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Electrode Property of Single-walled Carbon Nanotubes in All- solid-state Lithium Ion Battery using Polymer Electrolyte

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Abstract. Electrode properties of single-walled carbon nanotubes (SWCNTs) in an all-solid-state lithium ion battery were investigated using poly-ethylene oxide (PEO) solid electrolyte. Charge-discharge curves of SWCNTs in the solid electrolyte cell were successfully observed. It was found that PEO electrolyte decomposes on the surface of SWCNTs.

INTRODUCTION

Owing to its high energy density, lithium ion battery (LIB) has been used widely. However, since LIBs use flammable organic liquid electrolytes, there is a considerable risk of explosion and/or fire. To avoid the explosion and fire accidents, all-solid-state LIBs are now highly demanded. Furthermore, new electrode materials, which could not be used in usual LIBs because of side reactions with liquid electrolytes, would be usable in all-solid-state LIBs. Single-walled carbon nanotubes (SWCNTs) were expected as new electrode materials for LIBs because of their high electric conductivity and high specific surface area. Unfortunately, since carbonate electrolytes which are used in commercial LIBs easily decompose on the surface of SWCNTs, it had been judged that SWCNTs could not be used as electrode materials of LIBs¹⁻²⁾. However, SWCNTs might work as an electrode in all-solid-state LIBs, because the above-mentioned side reactions should not occur³⁾. So far, there have been few reports on all solid state LIBs using SWCNT electrodes. In the present paper, we investigate the electrode property of SWCNTs in a polymer electrolyte⁴⁻⁵⁾.

EXPERIMENTAL

We prepared solid electrolyte as follows. The [O]:[Li] = 8:1 mixture of poly-ethylene oxide (PEO, M.W.=1000000) and bis(trifluoro-methanesulfonyl)imide (LITFSI) was dissolved in acetonitrile in an argon gas filled dry box. The homogenized colloidal solution was cast and dried into a thin film at 80 °C for 12 h. The thickness of the solid electrolyte about was 100 μm⁶⁻⁸⁾. The ionic conductivities of the obtained film in the temperature range of 0-65 °C were measured with AC impedance technique using a potentiostat-galvanostat system (Autolab Co., Ltd.). The electrochemical stability of the electrolyte was measured by linear sweep voltammetry in the potential range of 0.01-4.5 V. For charge-discharge measurement of SWCNTs in solid electrolyte, we fabricated two electrode configuration cell consisting of SWCNT working and Li metal counter electrodes. We used high purity and high quality SWCNTs (Meijo Nano Carbon Co., Ltd., SO type) in the present study. The mean tube diameter of the SWCNTs was determined to be 1.48 nm by XRD pattern simulation. The XRD measurements were performed on a synchrotron radiation beam line BL-18C at the Photon Factory in High-Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The beam was monochromatized by Si(111) double monochromators and collimated by a pinhole collimator of 100 mm in diameter. The tube diameter and the value was confirmed by Raman (JASCO NRS-3300) and TEM (JEOL JEM-3010) measurements. We also observed charge-discharge curves of the same SWCNT sample in liquid electrolyte (ethylene carbonate (EC): diethyl carbonate (DEC) = 1:1).

RESULTS & DISCUSSION

The ionic conductivities of the electrolyte thin film determined by the AC impedance measurements at several temperatures are summarized in Fig. 1. The ionic conductivity value σ of the electrolyte having film thickness l and surface area A was calculated by the following equation.

$$\sigma = \frac{1}{\Omega} \times \frac{l}{A}$$

where R_b designates bulk resistance determined by Nyquist plots of AC impedance data. As shown in Fig. 1, the conductivity data can be divided in two regions having different activation energy ΔE_σ for ionic conduction evaluated from the following equation.

$$\log \sigma = \log \alpha + \frac{1}{2.303} \times \left(-\frac{\Delta E_\sigma}{KT} \right)$$

Where α is a frequency factor. It is plausible that segment motion of PEO polymer chains would reduce the activation energy in higher temperature region. Previous studies found that the ionic conduction behavior is different in the crystalline phase and amorphous phase of the PEO based electrolyte, and the ionic conductivity is higher in the amorphous phase than in the crystalline phase. Judging from the Fig. 1, the phase transformation temperature from crystalline to amorphous phase would be at around 60°C. The ionic conductivity at 65 °C was determined to be 1.70×10^{-3} S/cm. The determined value is as high as the previously reported value and is good enough to be used in all solid state LIBs⁹⁾.

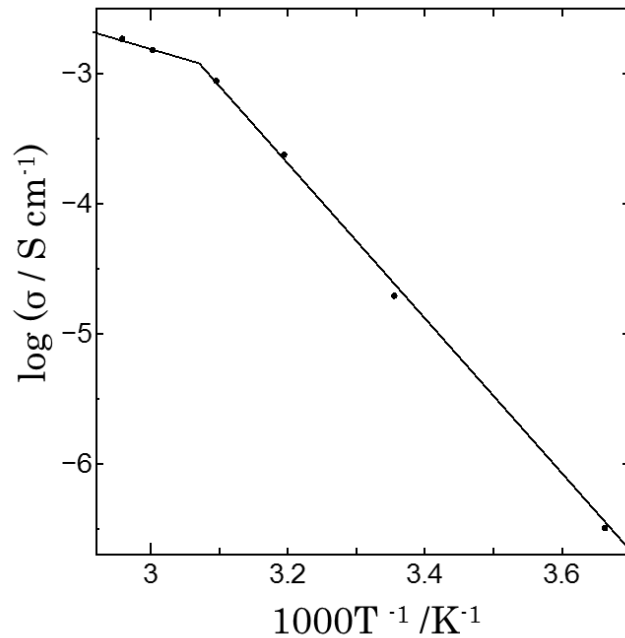


FIGURE 1. Temperature dependent conductivities of PEO-LITFSI electrolyte.

It was confirmed by the electrolyte stability measurement of PEO electrolyte that the electrolyte does not decompose up to 4.3 V (Fig. 2). Therefore, we can conduct charge-discharge experiment safely below 4.3 V.

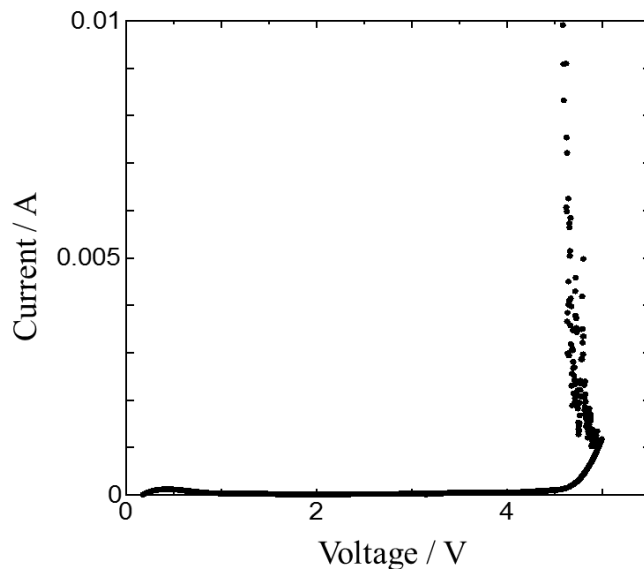


FIGURE 2. Linear sweep voltammogram of the used PEO-LITFSI polymer electrolyte at 65 °C.

Figures 3 and 4 show the observed charge-discharge curves of SWCNTs in liquid and solid electrolytes, respectively. The charge-discharge curve profiles observed in solid electrolyte cell (Fig. 4) are quite similar to those in liquid electrolyte cell (Fig. 3), although the charge and discharge capacities of solid electrolyte cell are much smaller than those of liquid electrolyte cell. Therefore, unfortunately, the decrease of irreversible capacity of SWCNTs by using solid electrolyte could not be achieved. This is probably due to that PEO electrolyte decomposes on the surface of SWCNTs as liquid carbonate electrolytes do¹⁰).

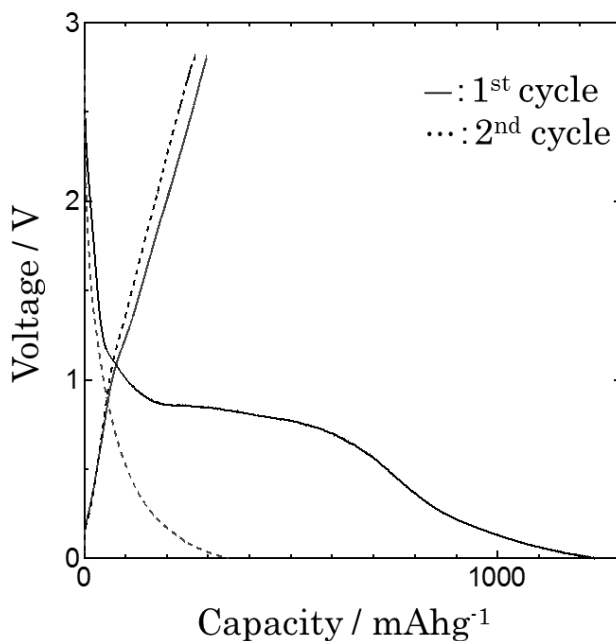


FIGURE 3. Charge-discharge curves of SWCNTs in liquid electrolyte cell at room temperature.

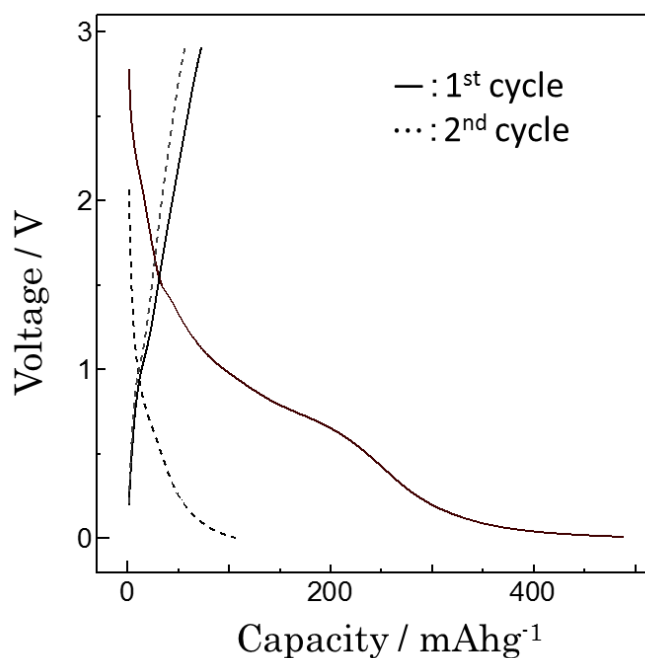


FIGURE 4. Charge-discharge curves of SWCNTs in solid polymer electrolyte cell at 65 °C.

Although it was found that Li ion insertion and extraction is possible in the system using SWCNT electrode and PEO electrolyte and that the reversible capacity of this system was as high as 100 mAh/g, it was concluded that SWCNT electrode is not appropriate for an all solid state LIB using PEO electrolyte because of the large irreversible capacity. To use SWCNTs as electrode active materials, non-polymer solid electrolytes should be used.

ACKNOWLEDGMENTS

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