Simple Synthesis and Supercapacitive Performances of NiMoS₄ Particles

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A simple method was used to prepare amorphous NiMoS₄ particles that were subsequently characterized with X-ray diffraction, X-ray fluorescence spectrum, scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectrum. The supercapacitive properties of NiMoS₄ were measured for the first time. It exhibits high capacitance and low charge ion transfer resistance owing to its accessible multiple valences, amorphous structure and high conductivity of sulfides.

Keywords: Amorphous; Capacitance; Charge Ion Transfer Resistance.

1. Introduction

Development of fast and efficient energy storage devices is still a challenge to meet extending from portable electronics to electrical vehicles [1]. Among these energy storage devices, supercapacitor has been attracted numerous attentions owing to the high powder density, fast charge/discharge process and good stability [2].

Transition metal oxides with high theoretical capacity have been widely used in the electrode materials. But the poor conductivity limits their practical applications. Surprisingly, the transition metal sulfides possess higher conductivity than the corresponding oxides [3]. Up to now, NiS and MoS₂ have been reported to own good supercapacitive performances. Moreover, the binary metal sulfides with their multiple redox reactions exhibit better electrochemical behaviors than single component metal sulfides. Therefore, the NiMoS₄ is predicted to own good supercapacitive properties. Moreover, to our best knowledge, there are very few reports for NiMoS₄ except for the applications in the sorbents for radioactive iodine [4] and dye-sensitized solar cells [5].

In this work, the NiMoS₄ was prepared by a very simple precipitation method and characterized by various characterization means. Then the electrochemical properties of NiMoS₄ were measured using a three-electrode setup in 1 M KOH.

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2. Experimental

2.1. Preparation of NiMoS₄
The excess of (NH₄)₂S reacted with (NH₄)₂MoO₄ with stirring at 70°C to prepare (NH₄)₂MoS₄. After about 40 min, the mixture was cooled in the fridge to allow (NH₄)₂MoS₄ to crystallize, and then it was separated by centrifugation. The obtained (NH₄)₂MoS₄ and NiCl₂·6H₂O were dispersed into the ethanol solution (0.125 volume fraction), and stirred at room temperature to obtain a NiMoS₄ precipitation. The precipitation was rinsed by distilled water and ethanol, and dried at room temperature to obtain NiMoS₄ powders.

2.2. Characterization
X-ray diffraction (XRD) patterns of (NH₄)₂MoS₄ and NiMoS₄ were measured with the given step (5° min⁻¹) using a D/MAX-2500 diffractometer (Japan) with a Cu Ka radiation reference target. X-ray fluorescence (XRF) spectrum of NiMoS₄ was used to determine the content of elements by S4 Pioneer spectrometer (Brucker). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements were conducted using S4800 microscope (Hitachi Limited, Japan) and Philips Tecnai G2F20 microscopy (Netherlands), respectively. X-ray photoelectron spectrum (XPS) measurement of NiMoS₄ was performed in a PHI1600 ESCA System spectrometer (PERKIN ELMER, USA). Typeset sub-subheadings in medium face italic and capitalize the first letter of the first word only. Section numbers to be in roman.

2.3. Characterization
The NiMoS₄ was blended with carbon black and polytetrafluoroethylene emulsion (60%) in a mass ratio of 75:15:10, and then the mixture was coated on Ni foam (1×1 cm²). The coated Ni foam was dried and pressed in a pressure of about 6 MPa to get a NiMoS₄ working electrode. The mass loading of active materials in the electrode was about 5 mg/cm².

The supercapacitive performances of NiMoS₄ were investigated using Galvano static charge/discharge (GCD) cycles and electrochemical impedance spectroscopy (EIS) by a three-electrode setup in 1 M KOH, using Hg/HgO and Pt mesh as the reference and auxiliary electrodes respectively. The corresponding specific capacitances of NiMoS₄ were evaluated based on the following equation:
\[
C = \frac{i \times \Delta t}{\Delta \mu \times m}
\]

Where \( C \) (F/g), \( i \) (A), \( \Delta t \) (s), \( \Delta \mu \) (V) and \( m \) (g) are specific capacitance, discharge current, discharge time, potential window, and mass of the active material.

3. Result and discussion

The prepared \((\text{NH}_4)_2\text{MoS}_4\) by the reaction between \((\text{NH}_4)_2\text{S}\) and \((\text{NH}_4)_2\text{MoO}_4\) was confirmed by XRD measurement. In Figure 1, all diffraction peaks of the prepared \((\text{NH}_4)_2\text{MoS}_4\) were in good accordance with those for the standard \((\text{NH}_4)_2\text{MoS}_4\) (JCPDS: 48-1662). When \(\text{NiCl}_2\) solution was added to the \((\text{NH}_4)_2\text{MoS}_4\) solution in a molar ratio of 1:1, the precipitation was observed immediately owing to the occurrence of a replacement reaction, further suggesting the formation of \(\text{NiMoS}_4\). No diffraction peaks were observed in the XRD pattern of the obtained \(\text{NiMoS}_4\) (Figure 1), confirming the amorphous structure of \(\text{NiMoS}_4\) nanoparticles. The composition of the obtained \(\text{NiMoS}_4\) was determined by XRF measurement. The molar ratio of Ni: Mo: S is about 1:1.03:4.01, which is very close to the chemical stoichiometry of \(\text{NiMoS}_4\), confirming the successful preparation of \(\text{NiMoS}_4\).

![Figure 1. XRD patterns of (NH₄)₂MoS₄ and NiMoS₄.](image)

SEM and TEM were used to observe the morphology and structure of \(\text{NiMoS}_4\). In the SEM image of Figure 2a, \(\text{NiMoS}_4\) consist of nanoparticles and there are some pores between nanoparticles, which can increase the contact between electrolyte and active material, contributing to the capacitance. In Figure 2b, some sheets are observed in the TEM image, which can be concluded that \(\text{NiMoS}_4\) nanoparticles are made of sheets. In addition, there are no diffraction fringes in the high-resolution TEM image of \(\text{NiMoS}_4\) (Figure 2c), also verifying that \(\text{NiMoS}_4\) is amorphous.
XPS analysis was also used to study the chemical composition of NiMoS₄. In the Ni core level spectrum (Figure 3a), the two main peaks at 873.2 and 855.9 eV are assigned to Ni 2p₁/₂ and Ni 2p₃/₂, confirming the +2 oxidation state of Ni. In Figure 3b, the Mo 3d₃/₂ and Mo 3d₅/₂ at 235.6 and 232.5 eV correspond to Mo⁶⁺. The S 2p peak at 162.8 eV is the characteristic of S²⁻. These results are in good accordance with NiMoS₄.

Considering the amorphous structure and accessible multiple valences, the prepared NiMoS₄ was used in the electrode material for supercapacitors.
4a shows the GCD curves at different current densities in the potential window of 0-0.6 V. The nonlinear discharge curves confirm the Faradic redox energy storage mechanism of NiMoS$_4$ [6]. The calculated specific capacitances of NiMoS$_4$ based on discharge curves were shown in Figure 3b. They are 283, 259, 230 and 206 F/g at 1.6, 1.8, 2.4 and 3 A/g, respectively. Obviously, the capacitances decrease with the increasing current densities, owing to that the electrolyte cannot fully contact the inner active materials at a high current density [7]. Moreover, the capacitances of NiMoS$_4$ are higher than those for the component sulfides like MoS$_2$ (122 F/g at 0.5 A/g [8]; 142 F/g at 0.59 A/g [9], 70 F/g at 1 A/g [10]) and NiS (250 F/g at 1 A/g [11]). In addition, they are also superior to those for the reported NiMoO$_4$ (161 F/g at 5 A/g) [12]. The high capacitance of NiMoS$_4$ may be on account of the multiple valences, high conductivity of sulfides, as well as the synergistic effect of Ni and Mo [13].

The EIS measurement was also used to understand the properties of NiMoS$_4$. Figure 4c exhibits the Nyquist plots of NiMoS$_4$. It can be found that the small impedance arc at the high frequency suggests a low charge transfer resistance in the NiMoS$_4$ electrode [14]. Moreover, the high phase angle at the low frequency reflects a low Warburg resistance, which will contribute to the diffusion of electrolyte into the electrode material, leading to a reversible Faradic redox.

![Figure 4. GCD curves (a); specific capacitances (b) and Nyquist plot (c) for NiMoS$_4$.](image)

4. Conclusion

In this work, NiMoS$_4$ was prepared through a simple and facile precipitation method and confirmed by various characterization methods, such as XRD, XRF, SEM, TEM and XPS measurements. The supercapacitive properties of the obtained NiMoS$_4$ were studied by GCD cycles and EIS measurement. The NiMoS$_4$ shows a low charge ion transfer resistance, and its specific capacitance reaches 283 F/g at a current density of 1.6 A/g.
References


