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Research Paper

Correlations of concentration changes of electrolyte salt with resistance and capacitance at the surface of a graphite electrode in a lithium ion battery studied by in situ microprobe Raman spectroscopy

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ABSTRACT

Concentration changes of electrolyte salt in practical lithium ion batteries occur due to various factors during operation, and the changes causes serious degradation of battery performance. It is important to identify elementary factors and how each of the factors induces the concentration changes in batteries by using a simplified system. The concentration of ions in the electrolyte solution between a highly oriented pyrolytic graphite (HOPG) electrode and a lithium foil electrode in a model battery was studied during charge/discharge cycles by in situ microprobe Raman spectroscopy. The concentration of ions decreased during de-intercalation of Li^+ from HOPG. The decreased concentration recovered during subsequent rest time with a time constant of several hours. The results of impedance spectroscopy showed that the cycle dependence of the resistance of the surface film on the graphite was similar to that of the time constant. On the other hand, the cycle dependence of the capacitance at the graphite surface and the cycle dependence of the charge transfer resistance at the graphite surface were similar to that of the degree of concentration change. The results suggest that the resistance of the surface film can be evaluated from the rate of the recovery.

1. Introduction

There has been an increasing demand for the development of superior batteries for use in electric cars and mobile electronic devices and for increased utilization of renewable energy. Much interest has been shown in lithium ion batteries due to their high power density. The potential of the graphite anode becomes sufficiently low for reduction of the electrolyte solution when the battery is charged. However, at the initial stage of charging, a surface film, called a solid electrolyte interphase (SEI), forms on the graphite [1–3]. The SEI is an insulator for electrons but is conductive for Li^+, and it therefore passivates further reduction of the electrolyte solution, resulting in stable charge/discharge cycles. The properties of the SEI are key factors for achieving good battery performance. However, the properties of the SEI and its origins are not yet fully understood because analysis of the SEI is difficult due to its very delicate and fragile nature both physically and chemically.

The concentration of ions in the electrolyte solution in the battery changes during charging and discharging [4–13], reflecting resistance to ion diffusion and the positions of diffusion barriers, and the changes in concentration has various negative effects such as lowering the reaction rate, decreasing the voltage and increasing the temperature, resulting in poor performance of batteries. Elucidation of the changes in concentrations of ions during operation of a battery is needed for the development of better batteries with high performance. Recent studies by in situ NMR measurement have shown that the concentration of ions in the SEI on Si/C increased during insertion of Li^+ into Si/C [12]. It was also shown that the concentration of the electrolyte salt changes during charging and discharging due to low permeability of the SEI for ion migration in a model cell with an HOPG electrode and an $LiFePO_4$ composite electrode [14]. Concentration changes of electrolyte salt in practical batteries are thought to be induced by various factors depending on active materials, electrolyte solution and pore

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structure of composite electrodes. Although it is difficult to fully understand the mechanism of concentration change, it is important to clarify the elementary factors that can cause concentration changes and how each factor causes concentration changes by using a simplified system.

The capacitance and resistance of the SEI and those at the surface of graphite electrodes in lithium ion batteries have been separately evaluated in many past works by electrochemical impedance spectroscopy [15–20]. In the present work, detailed kinetics of changes in the concentration of ions in the electrolyte solution in a model battery consisting of a highly oriented pyrolytic graphite (HOPG) electrode and a lithium foil electrode was studied by in situ ultrafine probe Raman spectroscopy. The capacitance and resistance were also measured by impedance spectroscopy, and their correlations with the concentration changes of electrolyte salt were investigated. The concentration of ions decreased during de-intercalation of Li^+ from HOPG and the concentration recovered during subsequent rest time with a time constant of several hours. The results of impedance spectroscopy showed that the cycle dependence of the degree of concentration change was similar to the cycle dependence of capacitance (constant phase element) at the surface of HOPG and that of the resistance to charge transfer at the surface of HOPG. The cycle dependence of the time constant was similar to that of the resistance of the SEI. The results suggest that the rate of recovery is determined by the resistance of the SEI; that is, the resistance can be evaluated from the time constant. The results provide important information for understanding phenomena in batteries and for evaluating the properties of the SEI to develop superior batteries.

2. Experimental

Analysis of the electrolyte solution in situ in deep narrow spaces is very difficult. We have recently developed the world's thinnest (cross-sectional area of about $30\,\mu m \times 60\,\mu m$) ultrafine fiber Raman probes with the highest spatial resolution of 23 μm [21] (much thinner than previous fiber Raman probes [22,23] ($> 600\,\mu m$)) to conduct in situ analysis of the concentration of ions in the electrolyte solution in deep narrow spaces between a highly oriented pyrolytic graphite (HOPG) electrode and an $LiFePO_4$ composite electrode inside model battery cells [14]. The details of the probe, the model cell and experiments are described in previous papers [21,14]. A model cell shown in Fig. 1a was made in a dry room where the dew point temperature was below −50 °C. The HOPG electrode, the Li electrode and the probe were inserted between very flat faces (±1 μm) of two SUS316 blocks, and the distance between the surfaces of the two electrodes was adjusted to 100 μm by sliding the two blocks by micrometers. Instead of previously used $LiFePO_4$ and $LiCoO_2$ composite electrodes [14,24,25] (commonly used in practical batteries), an Li electrode was used in the present study to conduct impedance spectroscopy at accurately controlled potentials of HOPG relative to Li. Two separator films were used to avoid a short circuit. In a previous work, multiple probes were used to study the dependence of concentration of the electrolyte salt on the distance from electrodes. In the present work, a single probe was used because no significant dependence of the concentration on the distance was observed when separator films were placed between the probe and electrodes (See Fig. S4 in supporting information). An electrolyte solution of $1\,mol\,dm^{-3}$ $LiClO_4$ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of 1:1 was used. A 532 nm laser light was introduced through the fiber probe into the cell, and Raman spectroscopy measurements were conducted during intercalation of Li^+ into HOPG and de-intercalation in the dry room. Impedance spectra were taken with Biologic VMP300 in a range of frequency from 3 MHz to 10 mHz with an amplitude of 10 mV.

Fig. 1b show a Raman spectrum of the electrolyte solution inside the battery (Fig. 1a) taken with the probe. Peaks at $718\,cm^{-1}$ and $730\,cm^{-1}$ were previously assigned as the symmetric ring deformation mode of EC and of solvated EC with Li^+ (EC-Li^+), respectively [26,27]. Peaks at $894\,cm^{-1}$ and $905\,cm^{-1}$ correspond to the ring breathing mode of EC and EC-Li^+, respectively, and the latter was overlapped with a peak of DEC. The peak at $935\,cm^{-1}$ was assigned [28] as the totally symmetric mode of ClO_4^-. In the present work, intensities of peaks at $718\,cm^{-1}$, $730\,cm^{-1}$ and $935\,cm^{-1}$ were analyzed.

3. Results and discussion

Fig. 2a shows the potential of HOPG vs Li and current during the 1st intercalation/de-intercalation cycle in a linear sweep voltammetry mode at a rate of 1 mV/s. The potential was first scanned to 0.01 V and then to 2.5 V. Fig. 2b and c show the areas of peaks of EC-Li^+ and ClO_4^- during this cycle, respectively. The area of each peak was obtained by summing counts in a window that includes the peak after subtraction of backgrounds (see page S2 in supporting information). The areas of the peaks are nearly proportional to the concentrations of Li^+ and ClO_4^-, respectively (See Figs. S2 and S3 in supporting information). During the decrease in potential, a current appeared at 0.84 V (indicated by a vertical dashed line at 0.29 day), and the areas of peaks of EC-Li^+ and ClO_4^- started to

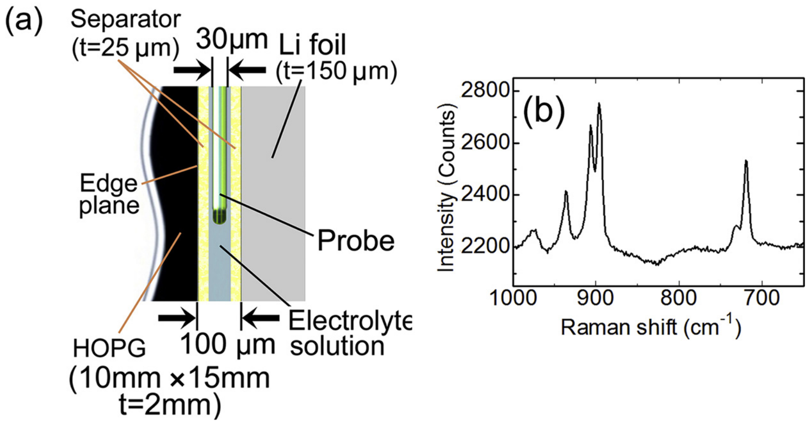

Fig. 1. Probe Raman spectroscopy inside the battery. (a) Structure of the battery. (b) Raman spectrum of the electrolyte solution inside the battery (Fig. 1a) before cycle test.