

Lithium-Ion Transfer at the Interface Between Electrolyte / Non-Graphitizable Carbon Electrode (3)

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Various kinds of carbonaceous material have been investigated to improve performance of lithium-ion batteries. Among them, non-graphitizable carbons are promising negative electrodes for lithium-ion batteries due to some attractive features such as higher Li capacity and easy monitoring of battery voltage during charge / discharge process. In addition, an isotropic structure of non-graphitizable carbons serves relatively large number of lithium-ion insertion sites on the surface, which is advantageous in interfacial lithium-ion transfer between electrode / electrolyte interface. Although much work has been done on electrochemical properties of non-graphitizable carbon electrodes, interfacial reactions between the electrode and electrolyte have been dismissed so far.

Fast interfacial lithium-ion transfer as well as fast lithium-ion transport through the electrodes and the electrolyte is required in high power use such as for HEV. We have previously studied that lithium-ion transfer at the interface between non-graphitizable carbon electrode and electrolyte, and as a result, lithium-ion transfer resistance at the interface were found to be very large and the activation energies for the lithium-ion transfer were clarified to be around 70 kJ/mol irrespective of electrolytes used¹⁾.

In this work, to elucidate lithium-ion kinetics at non-graphitizable carbon electrode, lithium-ion transfer at interface between oxidized non-graphitizable carbon electrode and electrolyte has been studied by AC impedance spectroscopy.

Non-graphitizable carbon prepared at 2273 K was heated at 773 K in the air for 1 h. Electrochemical properties of the heat-treated carbon were studied by cyclic voltammetry and AC impedance spectroscopy over the frequency range of 10 mHz -100 kHz employing a three-electrode cell. Electrolyte used was 1 mol dm⁻³ LiClO₄ dissolved in EC+DEC (1:1). Li metal was used as counter and reference electrodes.

Figure 1 shows the cyclic voltammograms of non-graphitizable carbon with and without heat treatment. Cathodic currents were observed for both samples below 0.9 V (vs. Li/Li⁺) due to insertion of lithium-ion into the non-graphitizable carbons and the corresponding anodic current identified as lithium-ion extraction appeared at around 0.6 V. The oxidation current of the heat-treated carbon was much larger than that of the pristine carbon.

AC impedance spectra of non-graphitizable carbons gave two semi-circles at the potential below 0.9 V. The semi-circle in the lower frequency region could be assigned to charge transfer resistance due to lithium-ion transfer at the interface between non-graphitizable carbon electrode and electrolyte¹⁾. The values of the interfacial lithium-ion transfer resistances, which were evaluated from the semi-circle in the lower frequency region, were extremely decreased by heat treatment. Figure 2 shows temperature dependency of charge transfer resistances at 0.8 V. The charge transfer resistances decreased with increasing temperature and showed Arrhenius-type

behavior. Activation energy for lithium-ion transfer resistances was determined by the least-squares method to be 47.9 kJ mol⁻¹ for heat-treated carbon, which was much smaller than 70.0 kJ mol⁻¹ of pristine carbon. These results indicate that surface structure of the non-graphitizable carbon, such as the size of pore openings²⁾ and flexibility of graphite-like layers for lithium-ion insertion, gives significant influences on interfacial lithium-ion kinetics.

Reference

- 1) T. Doi, T. Abe, K. Miyatake, Y. Iriyama and Z. Ogumi, Ext. Abst. 204th meeting of the Electrochemical Society, Orlando, Florida, No.249 (2003).
- 2) J. S. Xue and J. R. Dahn, *J. Electrochem Soc.*, **142**, 3668 (1995).

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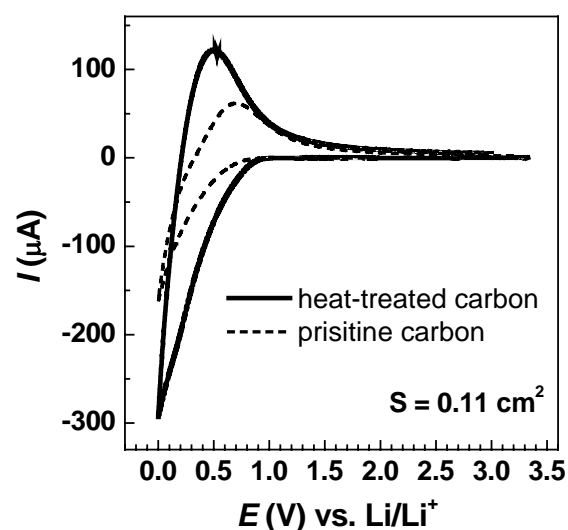


Fig.1 Cyclic voltammograms of non-graphitizable carbon with and without heat treatment. Sweep rate was 0.1 mV/s.

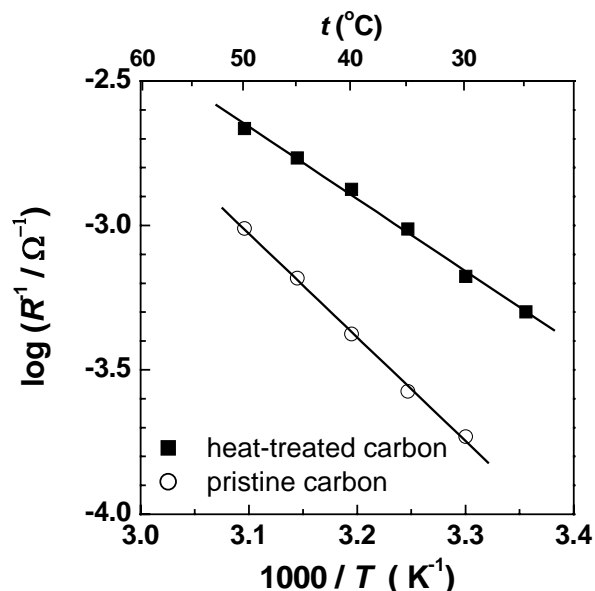


Fig.2 Temperature dependency of charge transfer resistances. Lines are drawn by a least-squares method.