

Condition That a Pure PC Electrolyte Is Stable during the Insertion of Li at the Well Graphitized Anode

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Introduction

Rapid improvement of performances of the portable electronic appliances used for IT technology is requiring Li-ion batteries to improve the working power, capacity and low price. Propylene carbonate (PC) is an excellent solvent giving rise to an electrolyte having high conductivity even at lower temperature and the price is low. But it cannot be used practically for any graphite based anode material since it decomposes vigorously at the anode during the Li charging process, which is ascribed to the solvent co-intercalation into the space of stacking graphite layers [1, 2].

We have found by chance, however, that PC does not decompose when a straight single fiber electrode was negatively polarized in an electrolyte comprised with pure PC and LiClO₄ [3]. Tentative explanation of the stabilization mechanism has proposed [3] but not proved yet. The purpose of the present study is to accumulate the experimental evidences in regard to the stabilization of PC at the graphitized electrode for elucidating the stabilization mechanism.

Experimental

Carbon fibers having different types of oxidized surface skin were examined (Petoca made, graphitized at 3110 °C). Highly oriented pyrolytic graphite (HOPG) was provided by NT-MDT (ZYA). Fabrication of a single fiber electrode is described elsewhere [3].

Pristine fibers and surface modified fibers were examined. The surface modification treatments were: mild oxidation, vacuum deposition of metal film, and that treated by mild oxidation. Electrochemical measurement was done mainly with a cyclic voltammetry with different scan rate in pure PC containing 1 M LiClO₄ in an argon flowing glove box.

Results and Discussion

Effect of the thickness of the protective skin

Comparison of CVs for fibers having a thick protective skin and a thin skin (Fig.1) showed no obvious difference between them. Even with a fiber whose skin was removed almost by mild oxidation revealed very stable CVs as shown in Fig.2. This implies that the suppression of PC decomposition does not caused by the skin layer.

Effect of a deposited metal film

Basically, the degree of the decomposition showed no effect due to the metal film deposition.

Effect of the potential scan rate

Even an electrolyte based on EC/DMC mixture

gave rise to a small initial irreversible capacity, but the specific amount of the capacity was clearly dependent on the scan rate, and the faster scan resulted in giving a suppressed irreversible capacity.

Effect of the uniformity of the potential distribution

Fabrication of the fiber electrode with a tilted direction induced the PC decomposition (Fig.3), implying the uniformity of the potential distribution is a key factor for controlling the decomposition.

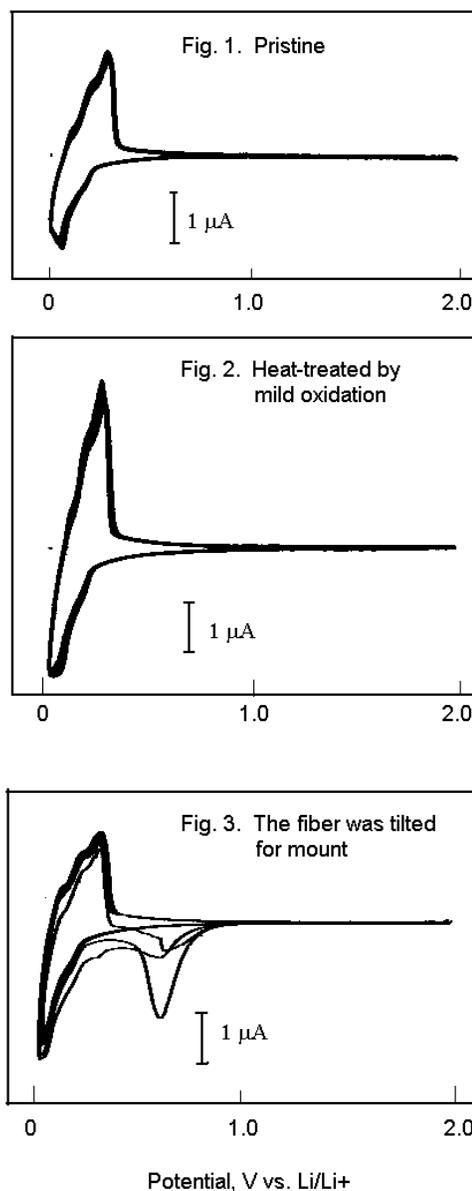


Fig. 1 (top) CV of a single graphitized carbon fiber having a thin skin in pure PC containing 1 M LiClO₄. Scan rate: 1 mV/s

Fig. 2 (middle) CV of a single graphitized carbon fiber in pure PC containing 1M LiClO₄. The fiber was mildly oxidized at 450 °C for 15 min. before measurement. Scan rate: 1 mV/s.

Fig. 3 (bottom) CV of a single graphitized carbon fiber in pure PC containing 1M LiClO₄. The fiber was mounted to the terminal with a tilted angle. Scan rate: 1 mV/s

References

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