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Construction of manganese-cobalt-sulfide anchored onto rGO/Ni foam with a high capacity for hybrid supercapacitors

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ABSTRACT

Ternary metal sulfides such as manganese-cobalt-sulfide (MCS) with the unique physical, chemical properties and high specific capacity can be used as energy storage material for supercapacitor. Herein, we prepared a MCS nanosheet array stick onto reduced graphene oxide (rGO)/Ni foam (MCS/rGO/NF) by a carefully controlled sulfurization time process. As the reaction time increased, the thickness of MCS/rGO/NF nanosheet arrays charged from thin to thick. After 3 h of sulfurization reaction (MCS/rGO/NF-3h), the nanosheets became rough due to the formation of some small sheets, and the composite showed the best electrochemical performance. The MCS/rGO/NF-3h composite exhibited a large specific capacity of 1356 C g^{-1} at a current density of 1 A g^{-1}, and a long-term cyclic stability of 92.9% at a current density of 10 A g^{-1} through 3000 cycles. Moreover, a hybrid supercapacitor (HSC) device was assembled using MCS/rGO/NF-3h and rGO as the positive and negative electrodes, respectively. The MCS/rGO/NF-3h//rGO HSC exhibited a high energy density of 45.4 W h kg^{-1} at a power density of 850.2 W kg^{-1}. The prominent electrochemical performance suggests that MCS/rGO/NF composites are promising electrode materials for energy storage applications.

1. Introduction

Owing to the massive consumption of energy and severe environmental pollution, new types of energy storage devices—green, cost-effective, and large energy storage capacity—are highly needed to solve the energy problems [1,2]. Supercapacitors (SCs) are regarded as potential energy reserve devices, because of their unique properties such as high power density, good cyclic stability, and fast charge/discharge rate [3,4]. Recently, SCs have been widely used in hybrid electric vehicles, portable electronics and emergency power systems [5–7]. To be specific, defined by the different energy storage mechanisms, SCs can be divided into two categories: electrical double-layer capacitors (EDLCs) and pseudocapacitors (PCs) [8–10]. However, the lower energy density and capacity of electrode materials limit their application. One effective solution is the use of Faradaic battery-type electrodes that increase the energy density via charge-transfer reactions occurring on the electrode surface. At present, several transition metal oxides and sulfides act as excellent active materials owing to diverse oxidation states, low cost, and higher energy storage capacity [11,12]. Among these materials, transition metal oxides have been widely investigated, which have a high theoretical capacity. However, it is well known that their application is restricted by poor conductivity and stability. Thus, advanced materials with good conductivity should be developed to enhance their electrochemical performance. Recently, transition metal sulfides are regarded as potential electrode materials for SCs because of their better electrical conductivity, thermal stability and various valences than transition metal oxides [13,14]. The electrical conductivity of transition metal sulfides is reported to be ~100 times superior than that of the transition metal oxides [15].

Transition metal sulfides have been applied to SCs as the electrode material, including binary metal sulfide such as NiS [13], CoS [16], CuS [17], MoS [18], and ternary metal sulfides such as $M_xCo_{3-x}S_4$ (M = Ni, Mn, Zn) [19], $NiCo_2S_4$ [20], manganese-cobalt-sulfide (MCS) [21], Zn-Co-S [22], and $CuCo_2S_4$ [23]. Among these transition metal sulfides, more attention has been paid to the pursuers of ternary metal sulfides due to their multiple Faradaic redox reactions and higher electrical conductivity than binary metal sulfides [14]. Until now, $NiCo_2S_4$ is one of the most studied

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ternary metal sulfides that displayed excellent specific capacity because of unique nanostructure and better conductivity [24]. Besides, MCS is also a promising electrode material exhibiting outstanding electrochemical performance. Significantly, manganese can transport more electrons due to a large number of oxidation states. Moreover, cobalt can provide a higher oxidation potential, leading to remarkable electrochemical performance [19]. Chen et al. synthesized $M_xCo_{3-x}S_4$ (M = Ni, Mn, Zn) hollow tubular structures, where $MnCo_2S_4$ HTS electrode exhibited a large specific capacity of 1094 F g^{-1} (10 A g^{-1}) [19]. Liu et al. prepared a hierarchical MCS core−shell nanostructure that exhibited a high specific capacity of 2067 F g^{-1} at the current density of 1 A g^{-1} [25]. An increasing number of studies about MCS indicate that MCS is a potential candidate owing to its higher electrochemical activity, excellent specific capacitance, and rate capability. However, the development of MCS electrode material is restricted by the slow ion/electron transfer rate and visible volume change during the redox reaction process [26]. To solve the abovementioned issues, the interactions between Faradaic and conductive materials are crucial for hybrid electrode materials to utilize the advantages of each component [27]. As one of the nanostructured carbons, reduced graphene oxide (rGO) has been widely applied to SCs as the electrode material because of its excellent electronic properties, chemical stability, higher specific surface area, more optimal mesopore size distribution, and better conductivity [28−30]. In addition, rGO can relieve conceivable volumetric changes during the conversion reactions, particularly in the processes of cyclic performance test [31]. Recently, rGO/transition metal sulfide hybrid electrodes such as rGO/Ni_3S_4 [31], MoS_2/rGO [32], and nickel cobalt sulfide-rGO [33] were reported to present better electrochemical performance than similar electrode materials without rGO. Based on the above considerations, excellent electrochemical performance is also expected in hybrid electrodes prepared by combining MCS with rGO. Furthermore, various synthetic conditions such as different types and amounts of sulfur sources, especially varying sulfurization time, have been used in the synthesis of metal sulfides exhibiting diverse porosity and morphology, leading to different electrochemical performance [34,35]. Hence, the morphology and electrochemical performance of MCS with rGO composites can be tuned by varying the sulfurization time, and it is important to determine the optimum sulfurization time for these electrode materials.

In this study, interconnected MCS nanosheets anchored onto rGO-coated Ni foam (MCS/rGO/NF) were prepared via a two-step hydrothermal treatment. The effect of different sulfurization times on the structure, morphology and capacity of composites was systematically investigated. The optimum electrochemical performance of MCS/rGO/NF composite was obtained when the sulfurization time was 3 h (MCS/rGO/NF-3h). The largest specific capacity of 1356 C g^{-1} at 1 A g^{-1} and an excellent life span with the retention capacity of 92.9% through 3000 cycles (10 A g^{-1}) were achieved. A hybrid supercapacitor (HSC) was fabricated using MCS/rGO/NF-3h composite and nitrogen-enriched rGO as the positive and the negative electrodes, respectively, showing a high energy density of 45.4 W h kg^{-1} at a power density of 850.2 W kg^{-1}. Excellent cycling stability was also achieved for the HSC device with 100% capacity retention through 4000 cycles at 3 A g^{-1}. Hence, MCS/rGO/NF composite can be regarded as one of the next-generation promising electrode materials for SCs.

2. Experimental

2.1. Synthesis of rGO/NF composite

GO was prepared by the modified Hummers way as previously reported [36]. The NF (6 cm × 5 cm) was successively cleaned with acetone, 3 M HCl solution, deionized water and ethanol by ultrasonication for 15 min each time. The rGO was coated on NF by the following method: 10 mg of GO was dissolved in 30 mL of distilled water under ultrasonication for 2 h. After a homogeneous solution was formed, 30 mg of ascorbic acid was dispersed into the solution. Then, the mixture in a beaker was heated over a water bath at 90 °C for 6 h. Afterwards, the sample was cleaned with deionized water and ethanol, and then dried at 60 °C for overnight.

2.2. Synthesis of MCS nanosheets on rGO/NF

All the chemical reagents were of analytical grade and used as received without further purification. MCS nanosheets were prepared on rGO/NF by a two-step hydrothermal method. In a typical process, $Mn(NO_3)_2$ (1 mmol), $Co(NO_3)_2\cdot6H_2O$ (2 mmol), $CO(NH_2)_2$ (12 mmol), and NH_4F (4 mmol) were added to 70 mL of a mixture of ethanol and deionized water (in 1:1 vol ratio) with appropriate stirring at room temperature for ~15 min. The precursor solution was moved into a 100-mL Teflon-lined autoclave. Then, the rGO/NF was placed into the autoclave and heated to 100 °C for 5 h. After the autoclave was cooled to room temperature, the samples were cleaned with deionized water and dried at 60 °C for overnight. $MnCo_2O_4$/rGO/NF (MCO/rGO/NF) nanosheets were obtained by annealing at 350 °C for 2 h under N_2 atmosphere. Then, 70 mL of 1 mmol $Na_2S\cdot9H_2O$ solution was moved into a 100-mL Teflon-lined autoclave, and the as-prepared precursors were added into the autoclave and heated at 120 °C for different times. The sulfurization time was 1, 3, 5 and 7 h, and the corresponding composites were denoted as MCS/rGO/NF-1h, MCS/rGO/NF-3h, MCS/rGO/NF-5h, and MCS/rGO/NF-7h. When the autoclave was cooled to room temperature, the prepared samples were cleaned with deionized water and dried at 60 °C for overnight. To promote sulfide crystallization, all the MCS/rGO/NF samples were heated at 350 °C for 2 h under N_2 atmosphere. The loadings of the active materials on NF were ~1.2 mg cm^{-2}.

2.3. Characterization of materials

The structures of samples were characterized by X-ray diffraction analysis (XRD, TD-3500 with Cu Kα radiation). The morphology of samples was observed by field-emission scanning electron microscopy (FESEM TESCAN, MIRA3) and high-resolution transmission electron microscopy (HRTEM JEOL, JEM-2100F). The composition and valence states of composites by X-ray photoelectron spectroscopy (XPS) using a K-Alpha electron spectrometer with Al Kα radiation. Nitrogen sorption isotherms were measured at 77.3 K on an automatic N_2 adsorption/desorption instrument (Quantachrome Autosorb Automated Gas Sorption System). Raman spectra were obtained using a Bruker Senterra equipped with a 532-nm wavelength laser.

2.4. Electrochemical measurements

A 660E electrochemical workstation was used to test the cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) curves and electrochemical impedance spectroscopy (EIS). The electrochemical measurements of the electrode materials were conducted in a three-electrode configuration using 2 M KOH electrolyte using the as-synthesis composite as the working electrode (2 cm × 1 cm), a Pt plate as the counter electrode and Hg/HgO as the reference electrode. CV curves were obtained in a voltage range from 0 to 0.7 V. GCD tests were measured at various current densities from 0 to 0.5 V. EIS was tested from 100 kHz to 0.01 Hz frequency range. The specific capacity (C_s) can be obtained by the following Eq. (1):