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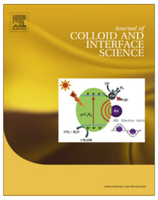

Regular Article

Moderated surface defects of Ni particles encapsulated with NiO nanofibers as supercapacitor with high capacitance and energy density

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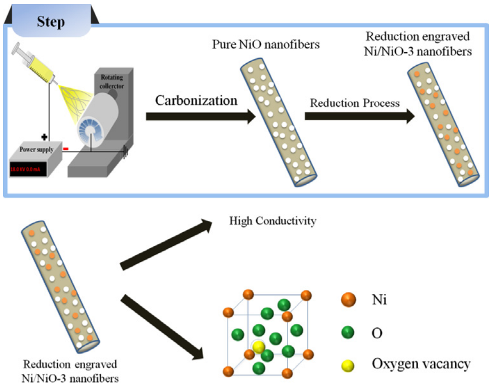
GRAPHICAL ABSTRACT



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ABSTRACT

Nickel oxide is a promising material for supercapacitors owing to its high theoretical specific capacitance; however, its practical capacitance is far below the theoretical limit. In this work, we report a novel Ni/NiO composite supported by carbon nanofibers as a pseudocapacitor electrode. Characterization of this sample by X-ray diffraction, transmission electron microscopy, scanning electron microscopy, X-ray photoelectron spectroscopy, Brunauer–Emmett–Teller analysis, and contact angle measurements revealed that Ni nanoparticles were uniformly dispersed on the surface of the nanofibers, leading to strong metal–metal oxide interactions and the formation of oxygen vacancies. Such three dimensional hetero-Ni/NiO components afford high conductivity owing to efficient electron transport and abundant surface defects (oxygen vacancies), which result in enhanced supercapacitor performance and energy density (ED). A moderate concentration of oxygen vacancies is crucial for achieving optimized electrochemical activity. As-prepared Ni/NiO-3 nanofibers generated high capacitances of 526 and 400 F/g at current densities of 1 and 10 A/g, respectively, with good stability (80% of the initial capacitance retained after 1000 cycles). Moreover, an ED as high as 65.8 Wh/kg was achieved at a power density of 900 W/kg, which is higher than those of NiO-based supercapacitors. This work provides a strategy for improving the potential of metal oxides for energy storage applications.

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1. Introduction

As promising energy storage devices, supercapacitors have attracted increasing attention [1–11]. Supercapacitors have numerous advantages over batteries, including high power density (PD) and charge–discharge stability [12–25]. Unfortunately, their applications are limited by a low energy density (ED). Therefore, the development of supercapacitors that combine high ED and high PD is necessary for advanced applications.

To date, a series of transition metal oxide/metal compounds has been studied as supercapacitor materials [26–28]. Among these, nickel oxide (NiO) has been widely researched because of its high theoretical specific capacity, good chemical stability, and low cost [29–33]. Although NiO has been reported to have a theoretical specific capacity of 3230 F/g [34], the practical capacity of NiO is still far below this value owing to its poor conductivity and low active surface area. To resolve this issue, various noble metals (e.g., Pt [35], Pd [36], Au [37], Ag [38], and Ru [39]) have been introduced to improve the electrochemical capacity. However, it is still not available because of the high cost. To achieve economic and environmental sustainability, the design and development of a cheap and efficient non-noble-metal material has become an urgent task. As one of the most common metals, nickel has been used widely both as a catalyst and a support in the field of electrochemical devices [40].

Oxygen vacancies, constituting one of the most familiar types of anion vacancy in three-dimensional crystalline materials, are widely considered to provide a useful approach for regulating the electronic configuration and intrinsic physicochemical properties of oxides [41]. Furthermore, synergistic effects between oxygen vacancies and metal oxides provide unexpected potential for optimizing the electrochemical properties of a material. Such oxygen vacancies can be confirmed by X-ray photoelectron spectroscopy (XPS). Additionally, a cooperative effect between nickel, NiO, oxygen vacancies, and a carbon nanofiber supporter has been shown to be beneficial for enhancing the electrochemical performance. It is probable that surface oxygen vacancies with unpaired electrons act as electron donors to significantly improve conductivity and accelerate the kinetics of surface redox reactions and thus enhance electrochemical performance [42].

When compared with other methods for fabricating nanofibers, electrospinning has attracted increasing attention owing to its simplicity, versatility, and low cost [43–47]. Electrospinning metal oxide fibers is a promising method for generating composite nanofibers with a high specific surface area, high crystallinity, and an increased number of active sites [48–49]. The resultant nanofibers are ideal for energy storage applications because the nanofibrous surface morphology provides a path for electron transport, which improves the energy storage capacity of the metal oxide.

Considering this, we designed oxygen-vacancy-enriched Ni/NiO composite nanofibers using electrospinning and a hydrogen reduction method. A reasonable strategy for achieving active materials with high electrochemical efficiency involves manipulation of the surface defects. The as-prepared Ni/NiO nanofibers exhibited a long cycle life (~80% of the initial capacitance retained after 1000 cycles) and high energy storage capacity. An asymmetric supercapacitor incorporating the Ni/NiO composite nanofibers was successfully constructed and shown to exhibit ultra-high supercapacitive performance.

2. Experimental

2.1. Chemicals

Nickel acetate $(CH_3COO)_2$-Ni·$4H_2O$, ethanol, dimethylformamide (DMF), poly(vinylpyrrolidone) (PVP, molecular weight 1 300 000), activated carbon black, poly(vinylidene fluoride) (PVDF), and N-methylpyrrolidinone (NMP) were purchased from Sigma-Aldrich. Ultra-pure water with a resistivity of 18.2 MΩ·cm was prepared using a water purification system. All chemicals were used as received without further purification.

2.2. Sample preparation

In a typical procedure, a known amount of PVP was efficiently dispersed in ethanol by stirring the solution overnight. To this PVP dispersion, an ~8 wt% NiAc solution (DMF/ethanol, 1:1 (v/v)) was added and stirred overnight. The as-prepared NiAc-PVP sol-gel was processed using an electrospinning apparatus (Nano NC) at an electric potential of 18 kV with a feed rate of 0.8 mL/h. As-spun fibers were collected on an aluminum substrate placed 15 cm from the syringe tip. Subsequently, the as-spun fibers were calcined at 600 °C for 180 min in air at a heating rate of 2 °C/min, resulting in the formation of NiO nanofibers. Then, the pure NiO fibers were subjected to hydrogen reduction at 400 °C for various times. The detail experimental conditions are summarized in Table S1. As-obtained samples were labeled as Ni fibers, Ni/NiO-1, Ni/NiO-2, Ni/NiO-3, Ni/NiO-4, Ni/NiO-5, and NiO fibers. To prepare the working electrode, as-prepared Ni/NiO composite nanofibers, activated carbon black, and PVDF were mixed at a weight ratio of 80:15:5 in NMP. The as-prepared slurry was spread onto a nickel foam at a weight loading of 2 mg/cm^2, and then pressed at 10 MPa for 1 min.

2.3. Characterization

The structures of the samples were examined using X-ray diffraction (XRD, D2 PHASER, Bruker). The morphologies of the samples were evaluated by scanning electron microscopy (SEM; Model SU8010, Hitachi Co., Ltd) and field-emission transmission electron microscopy (FE-TEM; JEM-2100F). The samples were also analyzed by XPS (VG Scientific Co., ESCA LAB MK-II). The specific surface areas were calculated using an adsorption analyzer (BEL BELSORP) based on adsorption data in the partial pressure (P/P_0) range of 0.02–0.25. Element Analyzer (Thermo EA1112) was used for oxygen element analysis. Electrochemical measurements, including cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS), were carried out using an Ivium electrochemical analyzer with a conventional three-electrode system, in which the modified nickel foam, a Ag/AgCl electrode, and platinum wire were employed as the working, reference, and counter electrodes, respectively. The conditions were as follows: 3 M KOH electrolyte, frequency range of 0.1 Hz–10 kHz, and an applied sine wave potential amplitude of 5 mV.

3. Results and discussion

Herein, we synthesized efficient Ni-engraved NiO nanofibers with oxygen vacancies and high conductivity using a two-step strategy. As shown in Fig. 1, pristine electrospun nanofibers were carbonized to obtain NiO nanofibers, which were subsequently treated by hydrogen reduction annealing. It should be noted that some of the particles on the surfaces of the nanofibers became black after the hydrogen reduction. As evidenced by the SEM and TEM images, the particles, which have diameters of about 20 nm, are randomly arranged and interconnected with each other.

The crystallographic properties of the Ni/NiO nanofibers were confirmed by XRD. Fig. 2(a) shows the XRD patterns of the fibers at the different processing phases. The peaks at 36.8°, 43.0°, 62.6°, 75.1°, and 79.0° correspond to the (111), (200), (220), (311), and (222) planes of the NiO crystal structure, respectively,