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Full Length Article

Ultrahigh volumetric capacitance and cycle stability via structure design and synergistic action between $CoMoO_4$ nanosheets and 3D porous Ni-Co film

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ABSTRACT

The rational design of the composites constituted by active materials and self-supported conductive current collectors has been turned out to be an effective way to achieve excellent electrochemical performance of supercapacitors. In this work, the 3D network-like continuous porous Ni-Co film (3DNC) with high conductivity and controllable porous structure was obtained through simple de-alloying and annealing processes, and then ultrathin $CoMoO_4$ nanosheets were homogeneously grown onto skeleton of 3DNC film by hydrothermal and low-temperature annealing processes. The 3DNC film exhibits considerable electrochemical performance, whose controllable pore structure insures optimized mass loading of $CoMoO_4$ and maximized space utilization of integrated electrode. The highly interconnected porous channels among the ultrathin $CoMoO_4$ nanosheets provide high ion-accessible effective surface area and fast ion diffusion path, which significantly increases the reaction kinetics of the $CoMoO_4$ nanosheets. Such outstanding structural advantages and the synergistic effect between $CoMoO_4$ nanosheets and 3DNC film result in desired electrochemical performance with an extremely high volumetric capacitance of 2601.3 F cm^{-3} (325.2 mAh cm^{-3}), excellent rate performance and superior cycle stability up to 20,000 cycles. The impressive results open an avenue toward the rational design of free-standing composites with high-performance electrochemical performance through both structure design and the synergistic action between active materials and conductive current collectors.

1. Introduction

Supercapacitors (SCs), one of the most promising green energy storage devices, have been attracting great attention in the future electrical energy storage fields due to their excellent power density, fast charge and discharge, superior cycle life, safety and environmental friendliness [1–4]. Considering the increasing demand for portable and wearable miniaturized electronic devices that are getting smaller and smaller, volumetric capacitance has been regarded as a critical factor in assessing the potential of SCs with limited space [5,6]. It is well known that volumetric capacitance is equal to the product of gravimetric capacitance and density ($C_{vol} = C_{wt}\rho$). Thereby, an effective strategy to realize excellent volumetric capacitance is to maximize gravimetric capacitance and packing density of electrode materials, especially porous carbon materials [7]. Unfortunately, the highly dense electrode structure generates the huge reduction in specific surface area (SSA) and the significant decrease in diffusion rate of electrolyte ions, resulting in lower gravimetric capacitance, which in turn leads to no significant increase, even a decrease in volumetric performance. In other words, maximizing the packing density cannot increase volumetric capacitance effectively [8]. In addition, the high cost and complex preparation processes have always limited widespread application of the MXene with high volumetric performance [9,10]. Thus, it remains a considerable challenge to design and synthesis low cost electrode materials with superior volumetric capacitance [11–13].

Recently, binary metal oxides have been reported to exhibit higher performance than single component oxides due to their feasible oxidation state [14–16]. Moreover, binary metal oxides also offer many advantages, such as low cost, abundant resources and environmental friendliness [17,18]. Binary metal oxides, such as $NiCo_2O_4$ [19], $ZnCo_2O_4$ [20], $MnMoO_4$ [21], $NiMoO_4$ [22] and $CoMoO_4$ [23,24], have been considered as promising candidates for high-performance SCs due to their high electrochemical performance. In particular, $CoMoO_4$, which combines the dual advantages of cobalt oxide (extremely high

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theoretical specific capacitance) and molybdenum oxide (rich polymorphism and reversible small ions storage) has received much interest as electrode for SCs or LIBs (Li-ion batteries) [25–27]. However, there are rare reports in the literature about binary metal oxides with high volumetric performance and long cycle life due to their poor stability and low conductivity [28–30].

Therefore, the integrated electrodes with nanostructured binary metal oxides nanoneedles, nanosheets, nanorods or nanowires and free-standing 3D porous conductive current collectors combined are highly desirable for high-performance SCs, which can ensure large active surface exposure in electrolyte, high conductivity of the electrode and high electrochemical utilization of active materials [31–34]. In order to achieve the superior volumetric performance and long cycle stability simultaneously without sacrificing gravimetric performance, an ideal free-standing conductive 3D current collector should meet two requirements: One is suitable pore structure and high conductivity, which can ensure high space utilization as much as possible for nanostructured active materials deposition without affecting the rapid transmission of electrons and ions [35]. The other is high specific capacitance contribution of the current collector. Nanoporous metal (NPM) obtained by dealloying is considered to be an ideal current collector. Owing to the internal continuous open structure, NPM exhibits high specific surface area and excellent electrical conductivity, resulting in high specific capacitance as an electrode alone. Furthermore, the pore size and composition of NPM can be adjusted by annealing and the composition of the precursor alloys, respectively. Compared with commonly used self-supported conductive current collectors with large pore size, such as metal foam [36,37], carbon cloth [38], 3D graphene foam [39] and stainless steel, NPM can effectively improve the space utilization of electrodes and increase the specific capacitance.

Herein, we designed and fabricated a free-standing 3D porous Ni-Co film (3DNC) with controllable pore size, excellent conductivity and high electrochemical performance through simple de-alloying and annealing processes, and then ultrathin $CoMoO_4$ nanosheets are homogeneously grown onto 3DNC skeleton by hydrothermal reaction and low-temperature annealing process. The as-prepared integrated electrode has an efficient mass loading of $CoMoO_4$ and the highly interconnected porous channels between the $CoMoO_4$ nanosheets, achieving the rapid and continuous transmission of ions and electrons, maximized space utilization and high ion-accessible effective surface area. Moreover, the 3DNC also provides higher capacitance for integrated electrode compared to other self-supported current collectors with large pore size. Owing to the rational structure design and efficient synergistic effect between $CoMoO_4$ and 3DNC film, the binder-free and self-supported integrated electrode exhibits excellent supercapacitor performance, especially outstanding volumetric capacitance and superior cycle stability.

2. Experimental

2.1. Synthesis of 3DNC films

$Ni_{20}Co_{10}Mn_{70}$ ingots were prepared by melting pure Ni, Co and Mn (> 99.9 at%) using an Ar-protected arc melting furnace. After annealing at 850 °C for 24 h for microstructure and composition homogenization, the ingots were cut into 2 mm plates and then cold-rolled to a thickness of ~110 μm at room temperature. Three-dimensional nanoporous Ni-Co film (3DNPNC: 1 × 1 cm^2) was obtained by chemically etching $Ni_{20}Co_{10}Mn_{70}$ film in a 1.5 M $(NH_4)_2SO_4$ aqueous solution at 50 °C for 20 h under Ar-protected flow, and subsequently rinsed thoroughly with water and ethanol and dried. Then, 3DNPNC was annealed in a tube furnace at 900 °C for 1, 2, 5, 15, 20 or 40 min under 20 Torr pressure with a mixture gas flow of Ar and H_2 with 500 and 200 sccm, respectively, and then cooled rapidly to room temperature under Ar gas flow at atmospheric pressure. These samples are denoted as 3DNC-x, where x is the annealing time in the tube furnace.

2.2. Synthesis of $CoMoO_4$/3DNC films

The above as-prepared 3DNC films were used as current collectors for the subsequent synthesis of $CoMoO_4$/3DNC composites via facile hydrothermal and low-temperature annealing methods. In a typical synthesis, 4 mmol of $Co(NO_3)_2{\cdot}6H_2O$ and 4 mmol of $Na_2MoO_4{\cdot}2H_2O$ were uniformly dissolved in 80 mL distilled water under constant magnetic stirring, and then the as-prepared solution was transferred into a 100 mL Teflon-lined stainless steel autoclave. Subsequently, a piece of 1 × 1 cm^2 3DNC film was immersed into the reaction solution, and the autoclave was sealed and maintained at 150 °C for 5 h. After the reaction was over, the film coated with light purple product was taken out from the autoclave and washed with deionized water several time, and then dried in a vacuum oven at 80 °C for 12 h to obtain $CoMoO_4{\cdot}xH_2O$/3DNC as precursor. Finally, the precursor was annealed at 350 °C for 2 h in Ar to obtain $CoMoO_4$/3DNC composites. The active material mass loading of $CoMoO_4$/3DNC-1, $CoMoO_4$/3DNC-2, $CoMoO_4$/3DNC-5 and $CoMoO_4$/3DNC-15 are 7.5, 6.3, 3.9 and 3.3 mg cm^{-2}, respectively, calculated by the weight difference of the initial and final mass of the film. And the corresponding densities are 3.87, 3.61, 3.52 and 3.45 g cm^{-3}, respectively. For comparison, pure $CoMoO_4$ powder was fabricated at the same conditions without 3DNC.

2.3. Material characterization

Scanning electron microscopy (SEM, Hitachi S4800) was used to characterize the morphology and structure of samples. Transmission electron microscopy (TEM) and scanning TEM (STEM) were performed on a FEI Tacnai G2 F20 with an EDS detector. X-ray diffraction (XRD) patterns were taken on a Rigaku D/max diffractometer with Cu Kα radiation at a wavelength of 1.5406 Å. The elemental composition was evaluated by X-ray photoelectron spectroscopy (XPS, PHI5000 VersaProbe).

2.4. Electrochemical characterization and calculations

The electrochemical measurements, including cyclic voltammetry (CV), galvanostatic charge and discharge (GCD) and electrochemical impedance spectroscopy (EIS, recorded in a frequency range from 0.01 Hz to 100 kHz) were carried out in a three electrode electrochemical system in 6 M KOH aqueous electrolyte, using the CHI660E (Chenhua China) electrochemical workstation at room temperature. The cycle stability was performed using Land 2001A charge/discharge system under the same conditions. The counter and reference electrodes were platinum plate and Hg/HgO electrodes, respectively. The $CoMoO_4$/3DNC films and 3DNC films can be used as the working electrode directly. The electrodes of $CoMoO_4$ power was fabricated by mixing the sample power, carbon black and poly (tetrafluoroethylene) with ethanol in a mass ratio of 80:10:10, and then the homogeneous slurry was coated on graphite paper and dried at 80 °C for 12 h. The thickness of the $CoMoO_4$ coated on graphite paper is 35 μm. The specific capacitance of as-prepared samples was calculated from galvanostatic charge/discharge curves using following equations [40,41]:

$$C_a = I\Delta t/S\Delta V \quad (1)$$

$$C_v = C_a/h \quad (2)$$

$$C_m = C_v/\rho \quad (3)$$

where C_a, C_v and C_m are areal capacitance (F cm^{-2}), volumetric capacitance (F cm^{-3}) and gravimetric capacitance (F g^{-1}), respectively. I, Δt, S, ΔV, h and ρ represent the discharge current (A), the discharge time (s), the area of electrode material (cm^2), the potential change (V) during the discharge, the thickness of electrode material (cm) and the density of electrode (mg cm^{-3}), respectively. The volumetric energy density (E_v) and volumetric power density (P_v) of the symmetric supercapacitor were estimated according to equations [7,42]: