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Influence of Fe doping on the crystal structure, electronic structure and supercapacitance performance of birnessite $[(Na, K)_x(Mn^{4+}, Mn^{3+})_2O_4\cdot 1.5H_2O]$ with high areal mass loading

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ABSTRACT

The supercapacitance performance of birnessite, which is a common layered manganese oxide mineral with the general formula of $(Na, K, Ca)_x(Mn^{4+}, Mn^{3+})_2O_4\cdot 1.5H_2O$, is greatly hindered by poor electrical conductivity, especially when the areal mass loading of the active materials is high enough for practical application. Heterogeneous atom doping is an effective way for improving the supercapacitance performance of birnessite. Herein, we mainly investigate the influence of Fe doping on the crystal structure, electronic structure and capacitance performance of birnessite $[(Na, K)_x(Mn^{4+}, Mn^{3+})_2O_4\cdot 1.5H_2O]$ in detail by combining the experiments and theoretical calculations/simulations. It is found that Fe atoms mainly substitute the central trivalent Mn in $[MnO_6]$ octahedral after doping without changing the crystalline phase of birnessite. Meanwhile, the particle size and surface area of Fe-doped birnessite continuously increase with the increase of the content of Fe dopant. On the other hand, the electronic conductivity of the doped birnessite firstly increases and then decreases with the increase of the Fe content due to the reduced indirect band gap and the increased number of the boundary/grain interfaces. Based on these results, the influences of Fe doping on the supercapacitance performance of birnessite electrode with very high areal mass loading of ~10–12 mg cm^{-2} are elaborately discussed related to morphology, structure, electrical conductivity, and ion diffusion properties.

1. Introduction

Supercapacitors have drawn great attentions as a typical energy storage system because of their extremely high power densities and reasonable energy densities [1–3]. In these systems, charge can be stored through two different mechanisms, i.e., electrical double-layer (non-farad process) and surface redox reactions (farad process), corresponding to electrical double-layer capacitors (EDLCs) and pseudocapacitors, respectively. Among various pseudocapacitor materials, manganese oxide (MnO_2), as one of the most promising candidate materials, draws increasing interest due to its extremely high theoretical capacitance (1370 F g^{-1}), low cost, and environmental friendliness [3,4]. Birnessite, which phase belongs to δ-MnO_2, usually shows better electrochemical capacitor performance owning to its fast ionic conductivities of the layered structure [5–10]. It have the triclinic structure (space group of $P\overline{1}$) with a general chemical formula of A $[M]_2O_4\cdot 1.5H_2O$, where A represents the interlayer cations such as Na^+, K^+ or Ca^{2+}; M is the central Mn in $[MnO_6]$ octahedra as Mn (III) or Mn (IV) [11–13]. The interlayered cations are incorporated into its structure to compensate the charge deficiency because of the replacement of Mn^{2+} and Mn^{3+} for Mn^{4+} in birnessite [14]. However, the electrical capacitor performances of birnessite are great hindered by poor electrical conductivities (10^{-5}-10^{-6} S cm^{-1}) and low mass transfer rates at electrolyte/electrode interface [8] [5,6]. Therefore, the utilization of the active materials in the electrode is quite low, leading to the actual specific

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capacitance of birnessite is much lower than the theoretical capacitance of MnO_2 [9]. This even become worse when the areal mass loading of birnessite is high enough for achieving high power and energy performance of the capacitor device in practical application [3,4]. In order to overcome these problems, highly conductive additives (such as carbon [8], carbon nanotubes [7], graphene [15], conductive polymers [16]) were incorporated with MnO_2 to form hybrid electrodes. The overall conductivity of these hybrid electrodes were increased, which improves the electrochemical performances [7,15,16]. Nevertheless, the intrinsic conductivity of birnessite was not improved in these hybrid electrodes. In contrast, heterogeneous atomic doping is an effective way to increase the intrinsic conductivity of birnessite [5,6,10,17–19]. Transition-metal elements were always selected as dopants due to the similar effective ionic radii, ionic charges, and crystal field environment between the transition metals and central Mn in $[MnO_6]$ octahedral. Junming Chen et al. reported an appropriate amount of nickel doping in ultrathin K-birnessite nanosheets can remarkable improve their specific capacitance and that 1.0 mol% nickel-doped K-birnessite nanosheets displayed the best specific capacitance of 337.9 $F\,g^{-1}$ at current density of 1 $A\,g^{-1}$ [10]. Guilin Wang et al. synthesized Ce-doped porous K-birnessite microspheres and found that 1.5% Ce-doped K-birnessite exhibited the best specific capacitance of 382.4 $F\,g^{-1}$ at current density of 1 $A\,g^{-1}$ [5]. Lihu Liu et al. showed that V-doped birnessite had the highest specific capacitance of 245 $F\,g^{-1}$ at current density of 0.1 $A\,g^{-1}$ with V/Mn molar ratio of 0.14:1 [6]. The improved electrochemical performance of doped birnessite usually attributes to the decreased particle size and improved electrical conductivity of birnessite after heterogeneous atomic doping [5,6,10,17–19]. Nevertheless, as a type of pseudocapacitor material, the crystal structure revolution (e.g. lattice parameters) and the mechanism of the change of electronic structure of birnessite originating from the doping are rarely discussed [6,10,20].

In the present work, we took Fe doped-birnessite as an example because one more electron in Fe 3d orbit (electron orbit configuration of Fe: $1s^22s^22p^63s^23p^64s^23d^6$) than Mn 3d orbit (electron orbit configuration of Mn: $1s^22s^22p^63s^23p^64s^23d^5$) is expected to donate electrons in the doped sample and the radii of Fe ion and Mn ion (Fe^{3+}: 0.645 Å; Mn^{3+}: 0.645 Å; Mn^{4+}: 0.530 Å at high-spin state) are similar. We investigated the influence of Fe doping on the crystal structure, morphology, electronic structure, and electrochemical performance of birnessite as supercapacitor material in detail. We found that Fe atoms mainly substituted the central trivalent Mn in $[MnO_6]$ octahedral after Fe doping without changing the crystalline phase of birnessite, but the particle size and surface area of Fe-doped birnessite continuously increase with the increase of the content of Fe dopant. In addition, the indirect band gap of birnessite decreased after the introduction of Fe into the structure of birnessite, leading to the increase of the electronic conductivity of doped samples. Nevertheless, the electronic conductivity decreased at high content of Fe doping due to the increase of the number of the boundary/grain interfaces. The supercapacitance performance of doped-birnessite was improved at low concentration of Fe dopant, but became worse at high Fe concentration. The reasons related to morphology, structure, electrical conductivity and ion diffusion of birnessite were concretely discussed.

2. Experimental

2.1. Chemicals

All chemical reagents with AR grade were purchased from Beijing Chemical Works without further purification.

2.2. Preparation of the undoped and doped birnessite

The undoped birnessite sample was prepared through two-step method [14]. In the first step, 50 mL of 5 M NaOH solution was added to 25 mL of 0.5 M $MnCl_2$ solution under vigorous stirring, followed by adding 50 mL of 0.2 M $KMnO_4$ dropwise into the slurry. The mixture was stirred drastically for 30 min at room temperature to form a brownish black suspension, which was aged for a day. In the second step, the suspension was transferred to a high pressure autoclave and maintained at 150 C for 12 h. Afterwards, the slurry was washed several times with distilled deionized water and freeze-dried for 24 h. The final product was donated as PB (short abbreviation for pristine birnessite). For Fe-doped samples, amount of $FeCl_3$ solutions were added in the first step according to the molar ratio between Fe and the sum of (Fe + Mn) as 0.01, 0.025, 0.05, 0.075 and 0.10. Others procedures were kept same as the undoped sample. The corresponding doped birnessite samples were donated as FeB-1, FeB-2.5, FeB-5, FeB-7.5 and FeB-10, respectively.

2.3. Characterizations

The crystal structure of as-prepared samples was determined by X-ray diffractometer (XRD, Bruker D8) utilizing Cu Kα radiation at voltage of 40 kV and current of 100 mA, and further refined by the Rietveld method using TOPAS software. The morphologies and elemental compositions of samples were characterized using a field-emission scanning electron microscopy (FESEM, MERLIN VP Compact, ZEISS, Germany). Valence and content of elements were confirmed by the X-Ray photoelectron spectrometer (XPS, ESCALab250, Thermo Scientific, Ltd) using a monochromatic Al Kα radiation with a power of 150 W. The BET surface areas of the samples were measured using a specific surface area analyzers (ASAP2020, Micromeritics). For the electrical conductivity test, 0.3 g sample was pressed at 10 MPa to form a plate with 13 mm diameter and ~1 mm thickness. Conductive silver ink was pasted on two flat surfaces of the plate as electrode, which was dried in an oven at 60 C for 20 min. The current-voltage curves were recorded using an electrochemical working station (Ivium-Vertex, Ivium Technologies, Holland) and the electrical conductivity was calculated using Ohm's law.

2.4. First-principles calculations

The effect of Fe doping on physical properties of birnessite was performed within first-principles calculations based on the density functional theory (DFT) framework. Fe-doped birnessite was modeled based on $NaMnO_2$ supercell, which has $P\bar{1}$ space group with the lattice parameter a = 2.951 Å, b = 2.955 Å and c = 7.33 Å for one formula unit per unit cell. The pseudopotentials were constructed by the electron configurations as Fe $3d^74s^1$ states, Na $2p^63s^1$ states, Mn $3p^63d^54s^2$ states, and O $2s^22p^4$ states. The generalized gradient approximation (GGA) with the PBEsol exchange-correlation functional for solid implemented in Vienna ab initio simulation program (VASP) was employed. After careful convergence tests for the total energy calculations, cut-off energy and Monkhorst-Pack mesh grid were chosen to be 500 eV and $5 \times 3 \times 4$ special k-point, respectively. The energy convergence tolerance was 1×10^{-6} eV/atom, while the force convergence tolerance was set to 0.01 eV/Å. All the structures were fully relaxed until reaching the convergence tolerance.