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Three-dimensional macroporous CNTs microspheres highly loaded with $NiCo_2O_4$ hollow nanospheres showing excellent lithium-ion storage performances

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ABSTRACT

Three-dimensional macroporous carbon nanotubes microspheres highly loaded with phase-pure $NiCo_2O_4$ hollow nanospheres are synthesized by the spray pyrolysis process and are characterized for potential use in lithium-ion batteries. Polystyrene nanobead template and the nanoscale Kirkendall diffusion process are first combined and are applied to the spray pyrolysis process to form macroporous $NiCo_2O_4$/carbon nanotubes composite microspheres with extremely high rate performance as anode materials for lithium-ion batteries. Metallic $NiCo_2$/carbon nanotubes composite microspheres—formed as intermediate products—are transformed into composite microspheres of phase-pure $NiCo_2O_4$ hollow nanospheres and carbon nanotubes by the nanoscale Kirkendall diffusion process. The mean size of the hollow $NiCo_2O_4$ nanospheres decorated on the carbon nanotubes backbone is 28 nm. The macroporous $NiCo_2O_4$/carbon nanotubes composite microspheres have discharge capacities of 840, 748, 677, 591, 514, 451, 391, 337, and 289 mA h g^{-1} at current densities of 0.5, 1, 2, 5, 10, 15, 20, 25, and 30 A g^{-1}, respectively. The discharge capacity of the macroporous $NiCo_2O_4$/carbon nanotubes microspheres for the 500th cycle at a current density of 3 A g^{-1} is 572 mA h g^{-1}. The uniquely structured hollow $NiCo_2O_4$ nanosphere/carbon nanotubes composite microspheres have superior cycling and rate performances for lithium-ion storage.

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1. Introduction

Hollow-structured transition metal compounds have attracted attention because of their well-defined interior voids, large surface area, and surface permeability, which make them promising candidates in a wide range of applications, such as energy storage, catalysis, drug delivery, photonics, and biotechnology [1–8]. In particular, when hollow structures are applied as anode materials for lithium- and sodium-ion batteries (LIBs and SIBs, respectively), the large void space in them is used to accommodate large volume changes during cycling and provide a short path length for lithium- and sodium-ion transport [9–13]. However, hollow-structured particles with low electrical conductivity and poor mechanical strength have been reported to exhibit relatively low volumetric energy density and poor cycling and rate performances [14–16].

Recently, nanostructured carbon composite materials of transition metal compounds with numerous empty nanovoids have been proposed as efficient electrode materials for LIBs and SIBs [17–21]. Carbonaceous materials with high electrical conductivity and structural flexibility, such as graphene, carbon nanotubes (CNTs), and graphitic carbon, improve the electrochemical properties of transition metal compounds [22–24]. In particular, carbon composite microspheres with uniform size distribution and non-aggregation characteristics are beneficial for the formation of electrodes with high packing densities. Kang et al. reported the preparation of uniform-structured composite microspheres with empty nanovoids by the spray pyrolysis process with and without the use of template additives [25–33]. Carbon composite microspheres with uniformly distributed empty nanovoids were also prepared using polystyrene (PS) nanobeads [27,28]. The decomposition of the PS nanobeads covered with carbon material and a transition metal compound under Ar atmosphere resulted in the

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formation of empty nanovoids. Application of the nanoscale Kirkendall diffusion process to the template-free spray pyrolysis process resulted in the synthesis of carbon composite microspheres consisting of metal-compound hollow nanospheres [29–33]. Metal nanoparticles uniformly decorated on amorphous carbon and reduced graphene oxide transformed into metal selenide (or sulfide) hollow nanospheres by the nanoscale Kirkendall diffusion process [29–33].

In the present study, we propose three-dimensional (3D) macroporous CNTs microspheres highly loaded with phase-pure $NiCo_2O_4$ hollow nanospheres. To the best of our knowledge, this is the first study to apply PS nanobeads in combination with nanoscale Kirkendall diffusion to the spray pyrolysis process in order to synthesize uniquely structured composite microspheres with extremely high rate performance as anode materials for LIBs. The PS nanobeads enabled the formation of macroporous CNTs microspheres for penetration of liquid electrolyte. Oxidation of $NiCo_2$ alloy nanoparticles by the nanoscale Kirkendall diffusion process resulted in the formation of phase-pure $NiCo_2O_4$ hollow nanospheres, which were then decorated on the CNTs backbone at a low oxidation temperature of 250 °C. The CNTs microspheres decorated with $NiCo_2O_4$ hollow nanospheres were found to have an ideal structure and their cycling and rate performances as anode materials for LIBs were superior to those of composite microspheres with densely structured nanoparticles.

2. Experimental section

2.1. Sample preparation

Macroporous 3D composite microspheres composed of CNTs and $NiCo_2O_4$ hollow nanospheres were prepared by a three-step process including spray pyrolysis. Precursor microspheres were prepared by spray pyrolysis from a spray solution of 0.005 M nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), 0.01 M cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), 100 nm PS nanobeads (3.0 g), and acid-treated MWCNTs (1 mg ml^{-1}) in 500 ml base solution. The MWCNTs were oxidized using a HNO_3/H_2SO_4 (1:3 v/v) solution at 70 °C and washed with distilled water. A schematic diagram of the spray pyrolysis process is shown in Fig. S1. The detailed procedure of the spray pyrolysis process has been described in our previous literature [34]. The first-step post-treatment process of the precursor microspheres synthesized at 700 °C was performed at 400 °C for 3 h under 10% H_2/Ar reducing atmosphere to produce CNT microspheres decorated with metallic $NiCo_2$ nanoparticles. Oxidation of $NiCo_2$ alloy during the second-step post-treatment process at 250 °C for 3 h under air atmosphere caused the formation of spinel $NiCo_2O_4$ hollow nanospheres, which resulted in the composite microspheres (referred to as H-$NiCo_2O_4$/CNT microspheres). For comparison purposes, composite microspheres with dense metal oxide nanoparticles of Ni and Co (referred to as D-NiCoO/CNT microspheres) were prepared by a one-step post-treatment of the precursor microspheres at 250 °C for 3 h under air atmosphere.

2.2. Characterizations

The crystal structures of the powders were investigated using XRD apparatus (X'pert Pro MPD) with Cu-Kα radiation (λ = 1.5418 Å) at the Korea Basic Science Institute (Daegu). The morphologies of the powders were investigated via field-emission SEM (FE-SEM, Hitachi S-4800) and HR-TEM (JEOL JEM-2100F) at a working voltage of 200 kV. The specific surface areas of the microspheres were calculated by a BET analysis of nitrogen adsorption measurements (TriStar 3000). XPS measurements of the microspheres were performed using the ESCALAB-250 spectrometer with Al-Kα radiation (1486.6 eV). To determine the amount of CNTs in the composite microspheres, TGA (TA Instruments SDT Q600) was performed in air at a heating rate of 10 °C min^{-1}.

2.3. Electrochemical measurements

The electrochemical properties of the composite microspheres were analyzed by constructing a 2032-type coin cell. The anode was prepared by mixing the active material, carbon black, and sodium carboxymethyl cellulose (CMC) in a weight ratio of 7:2:1. Lithium metal and a microporous polypropylene film were used as the counter electrode and the separator, respectively. The electrolyte was 1 M $LiPF_6$ dissolved in a mixture of fluoroethylene carbonate and dimethyl carbonate (FEC/DMC; 1:1 v/v). The discharge–charge characteristics of the samples were investigated by cycling in the 0.001–3 V potential range at various current densities. CVs were measured at a scan rate of 0.1 mV s^{-1}. The diameter of the negative electrode was 1.4 cm and the mass loading was approximately 1.2 mg cm^{-2}. EIS (Electrochemical Impedance Spectroscopy) measurements of the electrode were performed over a frequency range of 0.01 Hz–100 kHz.

3. Results and discussion

The formation mechanism of the 3D macroporous CNT microspheres highly loaded with phase-pure $NiCo_2O_4$ hollow nanospheres (referred to as H-$NiCo_2O_4$/CNT microspheres) is described in Scheme 1. Macroporous CNT microsphere decorated with (NiCo)O solid-solution nanocrystals were prepared from a single droplet containing nickel nitrate, cobalt nitrate, 100 nm PS nanobeads, and acid-treated multiwall CNTs (MWCNTs; Scheme 1a-①–③). The PS nanobeads improved the structural uniformity of CNT microspheres by improving the dispersion of CNTs with a low thickness and high aspect ratio. The decomposition of metal salts coated uniformly over CNTs and the subsequent crystal growth resulted in the formation of (NiCo)O nanocrystals. Reduction and alloying of the (NiCo)O nanocrystals under reducing atmosphere led to the formation of the $NiCo_2$ alloy nanocrystals, which, in turn, resulted in the formation of $NiCo_2$/CNT (Scheme 1a-④). The growth of the $NiCo_2$ alloy nanocrystals was restrained by the CNTs. The ultrafine $NiCo_2$ alloy nanocrystals transformed into the $NiCo_2O_4$ hollow nanospheres by nanoscale Kirkendall diffusion via an oxidation process under air atmosphere to form macroporous H-$NiCo_2O_4$/CNT microspheres (Scheme 1a-⑤). The formation of the $NiCo_2O_4$ hollow nanospheres by nanoscale Kirkendall diffusion is depicted in Scheme 1b. The surface oxidation of the alloy nanocrystals led to the formation of the core-shell structured nanoparticles. Kirkendall diffusion of the Ni and Co cations into the outer surface of the nanoparticles occurred simultaneously because of their similar sizes. The Ni and Co cations moved to the nanoparticle surface and combined with oxygen gas to form NiO and CoO phases, respectively. The spontaneous reaction of the highly reactive NiO and CoO nanoclusters resulted in the formation of the $NiCo_2O_4$ phase. The complete outward diffusion of the Ni and Co cations transformed the $NiCo_2$ alloy nanocrystals into phase-pure $NiCo_2O_4$ hollow nanospheres.

The morphologies and crystal structure of the precursor powders with a Ni:Co molar ratio of 1:2 prepared by spray pyrolysis at 700 °C are shown in Figs. S2 and S3, respectively. From the SEM images of crushed and uncrushed microspheres, the composite microspheres were confirmed to have a uniform and highly macroporous structure. The TEM and elemental mapping images confirmed the uniform distribution of ultrafine (NiCo)O nanocrystals all over the CNTs microsphere. The higher volume fraction

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