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Three-electrode button cell for EIS investigation of graphite electrode

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Abstract

Electrochemical impedance spectroscopy (EIS) has been used to study the graphite composite electrode/electrolyte interface in a newly designed three-electrode button-type cell. In order to follow the formation of the passivation film on graphite, several spectra have been plotted during the first reduction of the electrochemical system. Typical impedance spectra exhibit a high-frequency (HF) impedance loop, which does not evolve much over the scanned potential range. A middle-frequency (MF) loop appears as the cathodic polarization of the carbon electrode increases, whose characteristics are potential dependent. In the lower frequency (LF) region, a near vertical straight line is observed.

The attributions of each frequency region are discussed in the present paper.

Keywords: Electrochemical impedance spectroscopy (EIS); Passivation film; Graphite electrode; Lithium

1. Introduction

Electrochemical impedance spectroscopy (EIS) is a very employed technique to study the Li^+ insertion into carbon. All the authors dealing with the subject agree with the fact that the intercalation process is complex. It takes into account the lithium ions diffusion in liquid phase, their migration through passivation films formed on the graphite electrode, and lastly their finite space diffusion in the insertion material.

EIS allows to observe these different phenomena in a well-separated way in the frequency domains in so far as the time constants assigned to each of them are very different. The high-frequency (HF) loop observed on spectra concerning lithiated carbon/electrolyte interface is classically related to passivation films [1–9] formed on graphite and possibly on the current collector. In the middle-frequency (MF) region, the second loop is generally attributed to charge transfer and double-layer charging processes [1–10] and the lower frequency (LF) part is typically assigned to the diffusion in the solid phase [1–10].

2. Experimental

2.1. Button cells preparation

All experiments were performed on Li auxiliary electrode/electrolyte/Li reference electrode/electrolyte/graphite working electrode home-designed button cells (CR 2430 type). The working electrode is made of carbon and the auxiliary one is a 20 mm diameter lithium foil. The reference is made of a small stainless steel sheet covered with lithium. The separators made of a 20 mm diameter microporous polyethylene film are soaked with the electrolyte prior to use and are located between each electrodes in order to avoid any short-circuit.

Carbon electrodes are prepared as follows: the liquid mixture is made of 62.5 wt.% graphite (SFG6 Timcal), 12.5 wt.% PVDF (Kynar Flex 2821 Elf Atochem), 18.3 wt.% acetylene black, 16.6 wt.% dibutylphtalate (DBP) and acetone; 11 ml/g of carbon. The mechanically dispersed mixture is then spread on a polyethylene foil and laminated, then the acetone is evaporated. The plastifier (DBP) is removed by immersion in methanol. After solvent evacuation, the weight composition of the film shaped electrode is: graphite (75%), acetylene black (10%) and PVDF (15%). The typical electrode thickness is 150 μm. The electrode is then cut into discs of 14 mm diameter then dried under vacuum at 60°C for 12 h. It is then introduced

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under vacuum into a dry box filled with argon for cell assembly. The electrolyte used is 1 M $LiPF_6$ (provided by Elf Atochem) in EC:DMC 1:1 (Selectipur®, Merck). The EC/DMC mixture was first dried in the glove box over 3 Å molecular sieve (Roth) prior to use.

2.2. EIS measurements

EIS measurements were carried out using an electrochemical-regulation system (Solartron 1286 electrochemical interface) configured for potentiostatic control and a Solartron 1250 frequency response analyzer. The measurement set was controlled by a PC equipped with an HP 83200 IEEE board. The SAMDIE software developed in our laboratory [11] was used for data acquisition and plotting of impedance diagram. EIS measurements were performed with a 5 mV voltage magnitude in the 60 kHz–10 mHz frequency range in automatic sweep mode from high to low frequency with eight points per logarithmic decade.

When the imposed potential is the open-circuit voltage (OCV), it is first measured during a few minutes and then applied automatically. When the imposed potential is not the OCV, it is applied during several hours in order to attain steady state conditions, i.e. a negligible current, before measurements.

3. Results

3.1. Validation of the three-electrode cell configuration

In order to validate the cell configuration, three different EIS measurements were carried out: graphite electrode versus Li reference electrode (a) Li auxiliary electrode versus Li reference electrode; (b) graphite electrode versus Li auxiliary electrode; (c) Fig. 1 shows the results obtained. EIS data analyses clearly show that the sum of impedance spectra (a) and (b) is the same as the spectrum (c), i.e. $Z_c(\omega) = Z_a(\omega) + Z_b(\omega)$. It confirms that the contribution of the lithium/electrolyte interface cannot be neglected in a two-electrode cell, where the lithium plays both the roles of the auxiliary and reference electrodes. It also demonstrates that the EIS measurements performed on button-type three-electrode cells are correct.

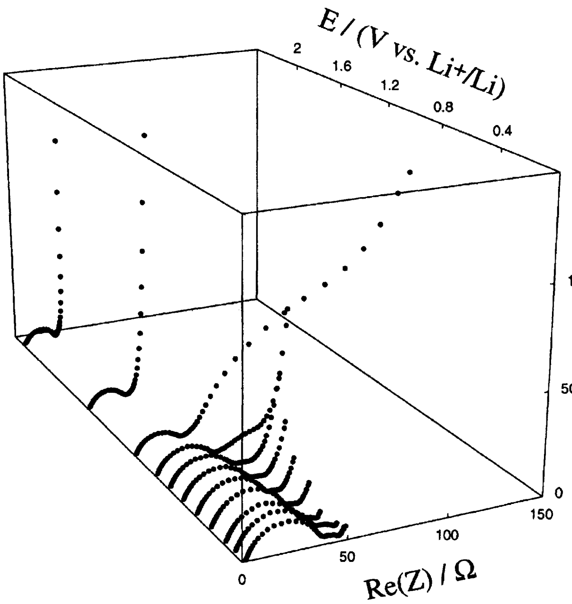

Fig. 2. Impedance spectra of the three-electrode cell at different potentials during the first intercalation of lithium ion into carbon.

3.2. EIS study of the first intercalation of lithium ion in graphite

It is now widely accepted that the capacity loss (irreversible capacity) during the first reduction of graphite is associated to side reactions and solid electrolyte interface (SEI) formation, which takes place mainly in the 0.8–0.7 V voltage range.

In order to better understand the passivation processes on the graphite surface, EIS measurements were performed at different potentials during the first intercalation of lithium in graphite.

Fig. 2 shows that a HF loop already appears at OCV ~2.3 V versus Li/Li$^+$ and that it does not change so much

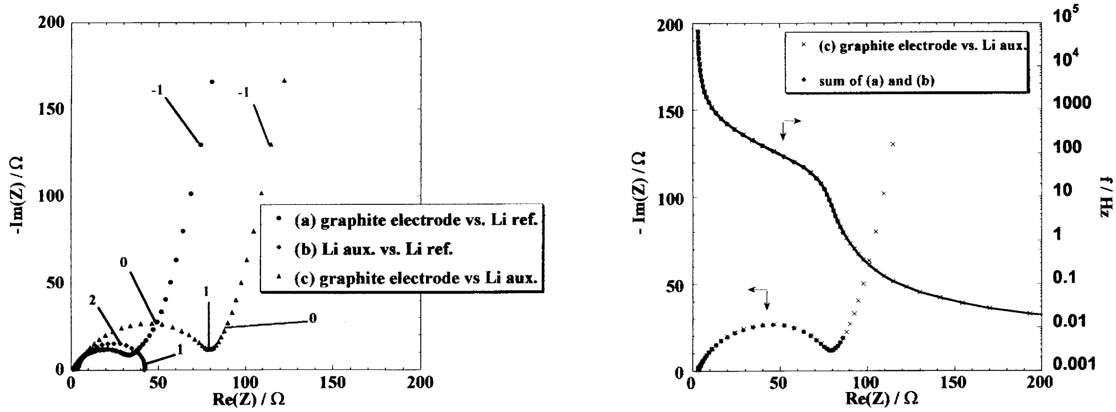

Fig. 1. OCV impedance spectra of the three-electrode cell.

with decreasing voltage. In the MF and LF domains, Fig. 2 shows that the EIS spectra strongly depend on the electrode potential. Indeed, as the potential decreases, a loop appears between the HF arc and the LF vertical straight line. The diameter of that MF loop decreases with the polarization potential of the graphite electrode.

EIS measurements have been performed with 100 mV potential steps in the (1.8–0.8 V versus Li/Li$^+$) range, first between 1.8 and 0.8 V versus Li/Li$^+$, then back from 0.8 to 1.8 V versus Li/Li$^+$. The third scan has been completed just like the first one. The results of the successive scans are depicted in Fig. 3.

The HF part does not vary much as the potential of the carbon electrode decreases or increases. On the other hand, the MF and LF region depend on the polarization potential of the graphite electrode. The potential range used here corresponds to the domain where irreversible loss of capacity begins to occur. Nevertheless, Fig. 3 clearly shows that the spectrum

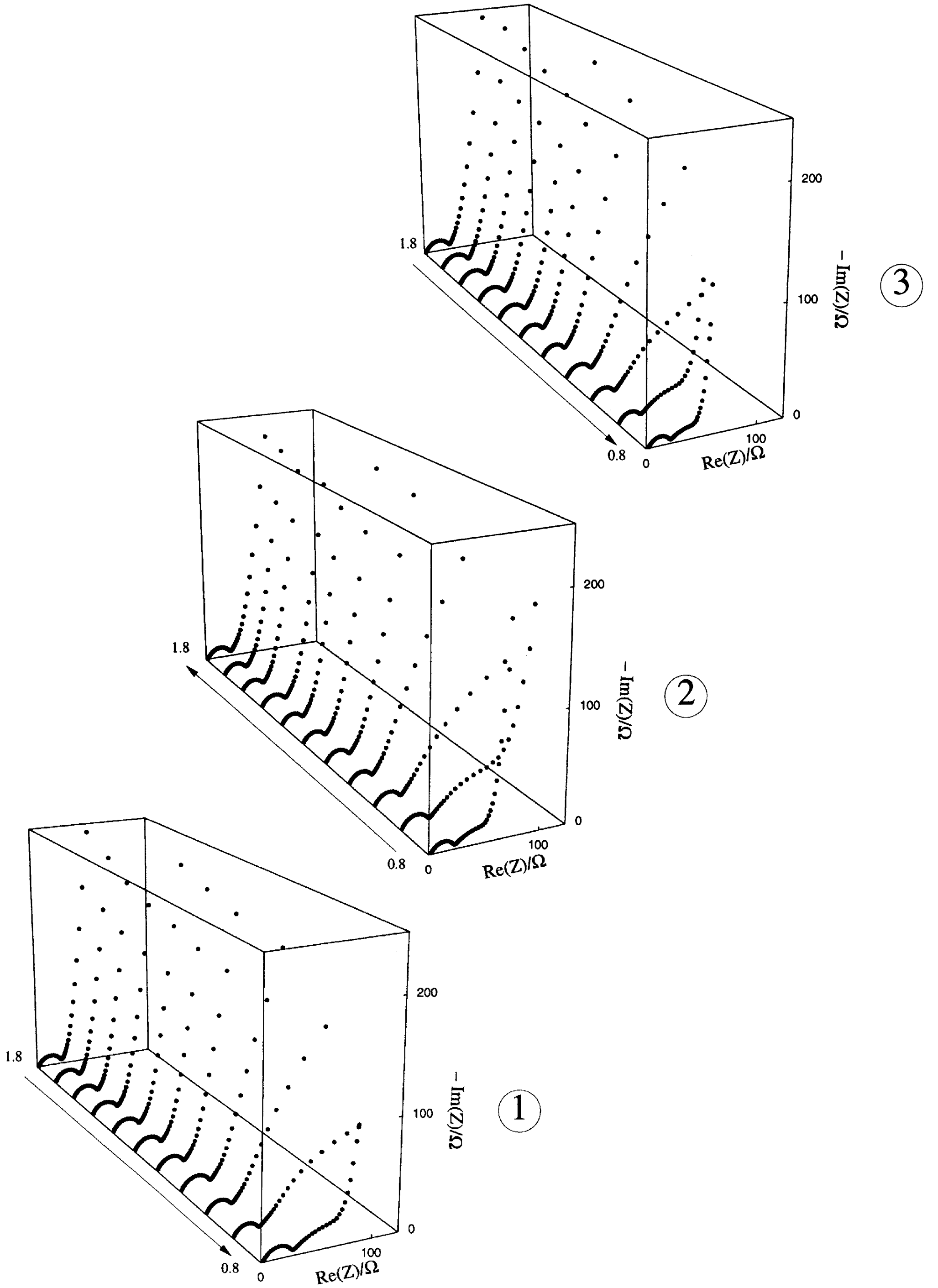

Fig. 3. Impedance spectra of the three-electrode cell over (1.8−0.8 V vs. Li$^+$/Li) potential range with different potentials scan directions.

obtained at a given potential is quite the same in case of the first, second or third scan. In other words, over the considered potential range, where irreversible reactions are supposed to occur (passivation film formation and side reactions), the spectra seem to be independent of the scan direction.

4. Discussion

In their recent work, Chang and Sohn [10] used EIS to study the Li^+ intercalation into graphitized carbon. For the authors, the HF arc observed on EIS spectra of the carbon working electrode versus Li reference electrode is associated with the collector/graphite interface rather than a passivation film on the graphite surface. As far as we are concerned, our results revealed that a HF arc exists at OCV, before lithium ion insertion. If the HF arc is assigned to the passivation film of the carbon electrode, then it means that the passivation film begins to form before the graphite electrode attains cathodic potentials from which it is supposed to grow. If the HF arc is not related to the passivation film, further experiments should allow us to identify this HF arc and to check the hypothesis suggested by Chang and Sohn.

In the MF and LF region, an appreciable change is observed depending on the polarization electrode potential. It is probably assigned to the insertion reaction. The MF arc is associated with the charge transfer while the LF straight line is due to the finite space diffusion.

5. Conclusion

The three-electrode button-type cell used in this work presents a correct configuration for EIS measurements. It allows to eliminate the contribution of the lithium auxiliary electrode/electrolyte interface and then to study the carbon/electrolyte interface only.

Interesting results have been highlighted. Indeed, EIS spectra of the carbon electrode versus lithium reference electrode reveal that a HF arc exists at OCV above the 0.8 V versus Li/Li^+ plateau, where passivation film formation and side reactions are generally assumed to occur. In the potential range of (1.8–0.8 V versus Li/Li^+), the impedance diagram does not depend on the potentials scan direction. Then, EIS measurements do not show any carbon electrode modifications whereas irreversible processes of loss of capacity occur in the considered potential range.

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