Polyoxovanadate-based MOFs Microsphere Constructed from 3-*D* Discrete Nano-sheets as Supercapacitor①

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ABSTRACT A novel polyoxovanadate-based MOFs microsphere, $[Ni(phen)V_2O_7]·H_2O$ (phen = 1,10-phenanthroline), constructed from 3-*D* discrete nano-sheets has been prepared and characterized by XRD, FT-IR, SEM and TEM. Electrochemical properties as supercapacitor of the as-prepared sample, such as CV, EIS, GCD and the cycle life test have also been studied. The as-prepared MOF (V, Ni) showed a high specific capacitance of 178.09 $F·g^{-1}$ at 1 $A·g^{-1}$ as well as good cycling stability and coulombic efficiency. This work proved that the novel MOFs based on polyoxovanadate hybrid material may serve as a promising electrode material for high-performance supercapacitor.

Keywords: MOFs microsphere, polyoxovanadate, discrete nano-sheets, supercapacitor;

DOI: 10.14102/j.cnki.0254–5861.2011–3053

1 INTRODUCTION

With the depletion and polluting effects of fossil fuels, the search for sustainable, clean, and green forms of energy sources is of a paramount importance[1-3]. Supercapacitors have attracted interest for future energy storage applications because of its high energy density and power density, fast charge-discharge rate and cycling stability[4-6]. Conventional materials for supercapacitors often have drawback such as poor conductivity, low energy density and low cycle life. How to fabricate high performance electrode materials is of great significance to scientific research and industrial application[7].

The metal-organic framework (MOF) material is a material having a plurality of skeleton structures combined by a metal ion and an organic ligand. MOF material has high specific surface area and high porosity, and is suitable for use in supercapacitors, which can effectively increase the contact area with the electrolyte, thereby achieving the purpose of improving the specific capacitance performance[8]. Polyoxometalates (POMs), a class of discrete anionic metal oxides, are composed of transition metals. POMs materials have been applied in various fields, including catalysis, electrochromic, magnetic, and energy storage. Simultaneously, polyoxometalates (POMs) with multi-electron redox properties, stability, and structural diversity are well-suited to achieve a high capacity for energy storage applications[9-11]. However, it is rarely applied in the field of supercapacitors[12, 13].

In light of above considerations, a novel MOF(V, Ni) microsphere constructed by 3-D nanosheets, namely $[Ni(phen)V_2O_7]·H_2O$ (phen is 1,10-phenanthroline), has been synthesized through one-step solvothermal method and characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM). In this study, the cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), galvanostatic charge-discharge (GCD) and the

Received 3 December 2020; accepted 7 April 2021

① This work was supported by the Natural Science Foundation of Fujian Province (No. 2020J01803), Fujian Provincial Key Laboratory of Featured Materials in Biochemical Industry (FJKL_FBCM202004) and the Fujian Provincial Key Laboratory of Ecotoxicological Effects and Control of New Pollutants (PY19001)

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cycle life test techniques were used to study the electrochemical properties of the sample as supercapacitor electrodes in 3M KOH electrolyte. In a three-electrode set-up, the MOF(V, Ni) composite delivered a specific capacitance of 178.09 $F\cdot g^{-1}$ at 1 $A\cdot g^{-1}$, and the capacitance retention rate is 130.66% after 2500 cycles, which makes them attractive for industry.

2 EXPERIMENTAL

2.1 Synthesis

Chemicals here are commercial sources and can be adopted without purification. A mixture of $Ni(CH_3COO)_2\cdot 4H_2O$ (1 mmol, 0.2489 g), NH_4VO_3 (1 mmol, 0.1170 g), 1,10-phenanthroline monohydrate (1 mmol, 0.1982 g) and anhydrous ethanol (60 mL) was heated at 140 ℃ in a Teflon-lined autoclave for 12 hours. Then, it was slowly cooled to ambient temperature, obtaining yellow precipitate by centrifugation. The resulting product was washed with ethanol and deionized water. Finally, the product was dried at 80 ℃ overnight to get the MOF(V, Ni) powders.

2.2 Structure determination

The crystallographic structure of the MOF(V, Ni) was characterized by XRD (Bruker D8 Advance diffractometer) with CuKα radiation (scanned range: 5～80°, scan rate: 8°/min). Fourier transform infrared spectroscopy (Thermo-Scientific NICOLET 360) was used to detect the structureof the sample. SEM (QUANTA 250) and TEM (Tecnai G2 20) were used to observe the morphology and microstructure of the sample.

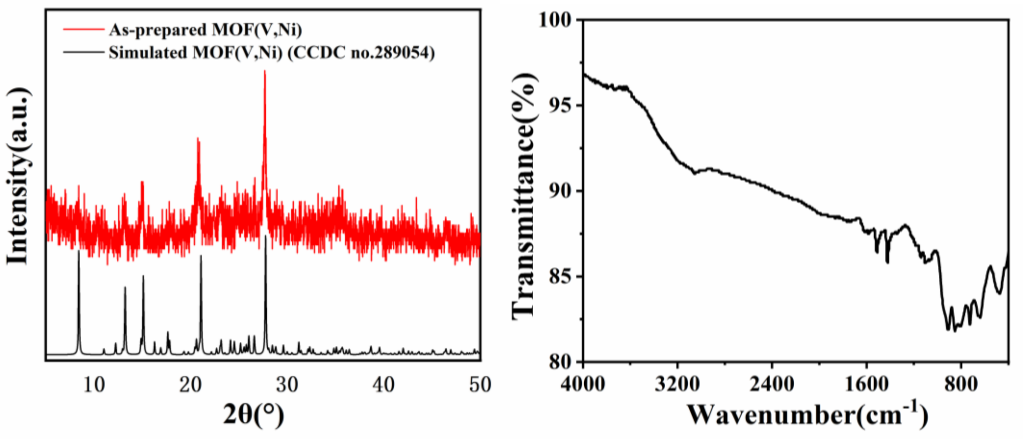
2.3 Electrochemical measurements

Electrochemical properties of MOF(V, Ni) were evaluated in a standard three-electrode test pool. For the working electrode, a mixture containing 5 mg active material, 1 mg acetylene black, and 1 mg PTFE binder was well mixed. Then, the mixture was pressed with several drops of alcohol to form a thin sheet. The loading mass of each nickel foam working electrode is about 5 mg. Platinum wire and a saturated calomel electrode served as the counter and reference electrodes, respectively. The electrolyte was 3 M KOH solution. CV, GCD and EIS were performed on an Electrochemical Workstation (Wuhan Koster Instrument Co., Ltd). The LAND test system CT2001A (Wuhan LAND Electronic Co., Ltd.) was used for the cycle life test and Coulomb efficiency performance of the sample.

3 RESULTS AND DISCUSSION

3.1 Structure and morphology analysis

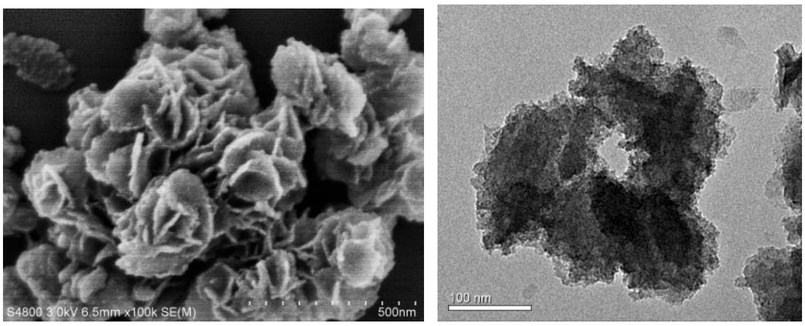
The crystal structure of MOF (V, Ni) was characterized using powder XRD. Fig. 1(a) shows the XRD spectra of MOF (V, Ni) and $[Ni(phen)V_2O_7]\cdot H_2O$ (CCDC 289054). All primary peaks of the sample are in good accordance with those of $[Ni(phen)V_2O_7]\cdot H_2O$ (CCDC 289054)[14]. FT-IR analysis was conducted to study the surface functional groups in MOF (V, Ni), as shown in Fig. 1(b). The bands at 1426, 1555, 1515, 1550 and 1645 cm^{-1} are the characteristic peaks of 1,10-phenanthroline for the as-pre- pared compound.



(a) (b)

Fig. 1. (a) XRD spectra and (b) FTIR spectra of MOF (V, Ni)

In order to study the morphology and microstructure characteristics of MOF (V, Ni), SEM and TEM were performed and the images are shown in Fig. 2. Clearly, these are uniformly distributed microspheres constructed from 3-*D* discrete nano-sheets with a rough surface and an average diameter of 0.15～0.35 μm. This 3-*D* discrete structure provides large specific surface area and potential ion transport channels for the energy storage of supercapacitors.



(a) (b)

Fig. 2. SEM (a) and TEM (b) images of MOF (V, Ni)

3. 2 Electrochemical performance

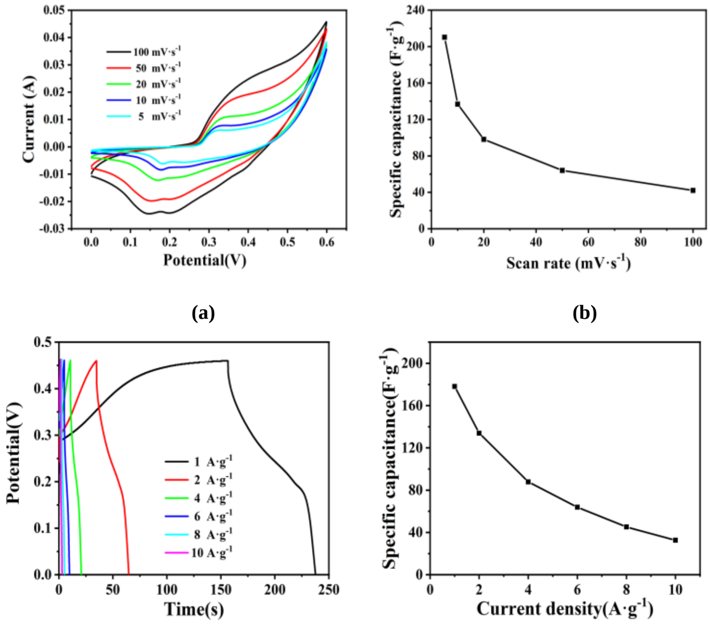
3. 2. 1 Cyclic voltammetry (CV) performance

CV curves and the estimation of specific capacitance through CV curves for the supercapacitor are shown in Fig. 3. Fig. 3(a) depicts the typical CVs curves of MOF(V, Ni) composite at various scan rates (5～100 mV·s^{-1}). Obviously, CV curves exhibit a pair of well-defined redox peaks ascribed to the typical pseudocapacitance behavior of MOF(V, Ni) during the charge-discharge process. With increasing the scan rate from 5 to 100 mV·s^{-1}, the slightly deviated redox peaks suggest excellent rate performance.

The specific capacitances at various scan rates are shown in Fig. 3(b). At the scan rates of 5, 10, 20, 50 and 100 mV·s^{-1}, the corresponding specific capacitances of MOF(V, Ni) are 210, 137, 98, 64 and 42 F·g^{-1}, respectively.

3. 2. 2 Galvanostatic charge-discharge (GCD) performance

The GCD curves of MOF (V, Ni) at different current densities are given in Fig. 3(c) and (d). With increasing the current density, GCD profiles exhibit similar shapes, indicating similar pseudocapacitance behavior. The approximately symmetric charge-discharge curves display excellent reversibility of the faradaic redox reactions and high coulombic efficiency. The specific capacitances at different current densities are shown in Fig. 3(d). The electrode had specific capacitances of 178, 134, 88, 64, 45 and 33 F·g^{-1} at current densities of 1, 2, 4, 6, 8 and 10 A·g^{-1}, respectively.



(c) (d)

Fig. 3. (a) CV curves at different scan rates, (b) the specific capacitance at different scan rates, (c) GCD curves at different densities, and (d) the specific capacitance at different current densities of the MOF (V, Ni) electrode

3. 2. 3 Electrochemical impedance spectroscopy (EIS) performance

EIS was carried out to further investigate the electron transfer and ion diffusion at the electrode/electrolyte interface, and the Nyquist plot is shown in Fig. 4. From high frequency region, the charge-transfer resistance is small, which revealed a high electrical conductivity and fast ion response originating of the MOF (V, Ni). From the low frequency region, the material has low resistance in KOH electrolyte, which may be due to the high electrochemical activity of different metals, large specific surface area and suitable pore size distribution in the electrode materials.

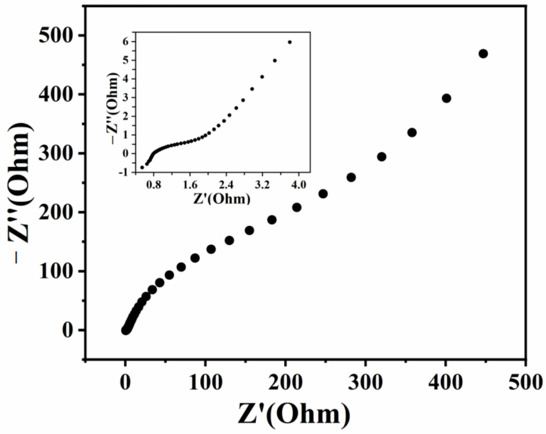


Fig. 4. EIS spectra of MOF (V, Ni) in 3 M KOH electrolyte

3. 2. 4 Cycle life test and coulomb efficiency performance

Long term stability is one of the main factors which determine the practical applications of the supercapacitor. Hence, the GCD cycling test has been done for 2500 cycles, and the values of specific capacitance and coulombic efficiency for various number of cycles are also shown in Fig. 5. From the cyclic stability curve of the specific capacitance, it can be seen that the specific capacitance increases steadily before 500 cycles mainly due to the activation of the electrode material[15]. There is a small fluctuation in the range of 500～2500 cycles, but it is basically in a stable state. Besides, an excellent coulombic efficiency of around 100% was observed. This experiment reveals that the MOF (V, Ni) has high stability as an electrode material for supercapacitors.

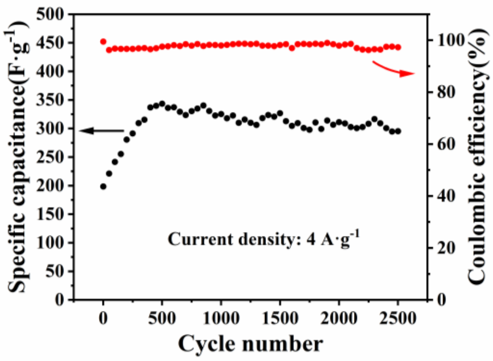


Fig. 5. Cycling performance and coulombic efficiency of the MOF (V, Ni) at 4 $A{\cdot}g^{-1}$ for 2500 cycles

4 CONCLUSION

In summary, we have successfully synthesized a novel MOF (V, Ni) microsphere constructed from 3-*D* discrete nano-sheets and tested for its electrochemical properties in a three-electrode system. The obtained results proved that the electrode has good capacitance, energy density and cycling stability in 3M KOH aqueous electrolyte. The electrode had specific capacitances of 178, 134, 88, 64, 45 and 33 $F{\cdot}g^{-1}$ at current densities of 1, 2, 4, 6, 8 and 10 $A{\cdot}g^{-1}$, respectively. This work proved that the novel MOFs based on polyoxovanadate hybrid material may serve as a promising electrode material for high-performance supercapacitor.

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