



Influence of vanadium doping on the supercapacitance performance of hexagonal birnessite



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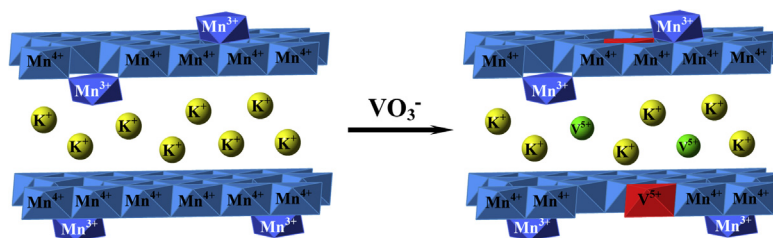
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HIGHLIGHTS

- V-doped birnessites are prepared by adding NH_4VO_3 to redox system of KMnO_4 and HCl .
- Mn(IV) and K^+ are partially substituted by V(V) in birnessite.
- Doping vanadium affects birnessite particle size and electrochemical properties.
- Doped birnessite ($\text{V/Mn} = 0.14:1$) exhibits a stable capacitance of 245 F g^{-1} .

GRAPHICAL ABSTRACT



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ABSTRACT

Nanostructured birnessite, promising candidate for supercapacitor electrode materials, shows greatly improved discharge capacity and cyclic stability with vanadium doping. The influence of vanadium doping on the physicochemical properties and supercapacitance performance of birnessite-type manganese oxides is investigated. Crystal structures, micromorphologies, bond lengths and chemical compositions of vanadium doped birnessites are characterized by XRD, SEM, XPS, TGA, and titration. The electrochemical properties are analyzed using galvanostatic charge–discharge test, cyclic voltammetry, and electrochemical impedance spectroscopy. The results exhibit that V/Mn molar ratio can reach 0.16:1 when Mn(IV) and K^+ are partially substituted by V(V) in birnessite. The thickness of disk-shaped crystal, bond length of Mn-O_1 and manganese average oxidation state decreases first and then increases with an increase in V/Mn molar ratio in synthesis system. Charge-transfer resistance decreases after doping vanadium, and increases with an increase in the content of vanadium in birnessite. Diffusion resistance increases first and then decreases due to the change of particle size and pore size distribution. The highest specific capacitance of 245 F g^{-1} is obtained with excellent cyclic stability for doped birnessite with V/Mn molar ratio of 0.14:1. Our study indicates that vanadium remarkably affects micromorphology, substructure, and electrochemical properties of manganese dioxides.

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1. Introduction

Supercapacitors, also known as electrochemical capacitors, have attracted increasingly attention due to their high power and reasonably high energy densities [1–3]. Compared with other supercapacitor electrode materials, such as conducting polymers, RuO_2 , IrO_2 , NiO and Fe_3O_4 , manganese oxides possess the

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advantages of high theoretical specific capacitance (1370 F g^{-1}), excellent cyclic stability, low cost of raw materials, low toxicity and environmentally friendly characteristics, and consequently have been considered as one of the most promising materials for supercapacitors [3–6]. During charge/discharge process, the redox reactions of manganese oxides involve surface adsorption, intercalation and deintercalation of electrolyte cations, such as H^+ , Li^+ , Na^+ and K^+ [3,5]. The practical specific capacitance was far lower than the theoretical value due to the limitation of poor conductivity of manganese oxides (10^{-5} – $10^{-6} \text{ S cm}^{-1}$) and low mass transfer rate at electrolyte/material interface, which was affected by crystal structures, chemical compositions, and micromorphologies [5,6].

To improve the electrochemical capacitance performance of manganese oxides, polyaniline and other transition metal oxides, such as NiO and PbO_2 were mixed as conductors [5,7,8], and alternatively nanosized manganese oxides were coated on carbon materials including nanotubes, nanographite, and graphene, which acted as template and highly conductive current collectors. The latter method improved the conductivity of manganese oxides and facilitated the fast transport of ions and electrons during charge–discharge processes [5], and the pseudocapacitance of MnO_2 encapsulated within CNTs was greatly enhanced to 1250 F g^{-1} [9]. It was reported that doping metallic elements, such as Al , Sn and Au , was also an important way to modify manganese oxide electrodes to enhance their electrochemical performance [5,10]. Physical vapor deposition was performed to synthesize a thick Au -doped MnO_2 film with a ultrahigh specific capacitance of 626 F g^{-1} at a scan rate of 5 mV s^{-1} [10]. Therefore, doping metallic ions and decreasing the particle size may remarkably improve the electrochemical capacitance performance of manganese oxides.

Vanadium pentoxide nanowires and $\text{VO}_x \cdot n\text{H}_2\text{O}$ powders were synthesized and exhibited the specific capacitances of 146 and 227.3 F g^{-1} , respectively [11,12]. Nanoporous structured V_2O_5 showed an excellent capacity, energy density, and cyclic stability due to its most accessible layered structure, high specific capacity, and mixed oxidation states [13–15]. Vanadium doping was also employed to improve the electrochemical performance of manganese oxides. As reported, the specific capacitance of V -doped amorphous MnO_x films increase linearly with the V atomic percentage, however, V -doping had significantly reduced the specific capacitance of the crystalline Mn_2O_3 films [16]. As for the former, the increase in specific capacitance after doping vanadium was attributed to the increase of electrical conductivity and film roughness (surface area) after charge–discharge cycling; as for the latter, doping vanadium prevented the phase transition although the electrical conductivity was increased [16]. However, the substitution of vanadium for manganese enhanced the electrical resistivity of tunneled manganese oxide cryptomelane [17]. The influence of vanadium substitution for manganese on the electrical resistivity of manganese oxides may be different due to the diversity crystal structures and doped sites [5,16,17].

As the most promising candidate for manganese oxide supercapacitor electrode materials, layered birnessite usually exhibits better electrochemical capacitance performance for fast ionic conductivities [5,18–21]. After doping vanadium, the capacitance properties of birnessite might be remarkably changed and optimized. However, the preparation, characterization and application of vanadium doped birnessite have not been reported. In our previous work, doping iron, cobalt and nickel in birnessite would decrease the thickness of the 2-dimensional disk-shaped crystal, and increase its specific surface area [22]. However, the influence of doping vanadium on the micromorphology, charge-transfer resistance, diffusion resistance and the corresponding electrochemical performance of birnessite was seldom studied. It is ambiguous whether the electrical resistivity or the mass transfer plays a key

role in improving the electrochemical performance of V -doped birnessite. Fully understanding the effect of vanadium doping on the electrical resistivity, mass transfer, and electrochemical properties of birnessite could lead to the development of more effective manganese oxide supercapacitor electrode materials.

In this work, V -doped birnessites were fabricated by adding NH_4VO_3 to the redox system of KMnO_4 and hydrochloric acid. The influence of doped vanadium content on the micromorphologies, manganese average oxidation state, substructure, and the corresponding electrochemical process was studied. The effect of reaction resistance and diffusion resistance on the electrochemical performance was compared to illustrate the key influential factors.

2. Experimental

2.1. Materials and chemicals

Manganese chloride tetrahydrate ($\geq 99.0\%$), hydrochloric acid (mass concentration: 36–38%), potassium permanganate ($\geq 99.0\%$) and sodium sulfate ($\geq 98.0\%$) were all purchased from China National Medicine Group Shanghai Chemical Reagent Company. Ammonium metavanadate ($\geq 99.0\%$) and was supplied by Xiamen XM-Innovation Chemical Co. Ltd., China. All reagents used were of analytical grade, unless otherwise noted. Deionized water was used in the experiment.

2.2. Preparation and characterization of V -doped birnessite

Vanadium doped birnessites were synthesized through the reduction of potassium permanganate by concentrated hydrochloric acid [23]. KMnO_4 of 0.2 mol was dissolved in 300 mL deionized water in a conical flask and boiled with an oil-bath heated at $100 \text{ }^\circ\text{C}$, and then 60 mL of 6 mol L^{-1} hydrochloric acid was added dropwisely to the boiling solution at 0.7 mL min^{-1} with vigorous stirring. The reaction lasted for 30 min, and then the suspension was aged for 12 h at $60 \text{ }^\circ\text{C}$. The mineral was washed with deionized water until filtrate conductivity was below $20.0 \text{ } \mu\text{S cm}^{-1}$, and subsequently dried in an oven at $60 \text{ }^\circ\text{C}$, and undoped birnessite was formed. To prepare V -doped birnessite, 0, 1.231, 2.600, 4.129 and 5.894 g NH_4VO_3 was added to KMnO_4 aqueous solution before dropping concentrated hydrochloric acid, achieved the molar ratios of $\text{V}/(\text{V} + \text{Mn})$ of 0, 0.05, 0.10, 0.15 and 0.20 in reaction system, respectively. The as-obtained samples were designated as HB, HB-V5%, HB-V10%, HB-V15% and HB-V20% corresponding to the molar ratios mentioned above, respectively.

The as-obtained samples were characterized by X-ray diffraction spectrometry (XRD, Bruker D8 Advance diffractometer with $\text{Cu K}\alpha$ radiation) at a scanning rate of $10^\circ \text{ min}^{-1}$. Fourier transform infrared spectroscopy (FTIR, Nicolet 8700) was used to identify the functional group of the products (made pellets with KBr powder) with a DTGS detector. Before and after charge–discharge tests, sample morphologies were characterized by scanning electron microscopy (SEM, JEOL, JSM-6700F Field Emission). BET surface area was tested and the pore size distribution of as-obtained samples was analyzed by Micromeritics ASAP2020 using nitrogen adsorption measurements. The contents of Mn and V in the samples were determined by atomic absorption spectroscopy (Varian AAS240FS). K content of the samples was determined by flame photometer (HG-3 blaze photometer). The average oxidation state (AOS) of manganese was measured by oxalic method [24]. The contents of crystal water in birnessites were calculated from the mass balance using thermo-gravimetric analysis (TGA) with NETZSCH TG 209 thermal analysis system.

At room temperature, the X-ray absorption spectroscopy (XAS) of birnessites was measured on 1W1B beamline at the Beijing

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