

## Lithium ion transfer at the interface between electrolyte / non-graphitizable carbon electrode

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Li-ion transfer at non-graphitizable carbon electrode / liquid (or polymer) electrolyte interface was studied by AC impedance spectroscopy. After potential cycling between 3.0-0 V one semi-circle was appeared at the potential of 3.0 V in the Nyquist plot and assigned to surface film resistance formed on non-graphitizable carbon electrode. At the potential below 0.9 V, impedance spectra gave two semi-circles. The semi-circle in the middle to lower frequency region can be identified as a charge transfer resistance due to lithium ion transfer at the interface between non-graphitizable carbon electrode and electrolyte. Temperature dependency of the resistance showed Arrhenius-type behavior and gave activation energy of about 73 kJ mol<sup>-1</sup> irrespective of electrolytes, indicating that high activation barrier exists at non-graphitizable carbon electrode / electrolyte interface for Li-ion transfer.

Key words: Non-graphitizable carbon, Lithium-ion transfer, Polymer electrolyte, Lithium ion battery

### 1. INTRODUCTION

Lithium ion batteries have been extensively studied because of their high performance and potentialities [1]. Carbonaceous materials with sp<sup>2</sup>-type structure have received considerable attention for use as negative electrodes of lithium ion batteries. Among them, highly crystallized graphite, which shows acceptably high capacity and very flat potential identical to lithium metal in charge/discharge process, has been generally employed for the commercial use [2]. Various kinds of carbonaceous materials still have been studied to improve the performance of lithium ion batteries. Non-graphitizable carbon is a promising candidate as a negative electrode of lithium-ion batteries for practical use in hybrid electric vehicles since the non-graphitizable carbon electrode gives gradual decrease (increase) in potential during lithium ion insertion (extraction), leading to the easiness of monitoring of battery voltage .

A number of studies have been done on electrochemical properties of non-graphitizable carbon electrode. Dahn et al. studied on the electrochemical behavior of some non-graphitizable carbons in liquid electrolyte, and reported that non-graphitizable carbon

showed higher reversible capacities than graphitic carbon (~372 mAh/g) [3,4]. Lithium insertion and extraction mechanism at non-graphitizable carbon electrode has been also reported [5-8].

Fast charge and discharge reactions are required for lithium ion batteries in high power use. Fast Li-ion transfer in the batteries as well as fast Li-ion transport through the electrodes and the electrolyte is required to achieve high rate performance. Therefore, kinetics of Li-ion transfer in the batteries should be understood. Little attention has been paid to lithium-ion transfer at interface between non-graphitizable carbon electrode and electrolyte

In the present work, Li-ion transfer at interface between non-graphitizable carbon electrode and electrolyte has been studied by AC impedance spectroscopy.

### 2. EXPERIMENTAL

Non-graphitizable carbon heated at 2273 K (GC-20, Tokai Carbon Co., LTD) was used as a working electrode. The non-graphitizable carbon was prepared from phenolic resin. Electrochemical properties of the non-graphitizable carbon electrode were studied by

cyclic voltammetry (HSV-100, Hokuto Denko Co.) employing a three-electrode cell, in which Li metal was used as counter and reference electrodes. Liquid electrolyte used was propylene carbonate (PC) containing  $1 \text{ mol dm}^{-3} \text{ LiClO}_4$ . Polymer electrolytes of copolymer (obtained from ethylene oxide, di(ethyleneglycol) methyl glycidyl ether (EM-2) and allyl glycidyl ether (AGE)) containing  $\text{LiBF}_4$  or  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  (LiTFSI) with a ratio of  $\text{Li}/\text{O} = 0.06$  were donated by Daiso Co., LTD. Ionic conductivity of polymer electrolytes were evaluated by AC impedance measurement in the frequency 100 kHz to 10 mHz employing two-electrode cell of stainless steel electrode / polymer electrolyte / stainless steel electrode in advance. Interfacial Li-ion transfer at the carbon electrode and liquid (or polymer) electrolyte was investigated by AC impedance spectroscopy employing VoltaLab40, Radiometer Analytical SAS. The electrode was swept to a given potential (ranging from 0.6 to 3.0 V) at  $1 \text{ mV s}^{-1}$  and kept at the potential to obtain steady-state, and then AC impedance spectra were obtained by applying a sine wave of 10 mV amplitude over the frequency range from 100 kHz to 10 mHz.

All experiments were conducted under argon atmosphere with a dew point below  $-60^\circ\text{C}$ .

### 3. Results & Discussion

Figure 1 shows cyclic voltammograms of non-graphitizable carbon in  $1 \text{ mol dm}^{-3} \text{ LiClO}_4 / \text{PC}$ . The cyclic voltammograms were measured with a sweep rate of  $0.1 \text{ mV s}^{-1}$  in the potential range between 0–3.0 V. A large cathodic current was observed below 0.9 V (vs.  $\text{Li}/\text{Li}^+$ ), which is ascribed to Li-ion insertion into the non-graphitizable carbon electrode and the corresponding anodic current assigned to lithium extraction appeared at around 0.7 V. Almost identical cyclic voltammograms were obtained using polymer electrolytes.

In Fig.2 are shown Nyquist plots at the given potentials ranging 0.6–3.0 V employing polymer electrolyte. The measurement was conducted at r.t. of c.a.  $25^\circ\text{C}$ . No semi-circle but only a line perpendicular to  $Z'$ -axis appeared at 3.0 V. Polymer electrolyte used in the present work shows high ionic conductivities even at r.t., giving no semi-circle in the Nyquist plot. From cyclic voltammogram, no Li-ion insertion and extraction occur at the potential of 3.0 V, and therefore, a blocking electrode behavior appeared. After potential cycling, one semi-circle was obtained at the same potential of 3.0 V, and up to 1.0 V, similar Nyquist plots were observed. No insertion and extraction of Li-ion at the non-graphitizable carbon electrode occurred above the

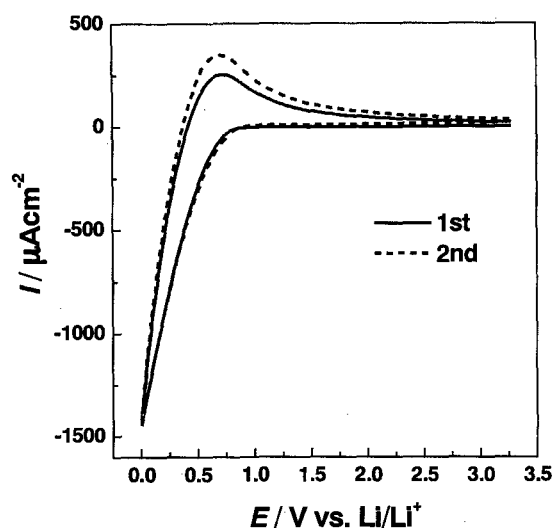


Fig.1. Cyclic voltammograms of non-graphitizable carbon electrode in  $1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC}$ .

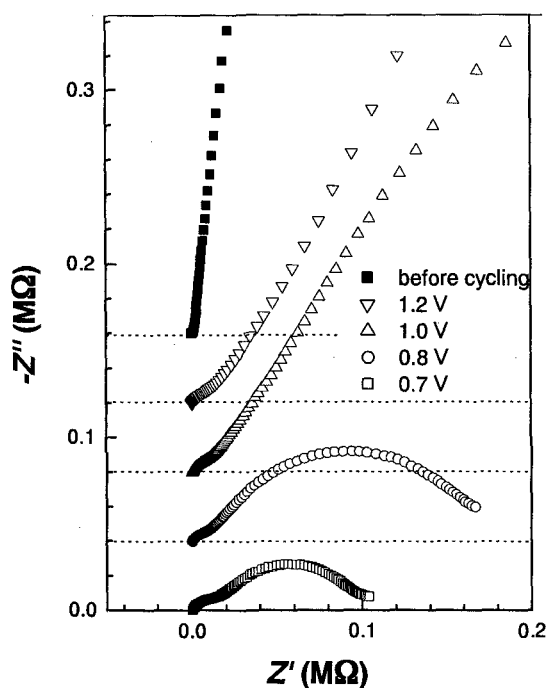


Fig.2. Impedance spectra of non-graphitizable carbon electrode in polymer electrolyte containing LiTFSI at potentials of 0.7, 0.8, 1.0, 1.2 and 3.0 V before cycling.

potential of 1.0 V and this semi-circle was not influenced by the electrode potentials, and therefore this semi-circle can be identified as a surface film resistance formed on non-graphitizable carbon electrode. At the potential below 0.9 V, another semi-circle appeared in the middle to lower frequency region. Resistances evaluated from the semi-circle in the lower frequency region were dependent on electrode potentials.

Therefore, it is reasonable to ascribe the semi-circle to a charge transfer resistance due to Li-ion transfer at the interface between non-graphitizable carbon electrode and electrolyte. Almost identical Nyquist plots were obtained irrespective of electrolytes.

In Fig.3 is shown the temperature dependency of Li-ion transfer resistances at 0.8 V. Charge transfer resistances decreased with increasing temperature and showed Arrhenius-type behavior. Activation energy for Li-ion transfer resistances was evaluated by the least-squares method to be  $74.7 \pm 1.8 \text{ kJ mol}^{-1}$  in PC based electrolyte,  $72.0 \pm 1.4 \text{ kJ mol}^{-1}$  in polymer electrolyte using LiTFSI as a salt, and  $75.8 \pm 1.5 \text{ kJ mol}^{-1}$  in polymer electrolyte using LiBF<sub>4</sub>. Irrespective of electrolytes used, almost the same large activation energies were obtained. These results are quite different from that obtained by Li-ion intercalation and de-intercalation at graphite electrode; activation energy for Li-ion transfer resistances at graphite electrode/ EC based electrolyte interface was smaller than the present values by around  $20 \text{ kJ mol}^{-1}$  [9-10]. Furthermore, activation energies for lithium ion transfer at lithium ion conductive electrolyte/electrolyte interface were reported to be dependent on the interaction between lithium ion and solvent in liquid electrolyte, namely, de-solvation process [11-13]. In contrast to the previous results obtained in our group, the present system seems to give another rate-determining step. By considering that the activation energies were independent of the electrolytes in the present work, the surface structure of the non-graphitizable carbon may give the large activation energies. This assumption can be proven by the surface modification of the non-graphitizable carbon. So far, HIP treatment of the non-graphitizable carbon was found to give smaller activation energies for lithium-ion transfer, leading to the conclusion that the above assumption is quite valid. The detail will be reported elsewhere [14].

#### 4. Conclusion

Li-ion transfer at the interface between non-graphitizable electrode and liquid (or polymer) electrolyte was studied. Existence of large activation barrier at non-graphitizable carbon electrode / electrolyte interface became explicit irrespective of electrolytes used. Improvement of rate performance of lithium ion batteries can be achieved by reducing the activation barriers at electrode / electrolyte interface by surface modification of electrode, which will be reported elsewhere.

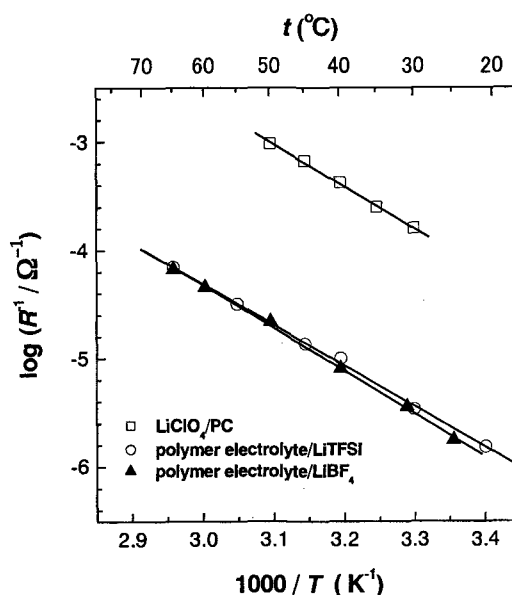


Fig.3. Temperature dependency of Li-ion transfer resistances. Lines are drawn by a least-squares method.

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