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Simple synthesis of novel phosphate electrode materials with unique microstructure and enhanced supercapacitive properties

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ABSTRACT

Flower-like $Ni_3P_2O_8$ and flower-like $Fe_3P_2O_8{\cdot}8H_2O$ have been successfully synthesized by a simple chemical precipitation method. X-ray diffraction (XRD) patterns reveal an amorphous phase formation of nickel phosphate ($Ni_3P_2O_8$) and pure monoclinic phase of $Fe_3P_2O_8{\cdot}8H_2O$. The novel flower-like $Ni_3P_2O_8$ and flower-like $Fe_3P_2O_8{\cdot}8H_2O$ when used for supercapacitor electrode materials exhibit a high specific capacitance (C_m) of 1464 F/g and 200 F/g at a current density of 0.5 A/g, respectively. Eventually, an asymmetric supercapacitor is fabricated using $Ni_3P_2O_8$ as positive electrode and $Fe_3P_2O_8{\cdot}8H_2O$ as negative electrode. A high specific capacitance of 94 F/g is achieved in the high-voltage region of 0 ~1.6 V, and a large energy density of 32.6 Wh/kg is delivered at power density of 420 W/kg. The findings demonstrate the important and great potential of developing metal phosphate based materials for supercapacitors.

1. Introduction

The energy-storage problem is one of the great challenges in the twenty-first century [1,2]. As the oil energy drying up and the emphasis on environmental protection and increased interest in renewable energy sources, researchers around the world have begun to research Li-ion batteries, fuel cells, and supercapacitors (ECs) to make a sustainable development [3,4]. Among these new energy devices, supercapacitors are considered as a promising candidate for energy storage due to high specific capacitance, long cycle life, and low maintenance cost. Generally, supercapacitors are classified into electrical double-layer capacitors (EDLCs) and pseudocapacitors depending on the charge storage mechanism. The EDLCs store energy via accumulating charge at the interface between electrode and electrolyte. Carbon-based materials, with high specific surface area, thermal stability, and electrical conductivity, are a class of typical materials employed in current commercial electric double layer capacitor [5,6]. Pseudocapacitor, storing energy by reversible redox reactions on electrode materials, usually exhibits a higher value of specific capacitance than electric double layer capacitance due to the presence of Faradaic process. Although compared with batteries, the ECs possess a longer cycle life, require a very simple charging circuit, experience no memory effect, and generally are much safer [6–8], they deliver an unsatisfactory energy density than batteries. So it is essential to increase the energy density of supercapacitors without sacrificing the high power density and steady cycle life [9–15]. It is well known that the energy density of the pseudocapacitors is direct proportion with the specific capacitance (C_m) and square of the cell voltage [16,17]. So it is important to increase the C_m and broaden the cell voltage of the supercapacitors.

A large number of experiments have approved that the electrode materials play a key role in the development of high performance supercapacitors. In recent years, transition metal oxides have been widely studied as pseudocapacitive materials due to their variable valence states, abundant resources, and environmental compatibility [18–20]. Among these transition metals oxides, the nickel oxides and their hydroxides or compounds have attracted much attention due to their huge actual capacitance (e.g. NiO – 1829 F/g [21], $Ni(OH)_2$ – 366.9 m^2/g [22], $NiCo_2O_4$ – 1278 F/g [23], $Ni_3V_2O_8$ – 1181 F/g [24], NiS – 2.64 F cm^2 [25]). In addition to the above materials, $Ni_3P_2O_8$ is an important inorganic phosphate with a two-dimensional layer open structure, which is benefit for improving effective specific surface area of materials. This inspired us to synthesize and investigate $Ni_3P_2O_8$ as a new positive electrode material for supercapacitors. On the other hand, although active carbon (AC) has been widely used as negative electrode, the lower theoretical capacitance (100–300 F/g) and narrow potential window in aqueous electrolyte are still difficult to fulfill the high-energy requirement. Furthermore, the low density of AC also limits the energy and power performances of

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these asymmetric supercapacitors [26–29]. In order to enhance the energy density of electrochemical capacitors, a new negative electrode material with high C_m and broaden working potential are highly desired. In this work, a new negative electrode material ($Fe_3P_2O_8{\cdot}8H_2O$) is fabricated to replace AC, and it exhibits excellent electrochemical performances including a preferable C_m (200 F/g) and broader potential window (0–1.3 V). Besides, iron compound have variable oxidation states, natural abundance, low cost, low toxicity, and environmental friendliness [30–37]. These advantages render $Fe_3P_2O_8{\cdot}8H_2O$ a promising candidate as negative electrode in asymmetrical supercapacitors.

Herein, amorphous $Ni_3P_2O_8$ is synthesized by a simple chemical precipitation method and served as positive electrode material of supercapacitors, and $Fe_3P_2O_8{\cdot}8H_2O$ is also synthesized by the same method to replace AC material. Then an asymmetric supercapacitor is assembled, the electrochemical properties of the $Fe_3P_2O_8{\cdot}8H_2O//Ni_3P_2O_8$ asymmetric supercapacitor were extensively investigated. A high C_m of 94 F/g is achieved at a current of 0.5 A/g and a large energy density of 32.6 Wh/kg is delivered at a power density of 420 W/kg.

2. Experimental

2.1. Synthesis of $Ni_3P_2O_8$ and $Fe_3P_2O_8{\cdot}8H_2O$

Nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$), ferrous sulfate ($FeSO_4{\cdot}7H_2O$), sodium phosphate monobasic anhydrous (NaH_2PO_4), polyvinylidene fluoride (PVDF), graphite, acetylene black, and sodium acetate (NaCOOH) were purchased from Sinopharm and used as received without further purification. For the typical synthesis of $Fe_3P_2O_8{\cdot}8H_2O$, 2 mmol of NaH_2PO_4 and 3 mmol of $FeSO_4{\cdot}7H_2O$ were dissolved in double distilled water (20 mL) with continuous stirring in order to make homogeneous solution, sodium acetate (NaCOOH) was added to adjust the pH (4–6) and stirred for an additional 1 h at room temperature. The resulting solution was filtered and washed 3 times using distilled water, and then the product was dried at 80 °C for 12 h in vacuum oven. $Ni_3P_2O_8$ was prepared by the same method.

2.2. Characterization of structure

The morphology of the samples was studied using a scanning electron microscope (SEM, JEOL, JSM-6701F, Japan). Crystallite structures were determined by X-ray diffraction (XRD) using a Rigaku D/MAX 2400 diffractometer (Japan) with Cu $K\alpha$ radiation ($\lambda = 0.15444$ nm) operating at 40 kV and 60 mA. The elemental surface composition of $Ni_3P_2O_8$ was analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5700, ESCA). The surface areas were investigated by volumetric nitrogen adsorption/desorption experiments (ASAP 2020) using a BJH algorithm for extraction of pore data.

2.3. Electrode preparation and characterization

For electrochemical measurement, 80 wt% of the active material was mixed with 7.5 wt% of acetylene black and 7.5 wt% of conducting graphite in an agate mortar until a homogeneous black powder was obtained. 5 wt% of polytetrafluoroethylene (PTFE) was added together with a few drops of ethanol. The resulting paste was pressed at 10 MPa into a nickel foam (Changsha Lyrun New Material Co. Ltd., grade 90 PPI, 2 mm thick), and then dried at 60 °C for 12 h in vacuum drying oven. Each electrode contained 4 mg of the electroactive material and had a geometric surface area of 1 cm^2. The electrochemical behaviors of the phosphate were investigated using three-electrode cells with 2 M KOH solution as the electrolyte. A platinum sheet electrode with a surface area of 2.25 cm^2 was used as the counter electrode and a saturated calomel electrode (SCE) served as the reference electrode. The cyclic voltammetry and charge–discharge tests were carried out using an electrochemical workstation (CHI660D, Shanghai, China) at room temperature. The cycling performance was tested using a CT2001A battery program controlling test system (China-Land Com. Ltd.). The C_m of the electrode was calculated from the following equation:

$$C_m = \frac{C}{m} = \frac{I \cdot \Delta t}{m \cdot \Delta V} \tag{1}$$

The energy density (E) was calculated from the following equation:

$$E_D = \int_0^Q V \mathrm{d}q = \frac{\int_0^{t_Q} V I \mathrm{d}t}{3600 \prod} \tag{2}$$

The power density (P) was calculated from the following equation:

$$P = \frac{E}{\Delta t} \tag{3}$$

where C (F) is the total capacitance, I (A) is discharge current, Δt (s) is the discharge time, ΔV (V) represents the potential window, C_m (F/g) is the specific capacitance, m (g) is the mass of the composite, E (Wh/kg) is the energy density, and P (W/kg) is the power density.

2.4. Preparation of the asymmetric supercapacitor

The asymmetric supercapacitor consisted of two electrically isolated electrodes: $Ni_3P_2O_8$ as the positive electrode and $Fe_3P_2O_8{\cdot}8H_2O$ as the negative electrode, and 80 wt% of active material was mixed with 7.5 wt% of acetylene black and 7.5 wt% of conducting graphite in an agate mortar until a homogeneous black powder was obtained. To this mixture, 5 wt% of polytetrafluoroethylene (PTFE) was added together with a few drops of ethanol. The resulting paste was pressed at 10 MPa into a nickel foam, then dried at 80 °C for 12 h, and joined together by a porous non-woven cloth separator soaked in 2 mol/L aqueous KOH solution. Each electrode has a geometric surface area of 1 cm^2. For the supercapacitor, the charge balance follows the relationship:

$$Q_+ \equiv Q_- \tag{4}$$

where Q_+ and Q_- represent the charge stored in positive electrode and negative electrode, respectively. Q of each electrode depends on C_m, the potential range of the charge/discharge tests (ΔE), and the mass of the electrode (m) according to the following equation:

$$Q = C_m \cdot m \cdot \Delta E \tag{5}$$

When $Q_+ = Q_-$, the ratio of the masses of the positive electrode (m_+) and negative electrode (m_-) will follow the equation:

$$\frac{m_+}{m_-} = \frac{C_{-m}}{C_{+m}} \cdot \frac{\Delta E_-}{\Delta E_+} \tag{6}$$

The SC of $Fe_3P_2O_8{\cdot}8H_2O$ and $Ni_3P_2O_8$ are 200 F/g and 1464 F/g. On the basis of the SC values and the potential windows found for the $Fe_3P_2O_8{\cdot}8H_2O$ and $Ni_3P_2O_8$ electrodes, the optimal mass ratio should be $m_+/m_- = 0.4098$ in the asymmetric supercapacitor.

3. Results and discussion

3.1. Structural analysis

The powder XRD patterns of $Ni_3P_2O_8$ and $Fe_3P_2O_8{\cdot}8H_2O$ are shown in Fig. 1. It can be seen from Fig. 1(a) that there is a broad peak at 30.328° without any other observable crystalline diffraction peaks, because the fabricated $Ni_3P_2O_8$ has short-range order