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Synthesis and electrochemical performance of ruthenium oxide-coated carbon nanofibers as anode materials for lithium secondary batteries

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ABSTRACT

In this study, ruthenium oxide (RuO_2) coated carbon nanofibers (CNFs) were synthesized and applied as anode materials of Li secondary batteries. The CNFs were grown on Ni foam via chemical vapor deposition (CVD) method after CNFs/Ni foam was put into the 0.01 M $RuCl_3$ solution. The ruthenium oxide-coated CNFs/Ni foam was dried in a dryer at 80 °C. The morphologies, compositions, and crystal quality of RuO_2/CNFs/Ni foam were characterized by SEM, EDS, XRD, Raman spectroscopy, and XPS. The electrochemical characteristics of RuO_2/CNFs/Ni foam as anode of Li secondary batteries were investigated using three-electrode cell. The RuO_2/CNFs/Ni foam was directly employed as a working electrode without any binder, and lithium foil was used as the counter and reference electrodes. $LiClO_4$ (1 M) was employed as electrolyte and dissolved in a mixture of propylene carbonate (PC): ethylene carbonate (EC) in a 1:1 volume ratio. The galvanostatic charge/discharge cycling and cyclic voltammetry measurements were carried out at room temperature by using a battery tester. In particular, synthesized RuO_2/CNFs/Ni foam showed the highest retention rate (47.4%). The initial capacity (494 mAh/g) was reduced to 234 mAh/g after 30 cycles.

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1. Introduction

With increasing demands for portable electronic devices, people are getting more interested in small secondary batteries such as Ni-hydrogen secondary battery or Li secondary battery. In general, transition metal oxides such as $LiCoO_2$, $LiNiO_2$, and $LiMn_2O_4$ are used for the cathode of the secondary battery and Li or carbon is used for anode. Organic solvent containing Li ion is used as the electrolyte between two electrodes. In total, Li secondary battery consists of cathode, anode, electrolyte, and separating membrane.

However, the Li secondary battery using metallic lithium has the following disadvantages during charge/discharge cycling: it is likely to form the crystal of dendrite, which causes risk of short circuit. Therefore, carbonized or graphitized carbon materials are used for anode [1,2,13,14].

Carbon nanofibers synthesized as carbon materials in this study have been highlighted as the carbon-based anode material of Li secondary batteries because the original technology for the energy storage device with energy reduction and eco-friendly high performance has been developed. The carbon nanofibers are carbon fibers with micro graphite crystal structures having excellent chemical stability, electrical conductivity, and high energy efficiency. Because they have a larger specific surface area than conventional carbon materials, they are expected to relatively easily react with ions as the anode material of Li secondary batteries [3–6,9–12].

However, the carbon-based anode material has some problems such as low charge/discharge capacity and efficiency because it has a high irreversible capacity. Thus, studies are actively being conducted on transition metal oxides as anode materials of Li secondary batteries. The transition metal oxides mitigate the degradation of undesirable electrolyte or electrode and improve the electron conductivity of the surfaces [7,8].

In this study, carbon nanofibers with excellent chemical stability and thermal conductivity are synthesized. We would like to improve the low capacity of the carbon nanofibers by coating it with ruthenium oxide (RuO_2) containing high capacity and to improve the efficiency and extend the life span of electrodes by suppressing the side reactions of electrolytes.

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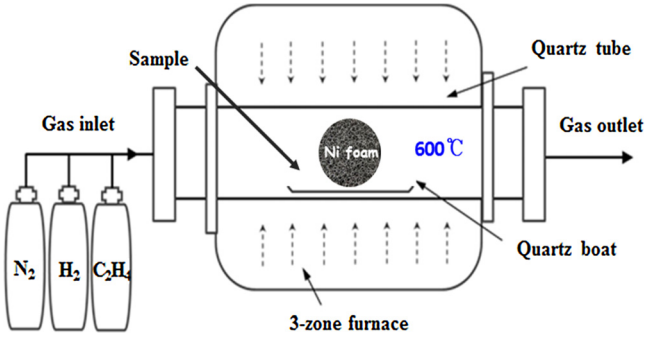

Fig. 1. Schematic diagram of CVD apparatus for the preparation of CNFs.

2. Experiment

2.1. Synthesis of carbon nanofibers

The synthesis of the carbon nanofibers was performed by chemical vapor deposition (CVD) method. CVD apparatus used for the synthesis is shown in Fig. 1.

In this study, carbon source used to synthesize carbon nanofibers was 20% ethylene (C_2H_4/N_2, Korea standard gas) gas. Gas phase reaction promotion gas and carrier gas were 20% hydrogen (H_2/N_2, Korea standard gas) gas, and high purity nitrogen (N_2, Korea standard gas) gas, respectively.

Carbon nanofibers were synthesized as follows: after Ni foam, the current collector, was put in the reactor, temperature was increased to 10 °C/min while nitrogen atmosphere was maintained. When it reached 600 °C, the temperature was maintained for 30 min/min and hydrogen gas was passed. For 10 min, a mixture of hydrogen gas and ethylene gas was passed. After the reaction was finished, it was cooled down to room temperature by passing nitrogen gas.

2.2. Preparation of ruthenium oxide-coated CNFs

$RuCl_3$ solution was used to coat the carbon nanofibers with ruthenium oxide. The dip-coating method was used to coat the carbon nanofibers synthesized by chemical vapor deposition in 0.01 M $RuCl_3$ solution, as shown in Fig. 2. After Ni foam was dip-coated in the ruthenium chloride solution and it was air-dried for 5 min, it was then dried for 12 h or more at 80 °C.

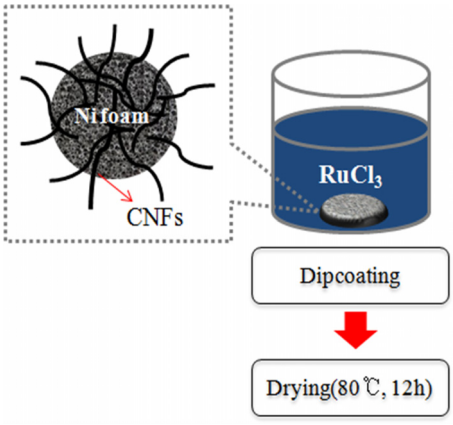

Fig. 2. Preparation process of ruthenium oxide coated CNFs.

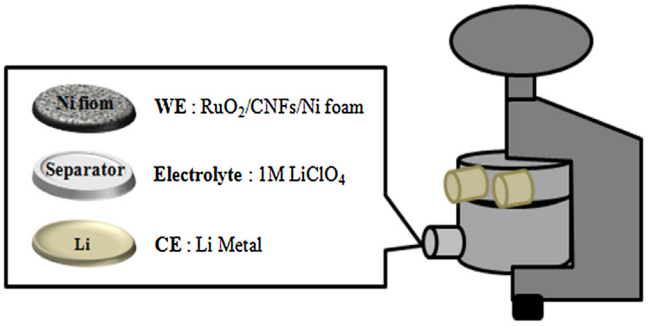

Fig. 3. Fabrication process of lithium secondary batteries.

2.3. Fabrication process of anode materials for lithium secondary batteries

Three-electrode cell was prepared by applying RuO_2/CNFs/Ni foam as anode active material of lithium secondary batteries. Three-electrode cell was assembled in the glove box filled with Ar gas. The scheme of cell assembly is shown in Fig. 3. It was assembled as a half cell. Prepared active materials were used as a working electrode. Lithium was used as counter and reference electrodes. A glass fiber separator was used as a separator membrane. $LiClO_4$ (1 M) was employed as electrolyte and dissolved in a mixture of EC(ethylene carbonate):PC(propylene carbonate) in a 1:1 volume ratio.

2.4. Analysis

The morphologies, compositions, and crystal quality of the prepared RuO_2/CNFs/Ni foam were characterized by scanning electron microscopy (SEM, Hitachi, S-4800), energy dispersive spectroscopy (EDS, Thermo ARL, ARL-3460), X-ray diffraction (XRD, PANalytical, X'pert PRO-MPD), Raman spectroscopy (Raman, Horiba Jobin-Yvon, LabRam HR), and X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, Multilab-2000). The electrochemical characteristics (Solartron, SI 1287) of RuO_2/CNFs/Ni foam as an anode of Li secondary batteries were investigated using cyclic voltammetry and galvanostatic charge/discharge.

3. Results and discussion

3.1. SEM

SEM images were measured to examine the morphologies of ruthenium oxide coated Ni foam, current collector, and ruthenium oxide-coated CNFs/Ni foam.

As the results of SEM image measurement, Fig. 4(a) shows that Ni foam was coated with ruthenium oxide while it was cracked. Sample (b) shows that carbon nanofibers were grown on the Ni foam. Carbon nanofibers were synthesized by contact of thermally decomposed hydrocarbon with metal catalytic particle such as Fe, Co, or Ni. It indicated that Ni foam, a current collector, played a role as a catalyst to grow carbon nanofibers. In addition, it showed that grown carbon nanofibers were coated with ruthenium oxide. Also, the growth of RuO_2/CNFs/Ni foam was verified with an average diameter of 100 nm.

3.2. EDS

EDS was performed to qualitatively and quantitatively analyze particular areas of ruthenium oxide-coated Ni foam and ruthenium oxide-coated CNFs/Ni foam. It is shown in Table 1. As (a) ruthenium oxide coated Ni foam and (b) ruthenium oxide coated CNFs/Ni foam

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