

Lithium-ion transfer at a solid polymer electrolyte/non-graphitizable carbon electrode interface

Takayuki Doi, Yasutoshi Iriyama, Takeshi Abe*, Zempachi Ogumi

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

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Abstract

Li-ion transfer at the interface between a non-graphitizable carbon electrode and a solid polymer electrolyte was studied by AC impedance spectroscopy. Non-graphitizable carbon prepared at 2273 K was used as a working electrode. After potential cycling between 0 and 3.0 V, Nyquist plots gave a semi-circle at 3.0 V versus Li/Li⁺. At this potential, no Li-ion insertion and extraction occurred, and therefore the semi-circle is due to surface film resistance. At potentials below 0.9 V, impedance spectra gave two semi-circles. The semi-circle in the lower frequency region can be assigned to the charge transfer resistance due to Li-ion transfer at the non-graphitizable carbon electrode/polymer electrolyte interface. The temperature-dependence of the resistance showed Arrhenius-type behavior and gave activation energy of about 70 kJ mol⁻¹ regardless of the electrolyte used, indicating that a high activation barrier exists at the non-graphitizable carbon electrode/electrolyte interface for Li-ion transfer. Non-graphitizable carbon heat-treated in air at 773 K gave lower activation energy for interfacial Li-ion transfer than pristine carbon. However, the activation energy for interfacial Li-ion transfer in the polymer electrolyte was still large compared to that obtained in the liquid electrolyte. These results suggest that a high energy barrier of activation for interfacial Li-ion transfer exists at the interface between the electrode and solid polymer electrolyte.

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1. Introduction

Li-ion batteries are now used in a wide variety of portable electronic devices due to their high energy densities. However, there is still a need to improve Li-ion batteries for use in hybrid electric vehicles (HEV) due to their high performance. The rate performance of Li-ion batteries should be improved because a high power density is required for use in HEV. Rapid charge and discharge reactions are required when Li-ion batteries are used for high power applications. Thus, Li-ion transfer must be very rapid in such batteries; fast interfacial Li-ion transfer as well as fast Li-ion transport through the electrodes and electrolyte is essential for improving the rate performance of Li-ion

batteries. We previously reported that interfacial Li-ion transfer between an electrode and electrolyte is a slow process [1–4], and Li-ion transfer at the electrode/electrolyte interface should also affect the rate performance of Li-ion batteries.

Highly crystallized graphite, which shows an acceptably high capacity and a very flat potential identical to Li metal in charge/discharge processes, has been generally used as a negative electrode in Li-ion batteries for commercial applications [5]. Various other carbonaceous materials must still be studied to enhance the performance of Li-ion batteries [6]. Among them, non-graphitizable carbon, in contrast to graphite, has an isotropic structure and presents a relatively large number of Li-ion insertion sites on the electrode surface [7]. Therefore, since its charge transfer resistance is expected to be relatively small, non-graphitizable carbon may be suitable for fast interfacial Li-ion transfer.

* Corresponding author. Tel.: +81 75 3832483; fax: +81 75 3832488.

E-mail address: abe@elech.kuic.kyoto-u.ac.jp (T. Abe).

A solid polymer electrolyte has received much attention for practical use in HEV due to their many advantages such as safety and high energy density compared to the present commercial Li-ion batteries, which use a liquid electrolyte [8,9]. However, since a solid polymer electrolyte, unlike a liquid electrolyte, provides a solid/solid interface with an active electrode material, the interface area between the electrode and electrolyte is small. This problem is a characteristic of Li-ion batteries using a solid electrolyte and must be solved for practical use; the small effective area gives large charge transfer resistance due to Li-ion transfer at the electrode/electrolyte interface [10]. Therefore, interfacial Li-ion transfer seems to dominate the rate performance of Li-ion batteries. However, interfacial Li-ion transfer is not yet well understood.

In the present paper, we report Li-ion transfer at the interface between a non-graphitizable carbon electrode and solid polymer electrolyte and discuss the high activation barrier for interfacial Li-ion transfer.

2. Experimental

A non-graphitizable carbon plate prepared from phenolic resin at 2273 K (GC-20, Tokai Carbon Co., Ltd.) was used as a working electrode. Its thickness was 160 μm . GC20 was heated to 773 K at a rate of 10 K min^{-1} under an air atmosphere and held at this temperature for 1 h. The electrochemical properties of the non-graphitizable carbon were studied by cyclic voltammetry (HSV-100, Hokuto Denko Co.) using a three-electrode cell. The effective electrode surface area was 1.0 cm^2 in polymer electrolyte or limited to 0.11 cm^2 by an O-ring in liquid electrolyte. Both the counter and reference electrodes were Li metal. Electrolyte solution was 1 mol dm^{-3} LiClO_4 dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume). A polymer electrolyte of copolymer (obtained from ethylene oxide, di(ethyleneglycol) methyl glycidyl ether and allyl glycidyl ether) containing LiBF_4 or $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (LiTFSI) with a Li/O ratio of 0.06 was donated by Daiso Co., Ltd [9]. The ionic conductivity of the polymer electrolyte was evaluated by AC impedance spectroscopy in the frequency range from 100 kHz to 10 mHz using a two-electrode cell consisting of a stainless steel electrode/polymer electrolyte/stainless steel electrode. Li-ion transfer at the interface between a non-graphitizable carbon electrode and electrolyte was investigated by AC impedance spectroscopy using a VoltaLab40 (Radiometer Analytical SAS). After potential cycling between 0 and 3.0 V, the electrode was swept to a given potential (ranging from 0.6 to 3.0 V) at 1 mV s^{-1} and kept at that potential to reach a steady-state. AC impedance spectra were then obtained by applying a sine wave with amplitude of 10 mV over a frequency range from 100 kHz to 10 mHz. The lowest electrode potential was limited to 0.6 V, since considerable time is needed to achieve a steady-state at potentials below 0.5 V. Unless otherwise stated, the potential is

given versus Li/Li^+ . All experiments were conducted under an argon atmosphere with a dew point below -60°C .

The surface structures of non-graphitizable carbons were studied by Raman spectroscopy (Jobin-Yvon, T-64000).

3. Results and discussion

Fig. 1 shows Raman spectra of GC20 with and without heat treatment at 773 K in air. Two main peaks appeared at around 1360 and 1600 cm^{-1} . Peaks at 1360 and 1580 cm^{-1} are well known as Raman active A_{1g} and E_{2g} mode frequencies. No obvious difference was observed between the spectra, indicating that the crystallinity of GC20 was not affected by heat treatment.

Fig. 2 shows a cyclic voltammogram of GC20 in a polymer electrolyte containing LiTFSI as a salt. The cyclic voltammogram was measured with a sweep rate of 0.1 mV s^{-1} in the potential range between 0 and 3.0 V. A large cathodic current was observed below 0.9 V, which is assigned to Li-ion insertion into the GC20 electrode, and a corresponding anodic current identified as Li-ion extraction appeared at around 0.7 V.

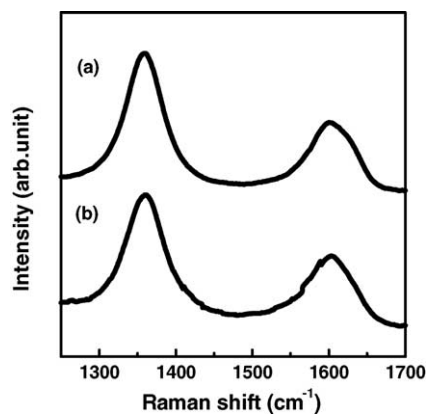


Fig. 1. Raman spectra of non-graphitizable carbon (a) with and (b) without heat treatment at 773 K in air.

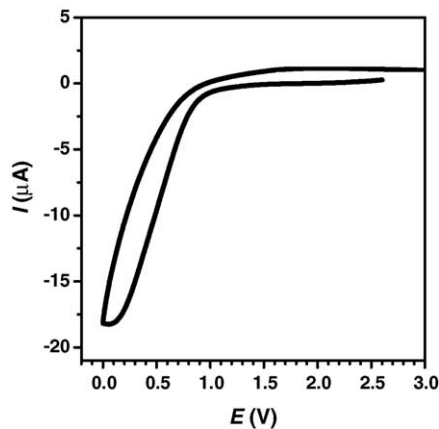


Fig. 2. Cyclic voltammogram of GC20 in LiTFSI-containing polymer electrolyte. Scan rate was 0.1 mV s^{-1} .

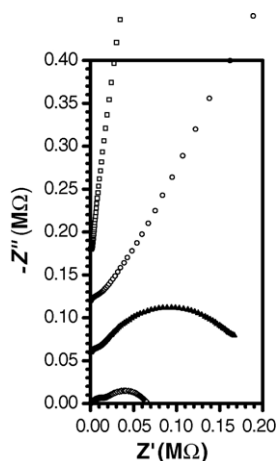


Fig. 3. Impedance spectra of GC20 electrode in LiTFSI-containing polymer electrolyte at potentials of 3.0 V before cycling (\square) and 1.2 V (\circ) 0.8 V (\triangle) and 0.6 V (\diamond) after potential cycling.

An almost identical cyclic voltammogram was obtained in a LiBF_4 -containing polymer electrolyte and a liquid electrolyte.

Fig. 3 shows Nyquist plots of GC20 at given potentials in the range 0.6–3.0 V in a polymer electrolyte using LiTFSI as a salt. No semi-circle was observed, but a line perpendicular to the Z' -axis appeared at 3.0 V. Each measurement was conducted at ca. 25 °C. The polymer electrolyte showed very high ionic conductivity even at a temperature as low as 25 °C. In addition, based on the cyclic voltammogram, no Li-ion insertion or extraction occurred at a potential of 3.0 V, and therefore blocking electrode behavior appeared. After potential cycling, one semi-circle was observed at the same potential of 3.0 V, and similar Nyquist plots were obtained at up to 1.0 V, as shown in Fig. 3. No oxidation and reduction current at the GC20 electrode was observed at potentials above 1.0 V, and this semi-circle was not influenced by the electrode potential. Therefore, this resistance is due to the surface film formed on the GC20 electrode. At potentials below 0.9 V, another semi-circle appeared in the lower frequency region. The resistance evaluated from the semi-circle in the lower frequency region depended on the electrode potential: the resistance decreased with a decrease in the electrode potential. Therefore, it is likely that the resistance can be ascribed to the charge transfer resistance due to Li-ion transfer at the interface between the non-graphitizable carbon electrode and electrolyte. Almost identical Nyquist plots were obtained in LiBF_4 -containing polymer electrolyte and EC+DEC-based electrolyte [4].

Fig. 4 shows the temperature-dependence of the Li-ion transfer resistance for GC20 at 0.8 V. Charge transfer resistance decreased with increasing temperature and showed Arrhenius-type behavior. The value of the resistance was much greater in polymer electrolyte than in liquid electrolyte, which is due to a much smaller interface area between the electrode and solid polymer electrolyte. The activation energy for Li-ion transfer resistance

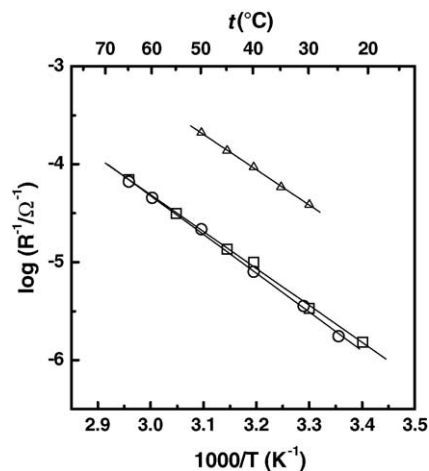


Fig. 4. Temperature-dependence of lithium-ion transfer resistance at the interface between GC20 electrode and electrolyte at 0.8 V. LiTFSI-containing polymer electrolyte (\square). LiBF_4 -containing polymer electrolyte (\circ). 1 mol dm^{-3} $\text{LiClO}_4/\text{EC}+\text{DEC}$ (\triangle). Lines were drawn using the least-squares method.

tance was determined by the least-squares method to be $72.0 \pm 1.4 \text{ kJ mol}^{-1}$ in LiTFSI-containing polymer electrolyte, $75.8 \pm 1.5 \text{ kJ mol}^{-1}$ in LiBF_4 -containing polymer electrolyte, and $68.7 \pm 1.8 \text{ kJ mol}^{-1}$ in EC+DEC-based electrolyte. Thus, nearly identical activation energies were obtained, which is quite different from the results obtained in Li-ion intercalation and de-intercalation at a graphite electrode; the activation energy for Li-ion transfer resistance at a graphite electrode/EC-based electrolyte interface was smaller than the present values by around 20 kJ mol^{-1} [11]. Our group previously showed that there were high activation barriers at the interface between electrode and electrolyte for Li-ion transfer and that the activation energies were responsible for the de-solvation of Li-ion [1,11]; the activation energies needed for Li-ion to transfer at an electrode/electrolyte interface are influenced by the solvent used in the electrolyte. In contrast, the present system seems to present another rate-determining step for Li-ion transfer at the electrode/electrolyte interface. Based on the finding that the activation energy was independent of the electrolyte, the surface structure of GC20 may be responsible for the large activation energy. This assumption can be examined by modifying the surface of GC20.

Fig. 5 shows the temperature-dependence of Li-ion transfer resistance for GC20 heat-treated at 773 K in air. The surface structure of carbon can be changed by mild oxidation [12,13], and we previously showed that heat treatment at 773 K in air resulted in a remarkable decrease in the resistance for interfacial Li-ion transfer [14]. The activation energy for Li-ion transfer resistance was evaluated to be $47.9 \pm 1.5 \text{ kJ mol}^{-1}$ in EC+DEC-based electrolyte. This value is much smaller than that obtained with pristine GC20 and almost identical to that obtained with a graphite electrode [11]. Consequently, the above assumption is considered to be valid. Hence, the surface structure

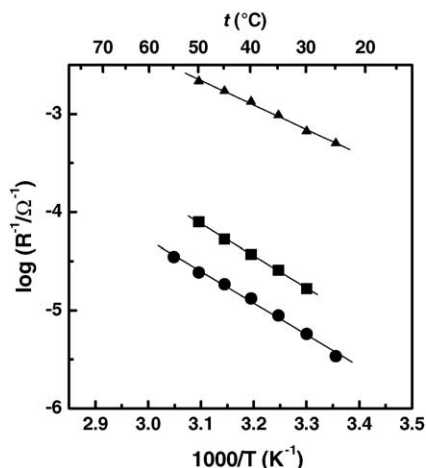


Fig. 5. Temperature-dependence of lithium-ion transfer resistance at the interface between heat-treated non-graphitizable carbon electrode and electrolyte at 0.8 V. LiTFSI-containing polymer electrolyte (■). LiBF₄-containing polymer electrolyte (●). 1 mol dm⁻³ LiClO₄/EC+DEC(▲). Lines were drawn using the least-squares method.

plays an important role in Li-ion kinetics at a GC20 electrode. The activation energy for Li-ion transfer resistance was 62.5 ± 1.1 kJ mol⁻¹ in LiTFSI-containing polymer electrolyte and 66.6 ± 2.4 kJ mol⁻¹ in LiBF₄-containing polymer electrolyte, which were also smaller than that obtained with pristine GC20. However, these values are still large compared to that obtained for Li-ion transfer in a liquid EC+DEC-based electrolyte or for Li-ion conduction through a polymer electrolyte (44.0 ± 0.9 kJ mol⁻¹ in LiTFSI-containing polymer electrolyte and 53.0 ± 1.9 kJ mol⁻¹ in LiBF₄-containing polymer electrolyte). Therefore, a large activation barrier for Li-ion transfer exists at an electrode/solid polymer electrolyte interface.

Based on the above results, decrease of activation barrier at interface between polymer electrolyte and electrode should be required for enhancement of rate performance of Li-ion batteries using solid polymer electrolytes.

4. Conclusion

Li-ion transfer at the interface between a non-graphitizable carbon electrode and a electrolyte was studied by AC impedance spectroscopy. At the interface between a GC20 electrode and electrolyte, a large activation barrier of more than 70 kJ mol⁻¹ was noted regardless of the electrolyte used.

Surface-modified GC20 that was subjected to heat treatment in air gave smaller activation energies for interfacial Li-ion transfer than that seen with pristine GC20. The present results show that the surface structure of non-graphitizable carbon should significantly affect the Li-ion transfer kinetics at the non-graphitizable carbon electrode/electrolyte interface. A high activation barrier was noted for Li-ion transfer at the interface between a surface-modified GC20 electrode and solid polymer electrolyte, which was much larger than that obtained in a liquid electrolyte or that for Li-ion transport within a polymer electrolyte. Thus, Li-ion transfer at an electrode/electrolyte interface significantly affects the rate performance of Li-ion batteries using a solid polymer electrolyte.

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