

Electrochemical oxidation behavior of carbon in non-aqueous solution

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Introduction:

Carbon materials are commonly employed as conductive additives in a positive electrode of lithium-ion batteries (LIB). These carbons are exposed to a strongly oxidative environment, and oxidation of carbon can take place. Therefore, carbons would not work as a conductive material due to carbon oxidation and it would cause degradation of LIBs. For the development of high-energy-density LIBs, higher working potential is recommended. Then, carbon will be exposed to a more strongly oxidative environment, resulting in the carbon oxidation problem in nonaqueous solution. Oxidative degradation of carbon materials in nonaqueous solution will be a serious issue. Carbon oxidation in aqueous solutions has been extensively studied for the understanding of the degradation of polymer electrolyte membrane fuel cells (PEMFC), and our group so far reported the oxidation behavior of carbon which served as a catalyst substrate in PEMFC.^[1] In contrast, few studies on carbon oxidation have been conducted in non-aqueous solutions. In this study, we report the oxidation behavior of carbon materials in nonaqueous solution by mainly using glassy carbons (GC).

Experimental:

Glassy carbon heat-treated at 2000 °C was used as a model electrode. A three-electrode cell equipped with Li metal as a reference electrode and Li metal as a counter electrode was employed for electrochemical measurements. The electrolyte solution was ethylene carbonate (EC) -diethyl carbonate (DEC) (1:1) mixture, containing 1 mol dm⁻³ LiClO₄. The GC electrode was held at 3.7, 4.0, 4.3, 4.7, and 5.0 V (vs. Li/Li⁺) for 10 hours. After keeping at each potential, each sample was held at 3.0 V (vs. Li/Li⁺) for 10 h. Then, the electric double layer capacitance of the GC electrode was studied by cyclic voltammetry. The surface composition was analysed by X-ray photoelectron spectroscopy (XPS). The surface morphology was observed by scanning electron microscope (SEM).

Results and discussion:

Figure 1 summarizes the results for surface analysis by XPS. Figure 1 shows the O/C ratios of a pristine GC and GCs after holding at 3.7, 4.0, 4.3, 4.7 and 5.0 V (vs. Li/Li⁺), followed by holding at 3.0 V (vs. Li/Li⁺). The O/C ratio of GCs surface increases as GCs were exposed to higher potentials. Hence, it was likely to consider that GCs were oxidized at high potential in non-aqueous solution and GC surface was more severely oxidized by the higher potentials.

Figure 2 shows cyclic voltammograms of GC before and after holding at 5.0 V (vs. Li/Li⁺) for 10 h. As shown in Fig. 2, the shapes of the cyclic voltammograms indicate the capacitive behavior and the currents corresponding to

redox reaction were not observed. The increase of electrical double layer capacitance suggests the increase of surface area, and therefore the surface of the GC held at 5.0 V (vs. Li/Li⁺) should be oxidized, which is in good agreement with the results of XPS.

Figure 3 shows SEM images of pristine GC and GC after holding at 5.0 V (vs. Li/Li⁺) for 10 h. On GC after holding at 5.0 V, a lot of pits were observed, as shown in Fig. 3 (b), which is caused by the oxidation.

As mentioned above, we showed the oxidation behavior of carbons by using the glass carbon electrodes in non-aqueous solutions. Oxidation behaviors of the commercialized conductive additives will be discussed in the conference.

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References

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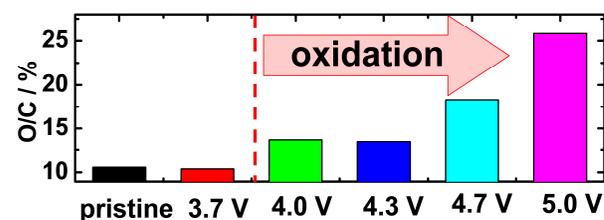


Fig. 1 O/C ratios of pristine GC and GCs held at 3.7, 4.0, 4.3, 4.7 and 5.0 V, followed by holding at 3.0 V in 1 mol dm⁻³ LiClO₄ / EC:DEC (1:1 by vol.).

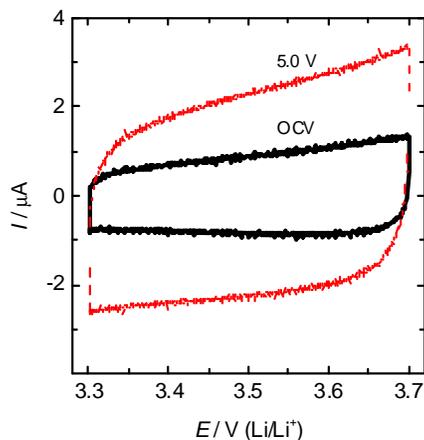


Fig.2 Cyclic voltammograms of GC before and after holding at 5.0 V for 10 hours, followed by holding at 3.0 V. Sweep rate was set at 100 mV s⁻¹.

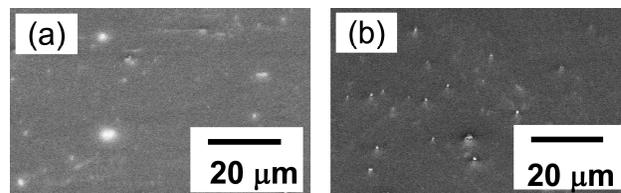


Fig. 3 SEM images of (a) pristine GC, (b) GC held at 5.0 V (vs. Li/Li⁺) for 10 h, followed by holding at 3.0 V (vs. Li/Li⁺).