

Studies of the first lithiation of graphite materials by electrochemical impedance spectroscopy

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Abstract First lithiation of graphite electrode in 1 mol/L LiPF₆-EC:DEC:DMC electrolyte was investigated by electrochemical impedance spectroscopy (EIS). The results illustrated that the first arc in the high-frequency range observed in the Nyquist diagram appears near 0.9 V in the initial lithiation of graphite electrode, and its diameter increases with the decrease of polarization potential. These EIS features were attributed to the formation and growth of SEI film. Appropriate equivalent circuit was proposed to fit the experimental EIS data. The fitting results revealed the process of the formation and growth of SEI film, and evaluated quantitatively the resistance of charge transfer, as well as the capacitance of double layer along with the increase of polarization potentials.

Keywords: lithium-ion batteries, impedance, graphite, SEI film.

Recently, lithium-ion batteries have attracted intensive research interests, especially with respect to the complex interfacial reactions between electrolyte and electrode. Carbonaceous materials are most widely employed as negative materials for lithium-ion batteries because lithium can randomly and stably intercalate or de-intercalate into them^[1]. During the first cathodic polarization (charge of the lithium-ion batteries), carbon-based negative electrodes undergo a surface passivation process at the interface with electrolyte. The passive film (also called solid electrolyte interphase,

SEI) growing in this process plays an important role in the cycleability of the negative electrode. The SEI film prevents lithium from being intercalated in the solvated state, which leads to the exfoliation (swelling) of the carbon. In addition, the SEI film also inhibits the further reduction of electrolyte by active lithium and thus limits the degradation of the electrolyte.

Electrochemical impedance spectroscopy, or EIS, is one of the most powerful tools to analyze electrochemical processes occurring at the electrode/electrolyte interfaces, and has been widely applied to the analysis of electrochemical lithium intercalation into carbonaceous materials including graphite. According to Aurbach *et al.*^[2], lithium insertion involves several processes that occur in series: diffusion of lithium ion in solutions, charge transfer, migration of lithium ions through the SEI films, and solid state diffusion of lithium ions into the graphite, which is often described as finite space or restricted diffusion. Thanks to the differences in their time constants, EIS is a suitable technique for these investigations, and can reflect all the above processes. The Nyquist diagram consists of two arcs, and a declined line. It is commonly considered that the first arc in the high-frequency range (HFA) observed in the Nyquist diagram is commonly attributed to the SEI film. If this is true, the formation and growth of the SEI film should be observed in the initial lithiation of graphite electrode. But Martinent *et al.*^[3] showed that during the first cathodic polarization of graphite in the potential range from 2.0 to 0.2 V, no important modification of the impedance spectra can be observed in the high-frequency region. Chang *et al.*^[4] attributed the HFA to the electrode/current collector interface, based on their finding that it does not show significant evolution in the potential range near 0.8 V versus Li⁺/Li, where the SEI film formation is considered to occur, and the resistance of the HFA is a function of the geometric area of electrode surface and does not depend on the amount of active material in the electrode. Holzapfel *et al.*^[5] also ascribed the HFA to the contact problems, but they considered that the contact problems may relate to the contact between the electrolyte and graphite, or graphite and graphite in the electrode bulk. The second arc in the medium frequency range (MFA) is generally attributed to the charge transfer step and the double layer capacitance, and the declined line in the low frequency range is related to diffusion of lithium ion inside the graphite.

In this study, we put emphasis upon the graphite

electrode in the first lithiation, and new results are presented concerning the unique features of the HFA in EIS. The formation and growth of the SEI film, the resistance of charge transfer, and the capacitance of double layer along with the increase of polarization potential were analyzed.

1 Experiment

All experiments were carried out in a three-electrode glass cell with lithium 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 was 1 mol/L $\text{LiPF}_6\text{:EC:DMC:DEC}$ (volume ratio 1:1:1, Guotaihuarong Co., Zhangjiagang, China).

EIS measurements were carried out in an electrochemical work station (CHI 660B, Chenhua Co., Shanghai, China). The amplitude of ac perturbation signal was 5 mV and the frequency range was from 10^5 to 10^{-2} Hz. The electrode was equilibrated at the given polarization potential for 1 h before the EIS measurements.

2 Results and discussion

2.1 The common EIS features of graphite electrode

Typical electrochemical impedance spectra of the graphite electrode in the initial lithiation are shown in Fig. 1. The Nyquist plots of the graphite electrode at 3.0 V show a sloping line in whole frequency range (Fig. 1(a)), and no arc can be observed in the high-frequency region, corresponding to the fact that there

is no initial formation of SEI film on the graphite electrode before lithiation. The sloping line bends toward the real axis and forms a semicircle at 2.0 V (Fig. 1(b)). The Nyquist plots at 1.5 and 1.0 V are similar (Fig. 1(c)), which include an arc in the high-frequency region and an inclined straight line in the low-frequency region. The above results illustrate that the formation and growth of the SEI film due to electrolyte reduction decomposition do not occur on the graphite electrode till electrode potential is below 1.0 V. The unique feature of the Nyquist plots 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 polarization potential (Fig. 1(d)), which corresponds to a generally accepted fact that the SEI film is formed near 0.8 V due to the decomposition of electrolyte solution species such as ethylene carbonate (EC) [6]. Thus the only explanation accounting for these observations is that the first arc in the high-frequency region observed in the Nyquist plots should be related to the SEI film. The Nyquist plots at and below 0.9 V are similar, consisting of three parts: the HFA relating to the SEI film, the MFA corresponding to the charge transfer step and the double layer capacitance, and the declined line in the low frequency region that depicts the diffusion phenomena.

In this study, our emphasis was put upon the variation of the HFA as well as the MFA along with the decrease of polarization potential. The EIS in the low frequency region has not been discussed, since a correct modeling of the low frequency part needs knowledge of the grain geometry and size distribution. Moreover, the HFA has not been observed in the Nyquist plots when electrode potentials were above 1.0 V, thus only the EIS experimental data below 0.9 V were simulated and analyzed.

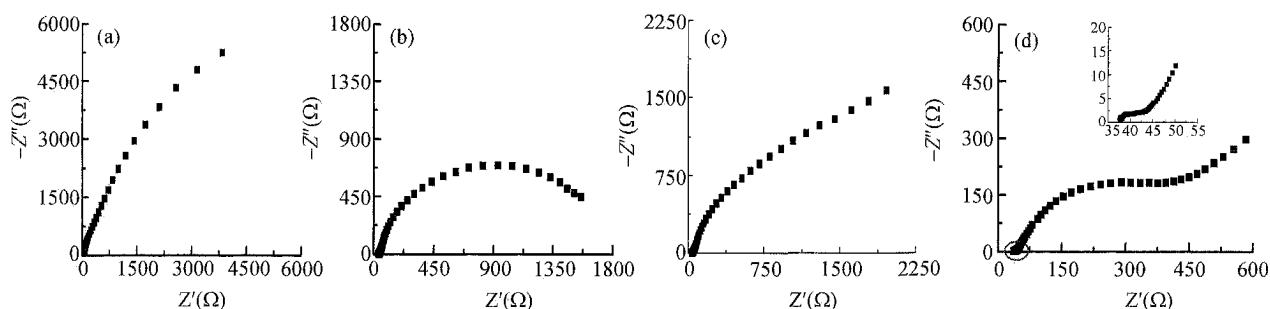


Fig. 1. Impedance spectra of the graphite electrode in the first lithiation in frequency range 10^5 – 10^{-2} Hz: (a) 3.0 V; (b) 2.0 V; (c) 1.5 V; (d) 0.9 V. The inset shows the spectra enlarged over a 10^5 –50 Hz frequency range.

2.2 Equivalent circuit proposed in EIS analysis

According to experimental results obtained in this work and those in ref. [7], an appropriate impedance model, as shown in Fig. 2, is proposed to model the impedance spectra of potentials below 1.0 V. In the equivalent circuit, R_s represents the ohmic resistance; R_{SEI} , and R_{ct} are the resistances of the SEI film and the charge transfer reaction, respectively; the capacitance of the SEI film, the capacitance of the double layer and the Warburg impedance are represented by the constant phase element (CPE) Q_{SEI} , Q_{dl} and Q_D , respectively. The CPE describes the non-ideal behavior of the composite electrode (porosity of the material, roughness of the surface), it can present a good compromise between the accuracy of the model and the number of parameters, and is fit for simulating the graphite electrode^[7]. The expression for the admittance response of CPE (Q) is

$$\frac{1}{Q} = Y_0 \omega^n \cos\left(\frac{n\pi}{2}\right) + j Y_0 \omega^n \sin\left(\frac{n\pi}{2}\right), \quad (1)$$

where ω is the angular frequency. A CPE represents a resistor when $n=0$, a capacitor with capacitance of C when $n=1$, an inductor when $n=-1$, and a Warburg resistance when $n=0.5$ ^[8]. In this study, Y_0 is considered to be a pseudo capacitance (pseudo- Y_0) when n lies between 0.5 and 1.

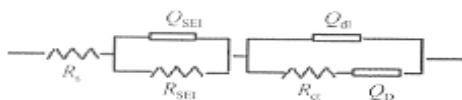


Fig. 2. Equivalent circuit used for analysis of impedance spectra of the graphite electrode in the first lithiation.

A step-by-step, and double-check fitting method was employed in the numerical analysis of the impedance spectra during the first lithium intercalation process. In this method, the fitted parameter values in the previous step (with lower lithium content) were used as initial values for the following step, and then the fitted parameters in the following step were used as initial values to fit the spectra of the previous step. The two processes were repeated until the values of the fitted parameters became the same by fitting in both the forward and backward directions. The relative standard deviation for all parameters fitted did not exceed 15%. The simulated impedance spectra in the first lithiation are compared with EIS experimental data at 0.5 V in Fig. 3, and equivalent circuit parameters are listed in Table 1, which demonstrates that the proposed model

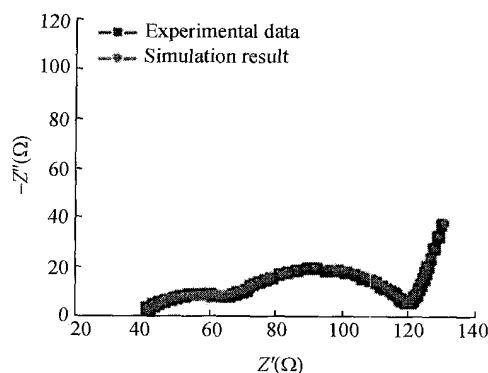


Fig. 3. A comparison of EIS experimental data at 0.5 V and simulation results using equivalent circuit of Fig. 2.

Table 1 Equivalent circuit parameters obtained from simulation of EIS experimental data at 0.5 V

Parameter	Value	Uncertainty
R_s	39.8	0.549%
R_{SEI}	30.69	2.650%
Q_{SEI-n}	0.5786	2.181%
Q_{SEI-Y_0}	0.2074E-06	13.595%
R_{ct}	50.6	1.599%
Q_{dl-n}	0.7952	1.240%
Q_{dl-Y_0}	0.1111E-03	8.771%
Q_D-n	0.8240	1.234%
Q_D-Y_0	0.1588	5.362%
χ^2	3.1711E-04	

can describe the experimental data satisfactorily.

2.3 The evolution of the HFA

The resistance and capacitance values corresponding to the migration of Li ions through the SEI film are frequently described in the literature by eqs. (2) and (3)

$$R = \rho l / S, \quad (2)$$

$$C = \varepsilon S / l, \quad (3)$$

where l is the thickness of the SEI film, S the electrode surface area, ρ the resistivity, and ε the permittivity of the SEI film. If we assume that the surface S , permittivity ε , and resistivity ρ remain constant, it is clear that a thickness increase will lead to a resistance increase, and to a decrease in capacitance. This is not always the case, the permittivity ε , and resistivity ρ are in fact variable along with the variation of the composition of the SEI film. It can be seen from Fig. 4 that, on charging from 0.9 to 0.8 V, R_{SEI} increases slowly, while Q_{SEI-Y_0} decreases slowly, implying the increase of the thickness of the SEI film. However, on further charging to 0.7 V, both R_{SEI} and Q_{SEI-Y_0} increase rapidly, reflecting a different formation mechanism of the SEI film in the

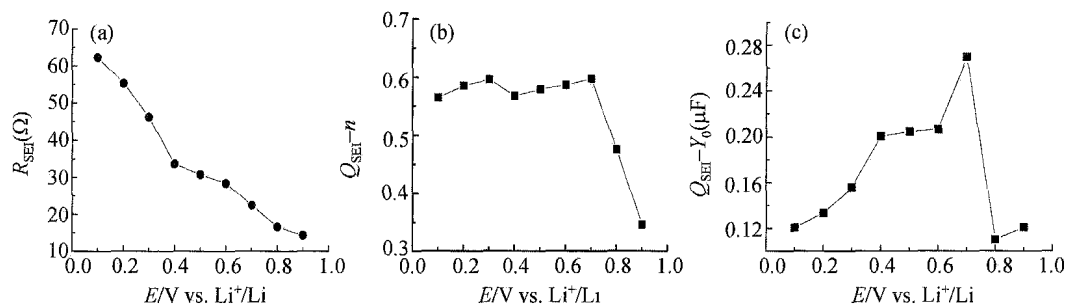


Fig. 4. Variation of parameters (R_{SEI} , $Q_{\text{SEI}-n}$, and $Q_{\text{SEI}-Y_0}$) obtained from fitting the experimental impedance spectra of graphite electrode in the initial lithiation.

above two potential regions. We speculated that a compact SEI film is formed between 0.9 and 0.8 V (low impedance and permittivity), and a highly porous SEI film is formed between 0.8 and 0.7 V (high impedance and permittivity). Therefore, although the thickness of the SEI film continually increases, $Q_{\text{SEI}-Y_0}$ still increases rapidly due to the increase of the permittivity. The above results correspond to those reported in ref. [9] that the reduction products of EC are different in different potential regions, the formation of Li_2CO_3 occurs at potentials between 1.0–0.8 V range, and that of lithium alkylcarbonates (ROCO_2Li) then follows at potentials below 0.8 V. When the electrode potential is changed from 0.9 to 0.7 V, $Q_{\text{SEI}-n}$ increases rapidly, indicating that the SEI film is rapidly formed on the surface of the graphite electrode. With the potential changing from 0.7 to 0.4 V, R_{SEI} first increases rapidly and then increases slowly; $Q_{\text{SEI}-Y_0}$ first decreases rapidly and then decreases slightly, which implies 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, thus the aging process of the SEI film dominates the electrode surface chemistry. The rapid decrease of $Q_{\text{SEI}-Y_0}$ between 0.7 and 0.6 V depicts the transformation between the formation of the SEI film due to the reduction of EC and the aging process of the SEI film. It is well known that all LiPF_6 solutions may be unavoidably contaminated by hundreds of ppm of HF, and in the aging process of the SEI film, HF reacts with both Li_2CO_3 and ROCO_2Li that are produced on carbon anode surfaces by the reduction of alkyl carbonate solvents such as EC. As a consequence, the Li_2CO_3 and ROCO_2Li will be substituted by LiF that is one of thermodynamic stable species of the SEI film and has poor ionic conductivity. The above processes result in not only the continuous increase of the R_{SEI} , but also the decrease of the homogeneity of the SEI film (the decrease of the $Q_{\text{SEI}-n}$)^[10].

Moreover, the decrease of the permittivity of the SEI film owing to the dissolution of ROCO_2Li leads to the decrease of $Q_{\text{SEI}-Y_0}$. The first rapid increase and then slight increase of the R_{SEI} as well as the first rapid decrease and then slight decrease of $Q_{\text{SEI}-Y_0}$ are probably due to the continual decrease of the concentration of the HF with the increase of elapsed time in the aging process. On charging from 0.3 to 0.01 V, R_{SEI} increases rapidly, and $Q_{\text{SEI}-Y_0}$ decreases slightly, which can be ascribed to two major factors. First, the aging process of the SEI film continually occurs; on the other hand, graphite increases in its volume upon Li insertion. This increase in volume stretches the SEI films on the edge planes of the graphite particles, through which Li-ions migrate into and from the active mass, and results in the cracking of the SEI film. Subsequently, the reactions of the active mass with electrolyte solution species occur to repair the cracking of the SEI film. The above cracking and repairing of the SEI film lead to an increase in the R_{SEI} and a decrease in the homogeneity of the SEI film^[11,12]. The increase of $Q_{\text{SEI}-n}$ between 0.4 and 0.3 V is obviously owing to the lithium ion intercalation, which reflects the transformation between the aging process of the SEI film and the lithium ion intercalation process.

2.4 Evolution of the MFA

It can be seen from Fig. 5 that the charge transfer resistance, R_{ct} , mostly decreases with the decrease of the polarization potential, indicating the dependence of the R_{ct} upon the electrode polarization potential. While the growth of the SEI film and lithium ion intercalation into graphite electrode also affects the charge transfer reactions. The R_{ct} at 0.8 V is obviously larger than that at 0.7 V, implying that the SEI film effectively prevents the reduction and decomposition of electrolyte solution species. During the following cathodic polarization below 0.7 V, the R_{ct} decreases again with the decrease of polarization potential, which indicates that a highly

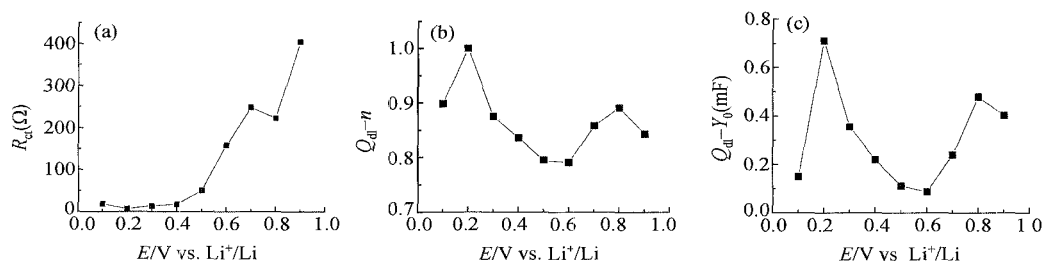


Fig. 5. Variation of parameters (R_{ct} , Q_{dl-n} , and Q_{dl-Y_0}) obtained from fitting the experimental impedance spectra of graphite electrode in the initial lithiation.

passivating SEI film was formed on the surface of graphite electrode above 0.7 V, in accordance with the results obtained in the high frequency range. The R_{ct} at 0.1 V is obviously larger than that at 0.2 V, probably because the increase of the amount of intercalated lithium ion results in the repulsion among them^[13,14]. The change of the CPE (Q_{dl}) parallel to R_{ct} clearly reflects the change of inhomogeneity of the charge transfer reaction induced by the formation and growth of the SEI film. Q_{dl-Y_0} and Q_{dl-n} vary accordingly to the variation of the SEI film described in the previous section.

3 Conclusions

EIS has been applied to investigating the formation of the SEI film on graphite electrode surface in the first lithiation. Impedance spectra were measured in a wide potential range from 3.0 to 0.01 V, and were analyzed on two regions of frequency, i.e. high- and middle-frequency regions.

The results demonstrated that the formation and the growth of the SEI film due to electrolyte reduction decomposition did not occur on the graphite electrode until electrode potentials were below 1.0 V. The HFA observed in the Nyquist plots is relevant to the SEI film. It is revealed that the SEI film is mainly produced between 1.0 and 0.7 V. The growth of the SEI film in the first lithiation of graphite materials may occur in three different steps: (1) the formation of the SEI film, (2) the aging process of the SEI film, and (3) the cracking and repairing of the SEI film.

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