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High-performance flexible all-solid-state asymmetric supercapacitors from nanostructured electrodes prepared by oxidation-assisted dealloying protocol

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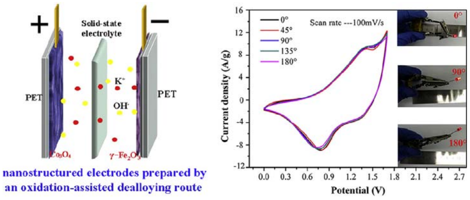
GRAPHICAL ABSTRACT



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ABSTRACT

Flexible all-solid-state energy storage devices that can function under considerably large mechanical deformation have shown great promise for portable electronics applications. However, conventional techniques are cumbersome in building cost-effective flexible all-solid-state energy storage devices, thus limiting their widespread applications. Here we report a flexible all-solid-state supercapacitor whose electrodes were prepared via a facile oxidation-assisted dealloying protocol for the first time. The electrodes demonstrate good flexibility and excellent performance. We assembled a prototype all-solid-state asymmetric supercapacitor (ASC) from the as-prepared Co_3O_4 flakes and γ-Fe_2O_3 nanoparticles as the positive and negative electrodes, respectively. The flexible ASC device possesses an extended operating voltage window of 1.7 V and a high energy density of 38.1 Wh/kg. We also demonstrated that four supercapacitor cells that were constructed in series illuminated 52 LEDs for at least 7 min. The ASC device has excellent power density and energy density that comparable to the art-of-the-state supercapacitors reported in the literature, and retains good charge and discharge performance under different bending conditions. The synthesis strategy reported here may be beneficial to the low-cost mass production of nanostructured electrode materials for energy storage applications.

1. Introduction

Increasing demand for portable consumer and wearable electronics urges the development of novel energy storage devices that are lightweight, flexible, of high power and energy densities [1–3]. In the past decades, supercapacitors have been attracting significant interest attention due to their high power density, exceptionally long cycling lifetime, excellent stability during cycling, and excellent safety liability [4,5]. Unfortunately, the energy density of commercially available supercapacitors is remarkably lower than those of batteries and fuel cells, which limits their application in next-generation portable devices [6]. Asymmetric supercapacitors (ASCs) are an effective approach for extending the operating voltage window of the powder sources [7–12]. The ASC generally consists of a battery-type Faradic electrode (cathode)

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as an energy source and a capacitor-type electrode (anode) as a power source. The ASC technology is expected to achieve an increased energy density and high cell voltage.

Despite great progress in improving the capacitance of cathode materials, the anode materials have been rarely investigated. Carbon-based nanomaterials are commonly used as anode in ASCs. However, the low specific capacitance of carbon materials severely limits the energy density for ASCs [13]. Metal oxide based anodes with nanostructures, such as MoO_3, Bi_2O_3 and Fe_2O_3, are promising electrode materials for ASCs because of their high specific capacitance, typically 2–3 times higher than that of carbon/graphite-based materials [14–16]. To prepare uniform metal oxide nanostructures, many strategies such as electrodeposition [17], hydrothermal reduction [18], solvothermal synthesis [19], sol–gel method [20] have been developed. These methods include meticulous chemical steps, excessive use of organic chemicals and operation at high temperatures. Recently, dealloying – a selective dissolution of one or more elements in an alloy – is used to fabricate nanoporous metals for application in supercapacitors [21–23]. Lang et al. [24] have developed a nanoporous Au/MnO_2 electrode by the combination of chemical dealloying and electroless plating, where MnO_2 grows on the internal surface of nanoporous channels. The nanocomposite-based supercapacitor exhibits a specific capacitance of constituent MnO_2, which is close to the theoretical value. The metal/oxide hybrid material has very high specific capacitance and energy density. However, to the best of our knowledge, the fabrication of nanoporous metal oxide by oxidation-assisted dealloying method for supercapacitors is still in its infancy. Low-cost nanoporous metal oxides such as NiO, Cu_2O and Fe_2O_3 with tunable pore sizes are clearly in great demand for energy storage applications. In these metal oxides, the porous supports offer a three-dimensional conductive pathway, facilitating charge transport effectively, while nano-sized pore channels, serving as reservoirs of electrolytes, provide short ion diffusion distance and have low resistance. Additionally, nanoporous architectures offer large effective surface areas, improving its specific capacitance [25–27].

In this work we report a simple oxidation-assisted dealloying process to produce Co_3O_4 with a 3D interconnected porous framework for cathode material and γ-Fe_2O_3 nanoparticles for anode material. A flexible all-solid-state ASC was constructed based on these low-cost Co_3O_4 and γ-Fe_2O_3 electrodes with KOH/poly vinyl alcohol (PVA) as electrolyte. The prototype device exhibited a high specific capacitance of 94.7 F/g at a current density of 0.7 A/g and an energy density of 38.1 Wh/kg.

2. Experimental section

2.1. Synthesis of the flexible Co_3O_4 positive electrode

The precursor ($Al_{65}Co_{35}$, at%) was designed according to the nominal composition of a single-phase Al_5Co_2 intermetallic compound. Fig. S1 shows the Al–Co binary phase diagram. $Al_{65}Co_{35}$ ingots were prepared by arc-melting pure bulk metals (Al, 99.99 wt%; Co, 99.99 wt%) in an argon atmosphere. Then, the ingots (about 35 g) were melted by high-frequency induction heating in a quartz glass tube and melt-spun onto a copper roller at a circumferential speed of 1500 rpm in a controlled argon atmosphere (as shown in Fig. S3). The as-spun alloy ribbons obtained are about 20–40 μm thick, 3–5 mm wide, and several centimeters long. Subsequently, the alloy ribbons were ball-milled in an agate tank (150 mL) using a planetary ball mill (QM-3SP04, Nanjing, China) under ambient conditions at 300 rpm for 6 h. The ball-to-ribbon weight ratio was maintained at 20:1.

The obtained $Al_{65}Co_{35}$ alloy powders were then dealloyed in a 0.2 wt% NaOH aqueous solution at 20 °C for 48 h. After dealloying, the powders were filtered with a filter paper and rinsed with distilled water for several times. The products were then dried in vacuum for 12 h at 70 °C and nanostructured Co_3O_4 flakes resulted. The flake-like Co_3O_4 powders (80 wt%), carbon black (10 wt%) and polyvinylidene-fluoride (PVDF, 10 wt%) were weighed and mixed in a mortar. A small amount of N-methylpyrrolidone (NMP) was then added to form a homogeneous mixture. The resulting mixture was coated onto a 25 mm × 15 mm Ni-foam and was dried at 70 °C for 12 h in vacuum. Finally, the positive electrode is pressed to 0.3 mm.

2.2. Fabrication of the flexible γ-Fe_2O_3 negative electrode

The precursor ($Al_{71}Fe_{29}$, at%) was designed according to the nominal composition of a single-phase Al_5Fe_2 intermetallic compound. Fig. S2 shows the Al–Fe binary phase diagram. A similar procedure described in fabrication of Co_3O_4 was used to prepare $Al_{71}Fe_{29}$ powder. The obtained $Al_{71}Fe_{29}$ alloy powders were dealloyed in a 2 wt% NaOH aqueous solution at 85 °C for 48 h. An identical drying procedure as described previously was used to prepare γ-Fe_2O_3 powders. Using γ-Fe_2O_3 (80 wt%), carbon black (10 wt%) and PVDF (10 wt%), the negative electrode 0.3 mm think was prepared, as per the procedures described in Section 2.1.

2.3. Assembly of the flexible all-solid-state supercapacitor

Polymeric PVA-KOH gel electrolyte was prepared by mixing 3 g KOH and 6 g PVA in 60 mL deionized water at 80 °C and stirring it using a magnetic stirrer until the solution became clear gel. Both positive and negative electrodes were dipped into the gel electrolyte solution for 3 min to absorb the gel electrolyte. After solidified at room temperature, two pieces of flexible electrodes were separated by the PVA-KOH gel film were used to assemble a flexible all-solid-state Co_3O_4//γ-Fe_2O_3 supercapacitor. The schematic diagram of the fabrication process of the flexible ASC supercapacitor is shown in Fig. 1.

2.4. Materials characterization

The crystal structure of the as-synthesized products were characterized by a Bruker Advance Eco X-ray powder diffractometer (XRD) with Cu-Kα radiation (λ = 1.5418 Å) in the 2θ range of 10°–80°. The morphology and microstructure of the samples were studied by transmission electron microscopy (TEM, Tecnai G2 F20) and scanning electron microscopy (SEM, JEOL JSM-6700). X-ray photoelectron spectra (XPS) were recorded on a Thermo VG ESCALALAB 250 X-ray photoelectron spectrometer using Al Kα X-rays as the excitation source. The specific surface area was measured by the multipoint Brunauer-Emmett-Teller (BET) method at 77.3 K with a quanta-chrome NOVA4200e system. The pore size distributions (PSD) were obtained by means of the Barrett-Joyner-Halenda (BJH) equation using the adsorption isotherm branch.

2.5. Electrochemical performance measurements

Electrodes were tested on a CHI660E electrochemical workstation in a three-electrode electrochemical cell using a 1 M KOH aqueous solution as electrolyte at room temperature. The Co_3O_4 electrode or γ-Fe_2O_3 electrode was used as the working electrode. A platinum plate and Ag/AgCl electrode were used as the counter and reference electrode, respectively. Cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) tests were conducted at different scan rates and current densities. Electrochemical impedance spectra (EIS) were measured in the frequency range of 0.01–1,00,000 Hz. The specific capacitance was derived from the discharge time as per the following equation [22]:

$$C = (I\cdot\Delta t)/(\Delta V\cdot m) \tag{1}$$

where I is the discharge current. Δt is the discharge time, ΔV represents the potential window and m is the mass of the electroactive materials.

The energy density (E) and power density (P) of the flexible all-solid-state ASC device were calculated using the following equations