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Impedance Characterization of the Film Formation Process at the Graphite Anodes

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Abstract In this paper, the formation mechanism of the passive SEI film at the natural graphite anodes was investigated with the electrochemical impedance spectroscopy (EIS). A characteristic semicircle was observed in the lower frequency range of the EIS spectrum for the irreversible charge process (lithium intercalation) at *ca.* 0.75V, 0.40V and 0.20V.

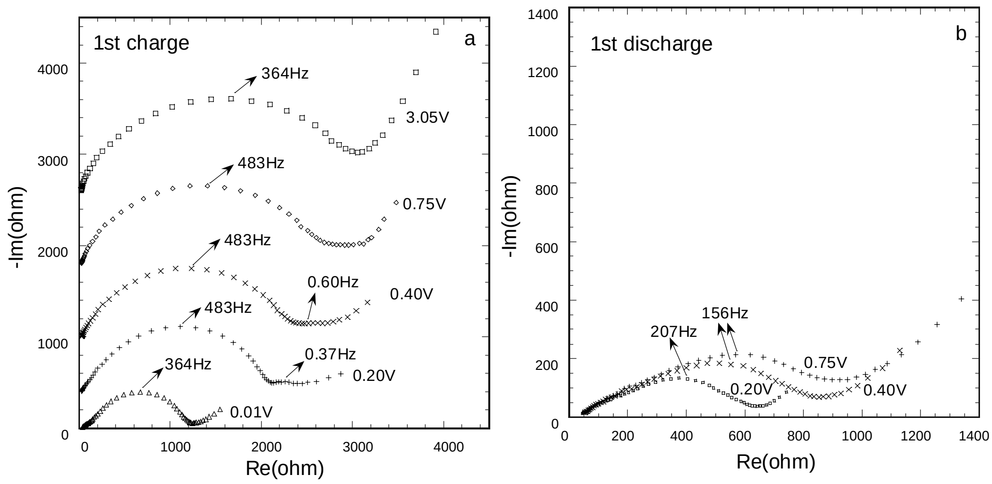
Keywords: Electrochemical impedance spectroscopy, surface film, graphite anodes, Li-ion battery.

A passive SEI (Solid electrolyte interface) film had been suggested to be formed on the graphite anodes with the irreversible capacity loss at *ca.* 1.20V in the first charge process by Fong *et al.* And the capacity loss at *ca.* 0.75V was originated from the electrolyte decomposition on the new surface created by the exfoliation of the graphite structure for solvent co-intercalation[1]. Aurbach *et al* studied the surface chemistry of the insulating film on the graphite electrodes in different electrolyte solutions[2]. But the formation process of the passive film on the graphite surface is still not very clear, especially for the variation of the electrode/electrolyte interface in the first cycle. For example, if a stable passive film (SEI) had been formed on the graphite surface, no exfoliation should occur. The film formation is a temporary process and *in-situ* study is not easy. The electrochemical impedance technique is a very useful tool for indirect study and analysis of the mechanism of this process[3-7].

The natural graphite investigated in this paper was obtained from Fujian, China (average size of the graphite powder is 15μm). The graphite electrodes were prepared by wet mixing the graphite powders with wt.5% PTFE (binder) and pressing the mixture under *ca*. 5 MP pressure into a thin tablet (*ca*. 0.30 cm^2 in geometry area). Half cells were constructed in a parallel plate configuration using the carbon tablets as the working electrodes, lithium foil as counter electrodes, microporous polypropylene as separators and 1 mol/L $LiClO_4$ EC/DEC solution (EC:DEC=3:7 in volume) as the electrolyte. To avoid the effect of the overvoltage at the counter electrode, another lithium foil was placed in the cell and used as the reference electrode. All the potentials were referred to the Li electrode. And the electrochemical cells were constructed in a *VAC* glove box (filled with dry argon gas) at room temperature. Electrochemical impedance measure-ments were performed with Zahner *Elektrik* IM6e (Electrochemical workstation, Germany). After the working electrode was charged or discharged galvanostaticly to the potential desired (in the rate of 20 hrs for $\Delta x=1$ in Li_xC_6), the impedance was measured under potentiostatic condition with 10 mV ac voltage (signal) in the frequency range from 1 MHz to 5 mHz. (8 points per decade above 66 Hz and 4 points per decade below 66 Hz).

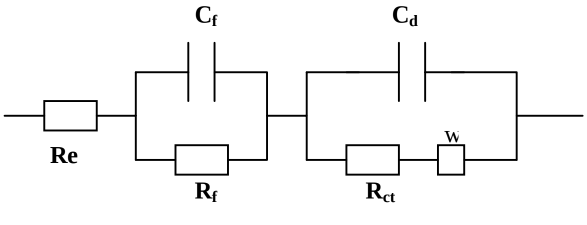
The EIS of the natural graphite electrode in the first cycle are shown in **Figure 1** (a and b). Three types of the EIS spectra can be distinguished in the first charge process (see **Figure 1** a), the EIS at *ca*. 3.05V(type I), the EIS at 0.75V, 0.40V and 0.20V(type II), and the EIS at 0.01V(type III). The EIS spectra in the first discharge process (**Figure 1** b) all belong to type III.

Figure 1 The EIS spectra of the natural graphite electrodes at different potentials in the first cycle (in a, the value of –Im in the EIS for 0.20V was offset by +400Ω, 0.40V by +1000Ω, 0.75V by +1800Ω, 3.05V by +2600Ω).



In the EIS spectrum of type I (at *ca*. 3.05V for the freshly prepared graphite anode), there are a depressed semicircle in the high and middle frequency range. No lithium intercalation should be expected at 3.05V for the freshly prepared electrodes. The semicircle should be corresponding to the electrode/electrolyte interface with a double layer capacitance in parallel to a charge transfer resistance, which may result from some surface reaction. And the depressed semicircle may be caused by the rough surface of the carbon electrodes.

Figure 2 The equivalent circuit used for the analysis of the type III EIS spectra in **Figure 1**.



unsymmetric flattened semicircle in the impedance plots. It is well known that a passive film should have been formed on the carbon electrode surface after the irreversible charge process is finished[1, 8]. The equivalent circuit for the electrode system with a passive film is shown in **Figure 2**. The equivalent circuit consists of two parallel circuits in series. R_e is the ohmic resistance of the electrolyte, R_{ct} and R_f are the charge transfer resistance and the resistance associated with the film respectively. W is the Warburg impedance, and C_d and C_f are the double layer capacitance and the film capacitance corresponding to R_{ct} and R_f respectively. The unsymmetric semicircle in the EIS of type III indicates that the time constants of the two parallel circuit of the electrode studied here are not well separated and the two semicircles emerged together. The high frequency part should mainly be contributed from R_f and C_f, because C_f should be much smaller than C_d.

The EIS of type II for the electrode at 0.75V, 0.40V and 0.20V in the first charge process is special and interesting. Different from the spectrum of type I and type III, there are two separated semicircles appeared in the higher and lower frequency range respectively. Compared with the EIS spectra of type III, the semicircle in the higher frequency range should result from C_d and R_{ct} and no passive film had been formed at this potential. Galvanostatic charge/discharge results show that there is still some irreversible capacity loss at *ca*. 0.40V and 0.20V, except at 0.75V for the graphite electrodes in the first charge process. So the second semicircle in the lower frequency range could be related to the irreversible reaction associated with the capacity loss at the graphite anodes. The irreversible reaction is the electrolyte decomposition on the graphite electrode surface and some gas (*eg*. ethane) is evoluted with the solvent decomposition[9-10]. Probably, a new interface between the carbon particles in the electrodes appears by the perturbation of the gas product, which results in the lower frequency semicircle. This is confirmed by the large capacitance value for the second semicircle estimated from the spectra. The approximate capacitance value was about 1mF, which is much larger than the value of C_d mentioned before (in the magnitude of 20μF)[11].

If the film was not very stable, or the electrolyte decomposition product on the graphite electrode surface can be easily dissolved by the electrolyte, the solvent molecules could be co-intercalated into the graphite with the Li^+ ions, and exfoliation occurred. So the irreversible capacity loss at *ca*. 0.75V in the first charge was resulted from the electrolyte decomposition both on the electrode surface before exfoliation and on the new surface exfoliated from solvent co-intercalation. As seen from **Figure 1**(a), the film formation process may begin at above 0.75V, and the SEI film could be formed with the irreversible capacity loss at *ca*. 0.75V, 0.40v and 0.20V until charging to 0.01V. In conclusion, a passive SEI film may be formed gradually with the decomposition of the electrolyte solvent on the graphite surface.

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