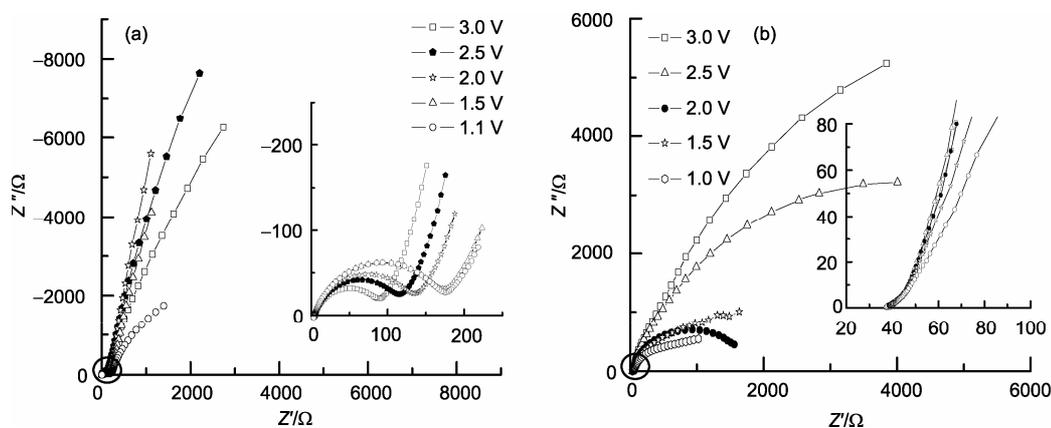
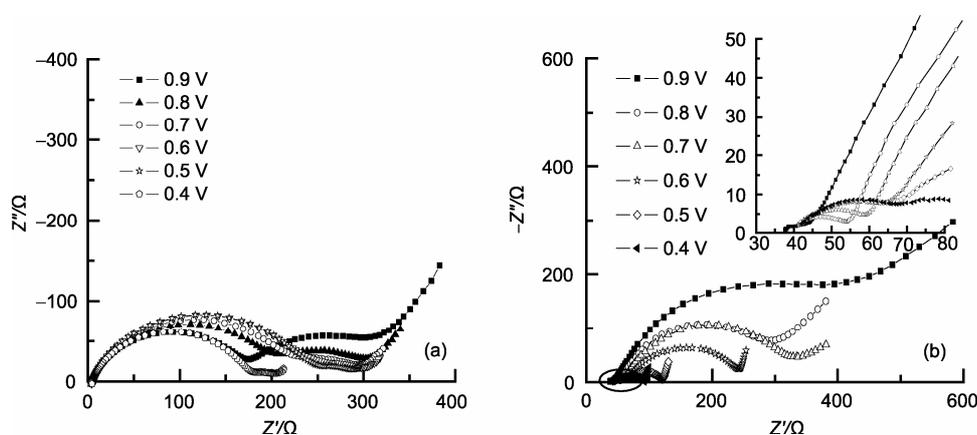

Figure 3 Nyquist plots of graphite electrode during the first lithiation at various potentials (3.0 — 1.0 V) in 1 mol·L^{-1} LiPF$_6$-EC：DEC：DMC electrolyte in different cells. (a) Two-electrode button cell; (b) three-electrode glass cell.

phite electrode when the electrode polarization potential is above 1.0 V, and also that the HF arc commonly appearing in the Nyquist plots of graphite electrode in the two-electrode button cell can be eliminated by the three-electrode glass cell.

If the HF arc in the Nyquist plots of graphite electrode in the two-electrode button cell is related not only to the contact problem, but also to the SEI films, an increase of the associated resistance at potentials between 1.0 and 0.5 V would be expected, where the SEI film formation is considered to occur according to the cyclic voltammetry results. But Chang et al[14,15]. reported that no important modification of the impedance graph can be noticed in the HF region during the first cathodic polarization of their graphite in the potential zone from 1.0 to 0.5 V. Whereas our results are quite different. Figure 4 shows the Nyquist plots of graphite electrode during the first lithiation at various potentials between 0.9 and 0.4 V in 1 mol·L^{-1} LiPF$_6$-EC：DEC：DMC electrolyte. As can be seen in Figure 4(a), the Nyquist plots of graphite electrode in the two-electrode button cell below 0.9 V consist of three parts, namely, the first arc in the highfrequency range, the second arc in the medium frequency (MF) range commonly ascribed to the charge transfer step, and an incline line in the low frequency range reflecting the solid state diffusion process of lithium ions into graphite materials. The diameter of the HF arc in the Nyquist plots of graphite electrode in the two-electrode button cell increases with the decrease of electrode polarization potential from 0.9 to 0.6 V. One may infer that the HF arc appearing in the Nyquist plots of graphite electrode in the two-electrode button cell below 0.9 V is related not only to the

contact problem, but also to the SEI films. In further charging process, the diameter of the HF arc remains almost invariant in the potential zone between 0.6 and 0.5 V, and decreases in the potential zone between 0.5 and 0.4 V. Thus it can be deduced that the decrease in diameter of the HF arc in the potential zone between 0.5 and 0.4 V may result from the variation of the contact resistance, because the resistance of the SEI film should increase or remain invariant with electrode polarization potential decreasing. As a consequence, the variation of the resistance of the SEI film with electrode polarization potential decreasing can not be discerned concretely, since the contact resistance varies with the decrease of electrode polarization potential.

It can be observed from Figure 4(b) that the unique feature of the Nyquist plots of graphite electrode in the three-electrode glass cell during the first lithiation at 0.9 V consists in that a depressed small semicircle appears in the high-frequency region and its diameter increases with the decrease of electrode polarization potential, which is much different from the Nyquist plots of graphite electrode in the two-electrode button cell during the first lithiation below 0.9 V. The observations correspond to a generally accepted fact that the SEI film is formed at potentials between 1.0 and 0.8 V due to the decomposition of electrolyte solution species such as EC[16–18]. Consequently, the unique explanation accounting for these observations is that the first arc in the high-frequency region observed in the Nyquist plots of graphite electrode in the three-electrode button cell should be related to the SEI film. The Nyquist plots at and below 0.9 V are similar, consisting of three parts: the HF arc relating to the SEI film, the MF arc relating to the charge

Figure 4 Nyquist plots of graphite electrode during the first lithiation at various potentials (0.9−0.4 V) in 1 mol·L^{-1} LiPF$_6$-EC：DEC：DMC electrolyte in different cells. (a) Two-electrode button cell; (b) three-electrode glass cell.

transfer step and the double layer capacitance, and the declined line in the low frequency region corresponding to diffusion phenomena. With the decrease of electrode polarization potential, the diameter of the HF arc in the Nyquist plots of graphite electrode in the three-electrode glass cell increases rapidly with electrode polarization potential decreasing from 1.0 to 0.6 V, indicating that the SEI film is rapidly formed on the surface of the graphite electrode, and the thickness of the SEI film also increases rapidly at the above potential region. When the electrode potential is changed from 0.6 to 0.4 V, the diameter of the HF arc in the Nyquist plots of graphite electrode in the three-electrode glass cell remains almost invariant, implying that a highly passivating SEI film has been formed on the surface of the graphite electrode. Such an SEI film can effectively prevent EC decomposition, and confirm that the SEI film of graphite electrode during the first lithiation is mainly formed in the potential region between 1.0 and 0.6 V, in accordance with the cyclic voltammetry results reported previously[13].

Figure 5 shows the Nyquist plots of graphite electrode during the first lithiation at various potentials (0.3－0.1 V) in 1 mol·L^{-1} LiPF$_6$-EC：DEC：DMC electrolyte. It can be seen from Figure 5(a) that, the diameter of the HF arc in the Nyquist plots of graphite electrode in the two-electrode button cell increases from 0.3 to 0.2 V, and decreases from 0.2 to 0.1 V, indicating that the variation of contact resistance depends significantly on the electrode polarization potential, and is randomly distributed. However, the diameter of the HF arc in the Nyquist plots of graphite electrode in the three-electrode glass cell remains almost invariant in potential region of 0.3－0.1 V, which is similar to that at potential region of 0.6－0.4 V. These results demonstrate that the SEI film

remains stable in potential region of 0.3－0.1 V, ensuring that the lithium ion can intercalate and de-intercalate into the graphite electrode reversibly. The above results and discussion demonstrate that the HF arc in the Nyquist plots of graphite electrode in the two-electrode button cell is related not only to the contact problems, but also to the SEI films, and the contact resistance can not remain invariant. Therefore, the study of the variation of EIS features of graphite electrode in the two-electrode button cell with the decrease of electrode polarization potential in the first lithiation can not be used to investigate the formation mechanism of the SEI film. Only when the contact resistance is eliminated, can the study of the variation of EIS features of graphite electrode with the decrease of electrode polarization potential in the first lithiation be used to investigate the formation mechanism of the SEI film. The HF arc in the Nyquist plots of graphite electrode in the three-electrode glass cell is related uniquely to the SEI films, so the formation and growth process of the SEI film can be obtained by analyzing the variation of EIS features of graphite electrode with the decrease of electrode polarization potential in the first lithiation.

3 Conclusions

The first lithiation of the graphite electrode was investigated by EIS and SEM in a two-electrode button cell and a three-electrode glass cell. The results demonstrate that the HF arc in the Nyquist plots of graphite electrode in the two-electrode button cell is related not only to the contact problems, but also to the SEI films, and the contact resistance can not remain invariant. Therefore, the variation of EIS feature of graphite electrode in the
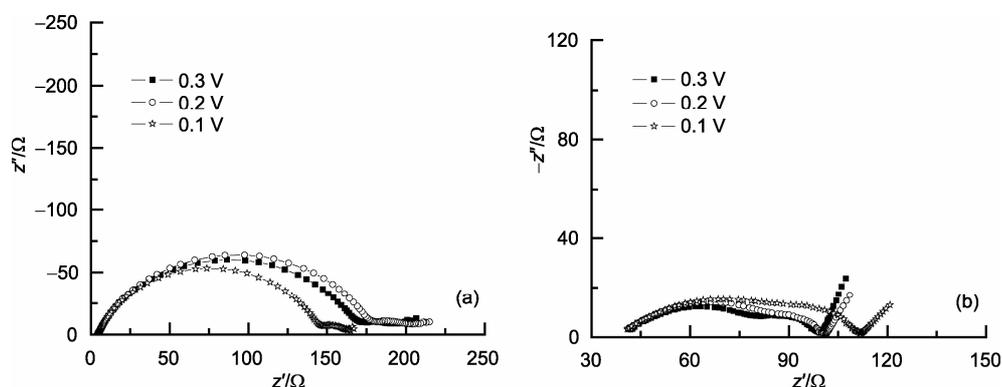
Figure 5 Nyquist plots of graphite electrode during the first lithiation at various potentials (0.3－0.1 V) in 1 mol·L^{-1} LiPF$_6$-EC:DEC:DMC electrolyte in different cells. (a) Two-electrode button cell; (b) three-electrode glass cell.

two-electrode button cell with the decrease of polarization potential in the first lithiation cannot be used to investigate the formation mechanism of the SEI film. However, the contact problem can be effectively eliminated in the three-electrode glass cell, thus the formation and growth process of the SEI film can be obtained by investigating the variation of EIS features of graphite electrode with the decrease of polarization potential in the first lithiation. Moreover, the results also point out that the SEI film of graphite electrode during first lithiation is mainly formed in the potential range of $1.0-0.6$ V.

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