Kinetic behavior of anion intercalation into graphite electrodes in organic solutions

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Energy storage systems for large electric devices, such as hybrid electric vehicles or electric vehicles, are requested to possess high power densities, as well as high energy densities. Lithium-ion secondary batteries (LIBs) are paid much attention as the power sources for the devices above, due to their high energy densities. In addition, a lot of studies to improve power densities are under investigation. Our group has focused on the Li⁺-ion transfer at the electrode/electrolyte interface and cleared that the weakening the interaction between Li⁺-ion and solvents was highly effective for fast charge and discharge reactions [1,2]. The results motivated us to study the electrochemical anion intercalation reaction into graphite electrodes. Since anion species are generally not solvated, the interaction with solvents is expected to be extremely small. In addition, anion intercalation into graphite usually occurs at high electrode potential over 4.5 V (Li⁺/Li), which indicates that the energy storage systems using anion intercalation reaction can possess both high power and energy densities. Although these systems are well known as hybrid capacitors or dual carbon cells and widely studied, the kinetics of anion intercalation has not been elucidated. In the present study, the kinetic behavior of anion intercalation reaction in organic electrolyte solutions is discussed.

Anion intercalation reaction was studied by use of the three-electrode beaker type cells. Highly oriented pyrolytic graphite (HOPG) bounded with Pt wire and Li metal were used as the working electrode and reference or counter electrodes, respectively. Electrolyte solution was consisted of propylene carbonate (PC) containing LiN(CF₃SO₂)₂ (LiTFSA). For electrochemical measurements, cyclic voltammometry and A.C. impedance method were conducted. To confirm the formation of graphite intercalation compounds, HOPG electrode after holding potential was investigated by X-ray diffraction (XRD) measurements. All cell fabrication and electrochemical measurements were conducted in Ar-filled glove box. Unless otherwise mentioned, all electrode potential was referred to Li⁺/Li.

Figure 1 shows the cyclic voltammogram of HOPG in 1 mol dm⁻³ LiTFSA-PC solution. Oxidation current and reduction current was observed around 4.5 V and 4.4 V, respectively. The redox currents showed good reversibility, which implies the intercalation and de-intercalation reaction of TFSA⁻ anion will be adjustable around 1 kHz and the following Warburg behavior was observed. Since the semi-circle did not appear at open circuit potential (ca. 3 V), it was ascribed to the charge transfer resistance (Rct).

The temperature dependency of Rct showed Arrhenius type behavior and the interfacial activation energy was calculated from the slope of it. As the result, the activation energy was evaluated to be 28 kJ mol⁻¹, which is almost half value compared with that of Li⁺-ion in organic carbonate solutions (ca. 55 kJ mol⁻¹), previously reported by the authors [2]. As described above, the large activation energy of Li⁺-ion is due to the de-solvation process, i.e., the interaction between Li⁺-ion and solvents. The small interfacial activation energy of TFSA⁻ anion will mean that the interaction with solvents is much weaker than that of Li⁺-ion. In general, anion species in organic solutions exist as “free anion”. Therefore, the interfacial activation energy can be arisen from the cleavage of small ion-dipole interaction with PC solvents or ion-phonon interaction with Li⁺-ion.

Based on the results and consideration, it will be concluded that the use of the anion intercalation into graphite electrode is attractive as the electrode reaction for next generation energy storage devices with high energy density and high power.

References


Fig.1 Cyclic voltammogram of HOPG in 1 mol dm⁻³ LiTFSA-PC. Scan rate was set at 1 mV sec⁻¹.

Complex impedance plots measured at 4.65 V is shown in Fig.2. One semi-circle with characteristic frequency of