



Three-dimensionally scaffolded Co_3O_4 nanosheet anodes with high rate performance

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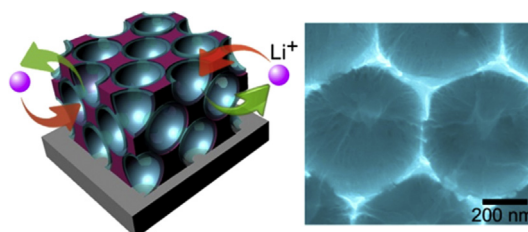
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HIGHLIGHTS

- Three-dimensionally scaffold-based anodes are fabricated.
- Thin nanosheets provide efficient pathways for electron and ion transportation.
- The Co_3O_4 anodes show attractive C-rate performance.
- The robust electrode structure provides high capacity retention.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 4 May 2015

Received in revised form

19 August 2015

Accepted 22 August 2015

Available online xxx

Keywords:

Mesostructured electrode

Anode

Secondary battery

High power

Nanostructure

ABSTRACT

Advances in secondary batteries are required for realization of many technologies. In particular, there remains a need for stable higher energy batteries. Here we suggest a new anode concept consisting of an ultrathin Co_3O_4 nanosheet-coated Ni inverse opal which provides high charge–discharge rate performance using a material system with potential for high energy densities. Via a hydrothermal process, about 4 nm thick Co_3O_4 nanosheets were grown throughout a three-dimensional Ni scaffold. This architecture provides efficient pathways for both lithium and electron transfer, enabling high charge–discharge rate performance. The scaffold also accommodates volume changes during cycling, which serves to reduce capacity fade. Because the scaffold has a low electrical resistance, and is three-dimensionally porous, it enables most of the electrochemically active nanomaterials to take part in lithiation–delithiation reactions, resulting in a near-theoretical capacity. On a Co_3O_4 basis, the $\text{Ni@Co}_3\text{O}_4$ electrode possesses a capacity of about 726 mAh g^{-1} at a current density of 500 mA g^{-1} after 50 cycles, which is about twice the theoretical capacity of graphite. The capacity is 487 mAh g^{-1} , even at a current density of 1786 mA g^{-1} .

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1. Introduction

Lithium-ion secondary batteries have found broad application since first commercialized in the early 1990s by Sony [1], and are

now being used for applications ranging from consumer electronics to electric vehicles and electrical grid storage [2–4]. Typically, graphite is used as an anode in Li-ion secondary batteries due to its attractive properties which include its low-cost, ease of processing, and good conductivity [5,6]. However, graphite possesses a theoretical capacity of 372 mAh g^{-1} , which limits the available energy density of commercial batteries. Graphite also presents a number of

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safety issues. The low lithium intercalation voltage at the graphite electrode can lead to lithium plating during cycling, which can cause fires and explosions [7]. This issue is particularly important during fast charging. Over the past decade, considerable efforts have been made to develop alternative electrodes with improved electrochemical performance [8–12]. Nanostructuring has been receiving attention for enhancing electrode performance, in particular due to the potential for providing electrodes with high surface areas and short electron and ion transport pathways. However, high surface areas may also lead to undesirable side reactions, which must be considered.

Since Tarascon first reported the use of a nanoscale transition metal oxide as an anode material [13], many transition metal oxides anodes have been considered [14,15]. Co_3O_4 is considered promising due to its high theoretical capacity of 890 mAh g^{-1} [16–20], which has led to a number of reports on the fabrication of Co_3O_4 -based anodes, including approaches based on redox precipitation [21], H_2O_2 -controlled hydrothermal processes [22], solvothermal [23] and molten salt [24] methods, and the electrochemical properties of nanostructured Co_3O_4 [25–29]. The electrical conductivity of Co_3O_4 is poor, and thus to form an anode which can be cycled at an appreciable rate, Co_3O_4 is usually mixed with an electrically conductive phase. Co_3O_4 -graphene composite structures have been of particular interest due to the excellent conductivity of graphene, and the two-dimensional (2D) nature of graphene, which provides a high contact area to Co_3O_4 [30–32]. For transition metal oxide systems in general, providing efficient pathways for electrons, is of particular importance, given the poor conductivities of both most transition metal oxides, and Li_2O , the product of the reaction with lithium. It is also important to avoid aggregation of the electrochemically active phase during the charge–discharge process and to accommodate any volume changes during cycling.

Here we present an ultrathin nanosheet-coated three-dimensional (3D) inverse opal anode, fabricated as outlined in Scheme 1. The Ni inverse opal scaffold was fabricated by electrodeposition of Ni metal through a sacrificial polystyrene opal template following our previous procedures [33,34]. Ultrathin Co_3O_4 nanosheets (4 nm thick) were hydrothermally grown onto the Ni scaffold followed by a heat treatment. As fabricated, the electrode provides a very short pathway for lithium and electrons in the Co_3O_4 , is mechanically stable, and provides good long-range electrical conductivity. Because the Co_3O_4 is attached to the surface of the porous 3D inverse opal, Co_3O_4 aggregation can be avoided, enabling most of the active nanomaterials to take part in the electrochemical reactions during the charge–discharge process.

2. Experimental

2.1. Ni inverse opal fabrication

The Ni inverse opal fabrication is similar to our previous reports [35,36] with some modifications. Typically, glass substrates were first cleaned with piranha solution (volume ratio of H_2SO_4 to H_2O_2 is 3:1; Caution, piranha is highly corrosive and potentially explosive) and coated with $\sim 5 \text{ nm Cr}$ and $\sim 60 \text{ nm Au}$ by e-beam evaporation (Temescal, Inc). To modify the surface of the substrate for polystyrene opal growth, the gold-coated substrate was immersed in a 0.5 mM aqueous solution of 3-mercaptopropylsulfonic acid, sodium salt (Sigma–Aldrich Corp.) for 2 h. Polystyrene spheres with a diameter of 600 nm (Molecular Probes) were dispersed in Millipore water to prepare a 0.2 wt\% suspension. After drying, the pre-treated substrate was placed vertically in a vial with the polystyrene suspension at $55 \text{ }^\circ\text{C}$ for deposition (Supplementary information Fig. S1a). The resulting polystyrene opal was sintered at $95 \text{ }^\circ\text{C}$ for 3 h to increase the pore size of the electrodeposited Ni

inverse opal. The Ni inverse opal was electrodeposited using current of 2 mA cm^{-2} in a commercial electroplating solution (Techni Nickel S, Technic Corp.), to an approximate size of $2 \text{ cm} \times 1 \text{ cm} \times 8 \text{ }\mu\text{m}$, as described in Fig. S1b. The sample was immersed in toluene (Sigma–Aldrich Corp.) to remove the polystyrene template. The resulting Ni inverse opal was rinsed alternately with ethanol and Millipore water, and dried in an oven at $\sim 60 \text{ }^\circ\text{C}$.

2.2. Co_3O_4 nanosheet growth

Ultrathin Co_3O_4 nanosheets were grown on the Ni inverse opal via a hydrothermal process followed by a heat treatment, similar to previous report [37] with some modifications optimized for our study at here. 1 mmol of $\text{Co}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$, 2 mmol of NH_4F , and 4 mmol of urea ($\text{CO}(\text{NH}_2)_2$) were dissolved into 40 mL of Millipore water under stirring for 15 min. This solution was transferred into a 50 mL Teflon-lined steel autoclave. A $1 \times 2 \text{ cm}^2$ Ni inverse opal coated substrate was inserted into the solution, Ni face up. The autoclave was sealed and heated in an oven at $110 \text{ }^\circ\text{C}$ for 6 h. The oven was turned off and allowed to naturally cool to room temperature. The substrate was removed from the autoclave, thoroughly washed with ethanol and Millipore water and dried in air at $50 \text{ }^\circ\text{C}$ for 2 h. The sample was then heat treated in a tube furnace at $400 \text{ }^\circ\text{C}$ for 1.5 h under ultrahigh purity Ar gas to crystallize Co_3O_4 (Ar was used to minimize oxidization of Ni scaffold). The ramp rate was $5 \text{ }^\circ\text{C min}^{-1}$. The furnace was then turned off and allowed to cool naturally.

Ni inverse opals coated with thick Co_3O_4 nanosheets and a Co_3O_4 thin film on Ni film substrate were also prepared for comparison of the electrochemical properties. A solution containing 5 mmol of $\text{Co}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$, 6 mmol of NH_4F , and 10 mmol of $\text{CO}(\text{NH}_2)_2$ in 40 mL of Millipore water was used to prepare the thick Co_3O_4 nanosheets for coating onto Ni inverse opal. Other procedures were the same as in the preparation of thin Co_3O_4 nanosheets. For the preparation of a Co_3O_4 thin film on Ni film substrate, electrodeposition of Ni was performed on a gold-coated glass substrate (no opal). Then, the Co_3O_4 film was grown on the Ni film through the same procedure as that used for preparing the Ni@ultrathin Co_3O_4 nanosheet inverse opal electrode.

2.3. Characterization

XRD was collected using a Philips X'pert MRD X-ray diffractometer (XRD) with Cu $K\alpha$ radiation (1.5418 \AA). Diffraction patterns were recorded at room temperature over the 2θ range of $10\text{--}80^\circ$. The XRD peaks were compared with Joint Committee on Powder Diffraction Standards (JCPDS). The morphology, structure and composition of the samples were investigated using a Hitachi S-4800 scanning electronic microscope (SEM), a Hitachi S-4700 SEM equipped with an Oxford INCA energy dispersive X-ray (EDX) analyzer, and a JEOL 2100 Cryo transmission electron microscope (TEM) operating at 200 kV . Elemental mappings were carried out on the Hitachi S-4700 SEM. Active material loading was determined via inductively coupled plasma (ICP) analysis using a PerkinElmer Elan DRCE ICP-MS.

2.4. Electrochemical measurements

Electrochemical tests were performed using two-electrode cells with lithium metal as the counter and reference electrodes using Princeton Applied Research Model 273A and Biologic VMP3 potentiostats. The Co_3O_4 -coated structures were set as the working electrodes. Cell assembly was performed in an Ar-filled glove box. A non-aqueous electrolyte consisting of 1 M of LiClO_4 into a 1:1 mass

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