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Preparation and electrochemical characterizations of poly(3,4-dioxyethylenethiophene)/$LiCoO_2$ composite cathode in lithium-ion battery

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Abstract

A composite electrode material, poly(3,4-ethylenedioxythiophene) (PEDOT)/$LiCoO_2$-carbon fibers (VGCF) from a continuous process of electrochemical deposition of 3,4-ethylenedioxythiophene (EDOT) monomer on the pre-formed $LiCoO_2$-VGCF electrode, was prepared and characterized to test its applicability in lithium-ion battery. Compared to the bare $LiCoO_2$-VGCF electrode, use of PEDOT/$LiCoO_2$-VGCF composite as cathode in lithium-ion battery has enhanced properties such as the cyclability, electrochemical stability, intercalation/deintercalation rate of lithium ion and rate capability. Scanning electron microscope shows the successful coating of PEDOT on the $LiCoO_2$ particles and the VGCF fibers. The differential scanning calorimetry (DSC) scans of the charged cathodes show that incorporation of PEDOT reduces the thermal stability of the cathode.

Keywords: Lithium-ion battery; Poly(3,4-ethylenedioxythiophene); $LiCoO_2$; Carbon fiber

1. Introduction

Lithium-ion batteries are key components of many portable electronic devices and also show promise for the use in electric vehicles. Due to their high energy density, flexible design, lithium ion batteries have preference over other secondary battery systems, nevertheless, many approaches to alleviate problems such as poor long-term cyclability, worse safety and rate capability [1–4] are still undergoing. Discovery of new composite systems to serve as electrode materials represents a reasonable approach and had been frequently attempted previously.

Electrically conductive polymers (ECPs) represent an interesting family of synthetic materials due to their high electron mobility inside the doped polymer chains [5–9]. The practical application of ECPs is often dependent on their stability in ambient conditions, in this aspect, great focus had been on polythiophenes (PThs) since they are generally stable in air and moisture. Poly(3,4-ethylenedioxythiophene) (PEDOT), as one member of PTh family, has gained great attention in view of its high electrical conductivity in the p-doped state, good thermal and chemical stability and fast electrochemical switching [7,8]. With this regard, PEDOT had been incorporated into metal oxides such as $LiMn_2O_4$ [10] and V_2O_5 [11–13] and to test their applicability in lithium-ion battery. In this aspect, EDOT monomer can be directly oxidized by the metal oxides to initiate polymerization and form PEDOT polymer into the inner layer of the metal oxides. Use of these PEDOT/metal oxide composites as electrodes showed drastic enhancement on capacity and charge/discharge behavior.

In this study, we attempted to combine PEDOT with vapor growth carbon fiber (VGCF)/$LiCoO_2$ and to test its capability to serve as cathode materials in lithium-ion battery.

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PEDOT polymer may be electropolymerized between the two kinds of particles to enhance the electronic conductivity of the resulting composite material [14]. Use of VGCF is due to its reported applications [15–17] as filler materials of the electrodes in lithium-ion battery. The unique properties of VGCF, such as the small diameter, large surface area, high electrical conductivity, and the very spacial network morphology on the electrodes, all contribute to the improved performance (e.g. the cycle characteristic) in lithium-ion battery. $LiCoO_2$ is the lithium-ion source and is frequently used due to its promising properties in lithium-ion battery. In this study, the PEDOT/$LiCoO_2$-VGCF composite cathode was readily prepared by a continuous process, i.e. direct electrochemical polymerization of EDOT to deposit PEDOT on the pre-formed $LiCoO_2$-VGCF electrode. The resulting PEDOT/$LiCoO_2$-VGCF composite was then used as cathode to test its applicability in lithium-ion battery. For comparison, analogous electrochemical characterizations with $LiCoO_2$-VGCF as cathode were also conducted to distinguish the role of the deposited PEDOT. The results provide the possibility to apply PEDOT/$LiCoO_2$-VGCF composite cathode in current commercial lithium-ion battery.

2. Experimental

$LiCoO_2$ (Nippon Chemical Industrial Co.) used in this work has an average particle size of 11.5 μm, and a Brunauer–Emmett–Teller (BET) surface area of $0.21\ m^2\ g^{-1}$. VGCF (diameter 150 nm, length 5–10 μm, Showa Denko) with a BET of $13\ m^2\ g^{-1}$ was used as the conductive carbon of the composite cathode. Electrodes were prepared by combining solid components of VGCF (5 wt.%), polyvinylidenedifluoride (5 wt.%, PVDF, Kureha Chemical Industry Co.) and $LiCoO_2$ (90 wt.%) in *N*-methylpyrolidinone (NMP, Merck) solvent of equal weight. The mixed slurry was then coated on an aluminum foil (20 μm, Nippon Foil Co.) and dried at 90 °C. The dried electrode was compressed by a roller at room temperature to make a smooth and compact film structure. The composite cathode electrode was required to store in the glove box (with its oxygen and humidity content maintained below 5 ppm) for more than 24 h before the electrochemical polymerization step.

The electrochemical deposition of PEDOT was performed by an Autolab electrochemical analyzer with a current sensitivity of 1 nA (Autolab PGSTAT30, Eco Chemie) [9]. A one-compartment three-electrode glass cell was used and the whole apparatus was settled in the glove box. The working electrode is the composite $LiCoO_2$-VGCF electrode prepared by the above procedure with a dimension of 1 cm × 1 cm. Both the counter and reference electrodes are lithium metal (FMC). PEDOT was deposited on the $LiCoO_2$-VGCF electrode in 1M $LiPF_6$ (Kanto Denka Kogyo Co. Ltd.)/propylene carbonate (PC, Ferro) solution with 0.05 M 3, 4-ethylenedioxy thiophene (EDOT) monomer by a constant current of 0.5 mA for 400 s (equal to 200 mC). The resulting composite electrode of PEDOT/$LiCoO_2$-VGCF was washed by PC for several times before further test for its capability as cathode materials in lithium-ion battery.

The composite cathodes of PEDOT/$LiCoO_2$-VGCF and $LiCoO_2$-VGCF electrodes were tested by repeated cyclic voltammetry (CV) at $50\ mV\ s^{-1}$ in 1 M electrolyte of $LiPF_6$ in ethylene carbonate: dimethyl carbonate (EC:DMC = 1:1) (Merck, LP 30). A three-electrode glass cell with lithium foil as counter and reference electrodes was used and operation was performed in a glove box. Otherwise, the electrodes were tested by CV at various scan rates in the same system in order to compare the ionic transfer rate of the two composite cathodes. Since the real applications of cathodes in lithium ion battery are the charge/discharge behavior at the constant current mode, the electrodes were therefore charged to 4200 mV at $0.1\ mA\ cm^{-2}$ before the subsequent discharge to 2700 mV at either rate of 0.1 or $1.0\ mA\ cm^{-2}$ to check the rate capability performance of the composites. The results should be consistent with those from the CV test.

Differential scanning calorimetry (DSC) experiments were carried out after charging the electrodes to 4.3 V at 0.1 C rate. A DSC Perkin-Elmer calorimeter was used. Approximately 4 mg of the cathode composite containing the electrolyte were hermetically sealed in an aluminum DSC pan in a glove box. The samples were analyzed in the DSC using a temperature scan rate of $10\ ^{\circ}C\ min^{-1}$ from 30 to 430 °C.

Surface morphology and surface composition of the composite electrodes were detected by scanning electron microscope (SEM, JEOL JSM35 model, operating at 20 kV) and energy dispersive spectroscopy (EDS), respectively. Specimen of PEDOT/$LiCoO_2$-VGCF was firstly washed by PC and then dried at 90 °C for 24 h before inspected by SEM. In contrast, $LiCoO_2$-VGCF specimen was inspected directly as its prepared status.

3. Results and discussion

The target material, PEDOT/$LiCoO_2$-VGCF cathode, was readily made by direct electrochemical deposition of EDOT to the preformed $LiCoO_2$-VGCF electrode. The successful incorporation of PEDOT into the $LiCoO_2$ and VGCF components can be verified by comparison of the surface morphology of $LiCoO_2$-VGCF and PEDOT/$LiCoO_2$-VGCF. SEM micrographs of different magnifications (4000× and 10,000×) shown in Fig. 1 were selected to focus on the $LiCoO_2$- and VGCF-rich areas, respectively. For the large $LiCoO_2$ particles in $LiCoO_2$-VGCF composite (Fig. 1a), several small $LiCoO_2$ scraps are visible on the surface area. On the contrary, the large $LiCoO_2$ particles in PEDOT/$LiCoO_2$-VGCF composite (Fig. 1c) show no traces of small $LiCoO_2$ fragments, which suggests the fact that the surfaces of $LiCoO_2$ in the PEDOT/$LiCoO_2$-VGCF sample are covered by the PEDOT polymer. VGCF fibers in $LiCoO_2$-