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Liquid phase synthesis of dendritic nickel carbide alloy with high conductivity for advanced energy storage

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ABSTRACT

Alloy materials have attracted increasing attentions because they possess superior electrical conductivity which can contribute to excellent electrochemical performance. Herein a dendritic Ni₃C alloy material has been prepared by the pyrolysis of nickel acetylacetonate employing oleylamine as a reductant and 1-octadecene or octadecane as the solvent. The current–voltage curves indicating that the electrical conductivity of Ni₃C is higher than that of nickel oxide. Electrochemical testing indicates that a high specific capacity of 390 C/g is found in alkaline electrolyte at 0.5 A/g, and deliver excellent rate characteristic as well as cycle life. The excellent electrochemical performance may be attributed to its high electrical conductivity and dendritic nanostructure that can promote diffusion of electrolyte ions. In addition, the AC//Ni₃C asymmetric supercapacitor has been assembled at a cell voltages between 0 and 1.6 V, achieving a maximum energy density of 37 Wh/kg (at a power density of 0.3995 kW/kg), and this manifests that the Ni₃C alloy is a promising electrode material for electrochemical energy storage.

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1. Introduction

It is a trend that electrochemically active electrode materials play an important role for high-performance supercapacitors. Therefore, numerous efforts from researchers have been made to develop the electrode materials that can possess low prices, less pollution and prominent energy storage capacity. Nickel oxide (NiO), as a common electrode material, has been treated as one of the most promising electrode materials for electrochemical capacitor applications on account of its superior theoretical specific capacitance [1], low cost, and outstanding thermal and chemical stability [2–4]. Nevertheless, the intrinsic high electrical resistances of nickel oxides restrict their charge–discharge rate in a higher current density which is adverse for high-power energy storage applications. Based on this consideration, many researchers have fabricated a mass of composite materials by adding the high-conductivity carbon-based materials, such as three-dimensional carbon nanotube networks supported nickel oxide [5], carbon nanotubes/NiO nanocomposites [6], microtubular carbonized kapok fiber/NiO composites [7]. Although these composites can improve the electrical conductivity to some extent, the effect is still unsatisfactory. Most commercial supercapacitors utilize carbon-based materials, owing to their large specific areas, high electrical con-

ductivity and low costs. But the specific capacitances of carbon-based supercapacitors are restricted by their less electrochemically active nature [8]. Therefore, it is a challenge to exploit new electrode materials with both high electrical conductivity and specific capacitances.

For recent years, transition metal carbides, are often referred to as “interstitial alloys” [9], which are prepared by integrating carbon atoms into the interstitial sites of their parent metals [10]. They have been considered as interesting active materials for electrodes owing to their high melting point, high electrical conductivity and chemical stability as well [9,11]. Among them, nickel carbides, as a sort of promising electrode material, hold a mass of metallic bonds between Ni and C elements. The Ni combined by metallic bonds could provide free electrons and greatly improving electrical conductivity [12,13]. The high electrical conductivity can result fast electron transfer for high-rate operation, leading to better rate capability. However, so far, there are almost no reports on applications in supercapacitors.

On the basis of mentioned above, a dendritic Ni₃C alloy material was synthesized via a liquid phase synthesis method. The obtained Ni₃C exhibits higher electrical conductivity than nickel oxides, and can achieve a high specific capacity, excellent rate capability and long cycle life. Furthermore, an asymmetric supercapacitor device based on Ni₃C as positive electrode and activated carbon (AC) as negative electrode was fabricated and displayed excellent cycling stability, upper energy and power density. It demonstrated

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that such an alloy material would be a potentially promising in energy storage system applications. Our study also provides a new thinking to explore other alloy material for electrochemical energy storage.

2. Experimental

2.1. Synthesis of the Ni₃C particles

Ni₃C particles were synthesized through the following process: 0.5 g acetylacetonate hydrate (Ni(acac)₂·xH₂O, 98%, TCI America), 5 mL of oleylamine (97% primary amine, Acros) and either 5 mL of 1-octadecene (ODE, 90%, Sigma-Aldrich) or 3.98 g of octadecane (ODA, 99%, Sigma-Aldrich) were mixed in a three-necked round-bottomed flask. The mixture was degassed before backfilling with nitrogen and then heated to 270/250 °C for 5/8 h. The product was purified using ethanol to flocculate, followed by redispersion in hexanes. So after cooling to room temperature, the product was centrifuged firstly with ethanol several times and centrifuged subsequently with normal hexane several times. Then the sample was dried at 80 °C for 12 h in vacuum oven [14].

2.2. Working electrode preparation

Electrode was prepared by coating electrode slurries (80 wt% active material, 7.5 wt% carbon black, 7.5 wt% conducting graphite and 5 wt% of polytetrafluoroethylene with a few drops of ethanol) on open-cell nickel foam, pressed at 10 MPa, and then dried at 60 °C for 12 h. Each electrode contained 4 mg of the electro-active material and had a geometric surface area of 1 cm². Electrical conductivity of samples is inspected by current–voltage (*I*–*V*) test; the working electrodes were prepared as follows: the sample (200 mg) was crushed into wafer in the mould; wafers held uniform diameter (~1 cm) and thickness (~2 mm); then put the wafer in the middle of two stainless steel sheets, and tested in the electrochemical working station.

2.3. Structure characterization and electrochemical measurements

Crystallite structures were determined by X-ray diffraction (XRD; D/MAX 2400, Rigaku, Japan). The microstructures were characterized with scanning electron microscopy (SEM, JEOL, JSM-6701F, Japan) and transmission electron microscope (TEM, JEOL, JEM-2010, Japan) equipped with Selected Area Electron Diffraction (SAED). The pore properties, including the BET surface area and pore size distribution were investigated volumetrically by ASAP 2020 nitrogen adsorption/desorption experiments. The chemical state of the products was investigated by X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo VG). The electrochemical properties of samples, including cyclic voltammetry (CV), galvanostatic charging and discharging (GCD) tests, electrochemical impedance spectrum (EIS) and cyclic stable were evaluated by a Chen-hua CHI 760D electrochemical workstation in a three-electrode cell in the 6M KOH aqueous electrolyte, in which platinum foil and saturated calomel electrodes were used as the counter and reference electrodes, respectively. The specific capacity values of a single electrode were calculated as follows: $C_m = (I \times \Delta t) / (\Delta V \times m)$, where C_m (C/g) is the charge capacity, I (A) is the discharge current, m (g) is the active material mass, Δt (s) is the discharge time.

2.4. Preparation of the asymmetric supercapacitor and the relevant calculations

The ASC was assembled using Ni₃C as the positive electrode ($m_+ = 4.0$ mg) and activated carbon as the negative electrode

($m_- = 4.13$ mg) in 6 M KOH. The mass loading for the positive and negative electrodes was optimized according to equation:

$$\frac{m_+}{m_-} = \frac{C_- \times \Delta V_-}{C_+ \times \Delta V_+} \quad (1)$$

And, the energy density E was calculated from the following equation:

$$E = \frac{1}{2} C_m \cdot \Delta V^2 \quad (2)$$

The power density P which was determined from the constant current charge/discharge cycles is as follows:

$$P = \frac{E}{\Delta t} \quad (3)$$

Here, E (Wh/kg) is the energy density, P (W/kg) is the power density.

The coulombic efficiency (η) is determined as following equation:

$$\eta = \frac{q_d}{q_c} \times 100\% \quad (4)$$

where q_d and q_c are discharge and charge specific capacity, respectively.

3. Results and discussion

3.1. Characterization of Ni₃C particles

The XRD patterns of Ni₃C samples with different synthesis conditions are presented in Fig. 1(a). It is found that the location of all diffraction peaks is consistent except for discrepant crystallinity, indicating that the uniform phase is synthesized at different reaction temperatures and times. Fig. 1(b) shows the XRD pattern of representative sample with 270 °C 8 h. The product possesses some legible diffraction peaks, which can be well indexed as (1 1 0), (0 0 6), (1 1 3), (1 1 6), (3 0 0), (1 1 9), (3 0 6), (2 2 3), (0 0 1 2), and (2 2 6) planes of rhombohedral Ni₃C (PDF #06-0697). SEM images indicate that the as-synthesized Ni₃C material consists of loosened particles structure (Fig. 1c). There are plentiful channels between particles, which facilitate access of electrolyte and avoid volume expansion in the process of Faradaic reaction. The average size of Ni₃C sample by Zetasizer Nano 3600 is 268.5 nm, which is larger than that of SEM results. It is because that the SEM test aims at observing the single particle by naked eye. When tests the precise average size of the sample by Zetasizer Nano 3600, sample is dissolved in water and tested. If the dispersibility of samples in water is bad, the average size is larger than that of SEM test results certainly. And there are many factors to decide the tested results by Zetasizer Nano 3600, such as temperature, concentration, dispersibility, the extent of the particles aggregates. The TEM images of Ni₃C (Fig. 1d and e) display the appearance of approximate dendritic structure with abundant gaps. The dendritic structure of Ni₃C can improve the specific surface area of material, which is benefit of improving the specific capacity of electrode material. The lattice fringes shown in Fig. 1(f) can be indexed to the (1 1 3) crystal planes of the rhombohedral phase, which further confirms the formation of crystalline Ni₃C. The blurry diffraction rings in SAED pattern indicate the polycrystalline nature of the Ni₃C particles (Fig. 1g).

To further ascertain the chemical bonding states of every element in Ni₃C, the sample is confirmed by XPS test. The typical Ni 2p, Ni 3p, O1s, C1s, Ni Auger signals are observed in the full spectrum (Fig. S1), which manifests that these elements exist in tested sample. The O element is derived from surface adsorption when the sample is exposed to the air. Results reveal that the sample consists of Ni and C elements on the surface, which is in line

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