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Self-supporting hierarchical rGO@Ni nanosheet@Co_3O_4 nanowire array and its application in high-rate batteries

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HIGHLIGHTS

- Self-supporting hierarchical rGO@Ni nanosheet@Co_3O_4 nanowire film is synthesized.
- The porous rGO-Ni substrate is really light-weight, only about 1.5 mg cm^{-1}.
- rGO-Ni-Co_3O_4 film shows better electrochemical performance than that on rGO film.

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ABSTRACT

To meet the design requirements for high-rate battery electrodes, self-supporting hierarchical rGO@Ni nanosheet@Co_3O_4 nanowire array film with light weight is synthesized via a series of controllable fabrication processes. Due to modifying the highly conductive nickel nanosheets onto the surface of rGO film, the energy storage performance of this hybrid film is enhanced, especially in rate capability. The whole high-rate battery, which is fabricated by using this film as the positive electrode, manifests the maximum energy density of 20.3 Wh kg^{-1} at a power density of 326 W kg^{-1} along with excellent capacity retention of 81.4% after 5000 cycles. Therefore, the rGO-Ni-Co_3O_4 hybrid film is a promising electrode material for flexible long-life cycling high-rate batteries.

1. Introduction

Over the past several years, as the global demand for energy and environmental protection is increasing, researchers have devoted intensive research to developing low-cost and environmental friendly energy storage devices [1,2]. Among various energy storage devices, supercapacitors have attracted a lot of attention, owing to their unique advantages, including higher energy density than conventional capacitors and higher power capability as well as long cycle life compared to lithium batteries [3–6]. The supercapacitors can be categorized into two types according to their energy storage mechanism: electrochemical double layer capacitors (EDLCs) and pseudo- capacitors [7,8]. Unlike the EDLCs, whose energy storage mechanism is similar to the conventional capacitors through electrostatic accumulation of charges in the electrochemical double-layer at the electrolyte/electrode interfaces, the pseudocapacitors store energy based on the continuous and fast reversible redox reactions of electroactive materials at the electrode surface, providing much higher specific capacitance than EDLCs [9,10].

Transition metal oxides/hydroxides have been widely explored as the electrode materials for pseudocapacitors [7,11–13]. Co_3O_4 is one of the most promising candidate materials owing to its easy availability and good pseudocapacitive behavior. However, its rate capability is limited by the low electric conductivity. To improve the electric conductivity and charge storage capability of Co_3O_4, composing the composites with well-conductive materials, such as carbon nanotube [14,15], graphene [16–20] and conducting polymers [21,22], is a feasible way.

Recently, Brousseet et al. [23] have discussed whether the Ni and Co-based electrodes are pseudocapacitive since their electrochemical performance exhibits some battery features, such as a flat discharge plateau. To avoid misunderstanding the definition of

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"capacitor", we consider it necessary to change the appellation for this Ni, Co-based application that we called pseudocapacitor in the past. In this present work, we would call it high-rate battery.

The electrode of high-rate battery is usually composed of current collector, binder, conductive additive and active material. As well known, the weight of current collectors (e.g. nickel foam and stainless steel foil) accounts for a large mass proportion in the device, far beyond the active material, but these current collectors cannot contribute to the capacity, and thus lead to low energy and power densities. So, it becomes a research hotspot to find a light-weight, high conductive current collector. Recently, the porous graphene film has been reported as an ideal substrate due to its light weight, high electric conductivity, large specific surface area, high mechanical flexibility and preeminent chemical stability [24–26]. However, these graphene films are usually reduced graphene oxide (rGO), not the pure graphene. They cannot be completely reduced, which contain some functional group, leading to the decrease in electric conductivity [24]. Therefore, modifying the rGO film to make it become a more efficient substrate for flexible high-rate battery applications attracts our attention. A common strategy is to composite rGO with highly conductive materials, such as metals.

Herein, we developed a rGO-Ni-Co_3O_4 hybrid film, which is light-weight, self-supporting and combines the superior capacity of Co_3O_4 with high conductivity of rGO-Ni. It is fabricated via a series of controllable processes. Firstly, the multilayered rGO sheets formed a self-supporting film as the substrate and the nickel nanosheets were coated on the surface of rGO film by chemical reduction from nickel hydroxide in H_2/Ar atmosphere. Subsequently, the Co_3O_4 nanowires were uniformly grown onto the hybrid matrix by a facile hydrothermal method followed annealing. As the positive electrode for high-rate batteries, the rGO-Ni-Co_3O_4 film provided not only a high capacity but also a superior rate capability compared to the rGO-Co_3O_4 electrode. We also fabricated a whole battery using this hybrid film as the positive electrode and activated carbon as the negative electrode, which presented high energy and power densities as well as long cycle life.

2. Experimental

2.1. Preparation of rGO-Ni-Co_3O_4 hybrid film

All reagents were of analytical grade and used without further purification. The free-standing graphene oxide (GO) membrane was prepared by stationary evaporation and leavening methods [27–29]. 100 mg GO, prepared from flake graphite through the modified Hummers' method [30], was dissolved into 50 mL distilled water via ultrasonic treatment to form a stable GO suspension, which was then heated at 80 °C for 40 min in water bath. After a period of time, a smooth and stable film was appeared at the liquid/air interface. The GO membrane was taken out of from the beaker and let it air-dry. After that, to obtain the rGO membrane, hydrazine hydrate with GO membrane was added into a petri dish, which was heated to 90 °C for 16 h.

The Ni coating on the rGO membrane was reduced from $Ni(OH)_2$ nanosheets, which was synthesized by using a facial hydrothermal method. In a typical synthesis of Ni nanosheets, an aqueous solution containing 0.05 M $Ni(Ac)_2 \cdot 4H_2O$ and 0.15 M hexamethylenetetramine (HMT) was transferred into a Teflon-lined stainless autoclave with GO membrane [31]. After growth at 120 °C for 5 h, the obtained $Ni(OH)_2$ nanosheets were washed with ethanol and distilled water before dried. Then, the sample was annealed at 350 °C for 1 h in Ar and followed to be annealed at 450 °C for 2 h in gas mixture (10% H_2 + 90% Ar) to form Ni nanosheet arrays on the rGO membrane [32].

The rGO-Ni-Co_3O_4 hybrid membrane was fabricated by a facial hydrothermal route. 10 mmol of $Co(NO_3)_2$, 20 mmol NH_4F and 50 mmol of $CO(NH_2)_2$ were dissolved in 70 mL of distilled water to form a homogeneous solution, which was transferred into Teflon-lined stainless steel autoclave with a piece of the as-prepared rGO-Ni membrane. The autoclave was heated to 120 °C inside a conventional oven for 9 h and then cooled to room temperature naturally. Subsequently, the obtained product was rinsed with distilled water several times and annealed at 350 °C in argon for 2 h leading to the formation of Co_3O_4 [33]. The Co_3O_4 nanowire arrays grown on the as-prepared rGO film without Ni coating named as rGO-Co_3O_4 and on rGO film reduced in H_2/Ar atmosphere named as rGO(H_2)-Co_3O_4 were prepared for comparison in electrochemical performance.

2.2. Materials characterization and electrochemical measurements

The microstructure and morphology of the products were characterized by X-ray diffraction (XRD, Rigaku D/max 2550 PC, CuKα), scanning electron microscopy (SEM, Hitachi S-4700), and transmission electron microscopy (TEM, FEI Tecnai G^2 F20 at 200 kV). The Raman spectra were measured on a JobinYvon Labor Raman HR-800 using Ar-ion laser of 514.5 nm.

The electrochemical measurements were carried out in a three-electrode electrochemical cell containing 6 M KOH aqueous solution as the electrolyte. All the tests were conducted at 20 °C. Cyclic voltammetry (CV) measurements and the galvanostatic charge–discharge tests were performed on a CHI660e electrochemical workstation (Chenhua, Shanghai). CV measurements were carried out at different scanning rates between 0 V and 0.7 V, rGO-Ni-Co_3O_4, rGO(H_2)-Co_3O_4 and rGO-Co_3O_4 films as the working electrode, Hg/HgO as the reference electrode and a Pt foil as the counter-electrode. Electrochemical impedance spectroscopy (EIS) measurements were carried out on this apparatus with a superimposed 5 mV sinusoidal voltage in the frequency range of 100 kHz to 0.01 Hz.

The electrochemical measurements of the whole battery were carried out in a two-electrode electrochemical cell containing 6 M KOH aqueous solution as the electrolyte. The whole battery was assembled using the rGO-Ni-Co_3O_4 as positive electrode, the carbon black electrode as negative electrode and the cellulose acetate as separator. The negative electrode was prepared by mixing active carbon, acetylene black and PTFE in an 80: 15: 5 mass ratio and then pressed onto nickel foam followed drying overnight. CV measurements were carried out at different scanning rates between 0 V and 1 V on a CHI660e electrochemical workstation (Chenhua, Shanghai). Galvanostatic charge–discharge tests were conducted on a LAND battery program-control test system between 0 and 0.8 V. Electrochemical impedance spectroscopy (EIS) measurements were carried out on this apparatus with a superimposed 5 mV sinusoidal voltage in the frequency range of 100 kHz to 0.01 Hz.

3. Results and discussion

3.1. Material characterization

The process for synthesizing rGO-Ni-Co_3O_4 hybrid composites as the electrode of high-rate batteries involves three key steps, which is shown in Fig. 1. First, the free-standing GO film was received through evaporating aqueous GO slurry, which was obtained from graphite powder according to the modified Hummers' method. During the evaporation process, the GO nanosheets aggregated together via interlayer van der Waals' forces at the interface between the hydrosol and atmosphere, resulting in the