A stable structure zinc manganese oxide (ZnMn$_2$O$_4$) synthesized via a facile coprecipitation method as high performance air electrode catalyst for potassium-oxide batteries

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Abstract: Potassium-oxygen batteries as promising energy storage system have been widely concerned at present. In this paper, we obtain a zinc manganese oxide (ZnMn$_2$O$_4$) catalyst via a facile coprecipitation method. XRD and Raman tests show that ZnMn$_2$O$_4$ at the Zn and Mn molar ratio to 1:2 along with hot-heat treatment at 150 °C has a higher crystallinity and lower heterophase content. SEM observes that ZnMn$_2$O$_4$ material shows uniform spherical morphology with loose arrangement, which can be beneficial to mass transfer and discharge products storage. Electrochemical test results display that air electrode with ZnMn$_2$O$_4$ as catalyst has rapid electron and ion transfer speed and successfully carries out the charge and discharge process in the potassium-oxygen battery system.

1. Introduction

Metal-air batteries owing to rather high energy density are regarded as a promising energy storage system and are widely concerned in the field of new energy vehicles [1]. Compared with lithium, potassium in the earth's crust is more abundant and potassium has similar electronegativity to lithium. Therefore, potassium-oxygen battery has been seen the next-generation energy storage system [2, 3]. Like lithium-oxygen batteries, potassium-oxygen batteries also require highly active catalysts for air electrode because of the more stable K-O bond structure [4-6]. Among many catalysts, manganese based metal compounds are the most commonly used transition metal oxide catalyst materials owing to their excellent catalytic performance and low price. And manganese based metal compounds via doping modification can improve the defect sites, and then increase the coordination space on the d orbital in order to achieve higher catalytic activity [7,8].

Just because of this, in this paper zinc manganese oxide (ZnMn$_2$O$_4$) catalysts are synthesized by homogeneous precipitation method and used as the air electrode catalyst for potassium-oxygen batteries. This research shows that zinc manganese oxide (ZnMn$_2$O$_4$) as catalyst can make air electrode carry out the charge and discharge process in the potassium-oxygen battery system.
2. Materials and Methods

2.1 Synthesis of zinc manganese oxide (ZnMn₂O₄) catalysts by homogeneous precipitation method

Firstly, 0.04 mol.L⁻¹ zinc acetate and manganese acetate mixed solution was prepared by zinc acetate and manganese acetate molar ratio to 1:1, 1:2 and 1:3, respectively. Then, 0.2 mol.L⁻¹ sodium carbonate solution with 0.1%~0.2% ammonia was used as the sodium carbonate ammonia mixed solution after uniform mixing. After that, the same volume of sodium carbonate ammonia mixed solution with continuous stirring was added to zinc acetate manganese acetate mixed solution using a peristaltic pump at a speed of 100 mL.min⁻¹. After sedimentation, the supernatant was discarded and centrifuged to retain the sediment. At last, Zinc manganese oxide (ZnMn₂O₄) can be obtained by calcining above-mentioned precipitate after sufficient drying in a muffle furnace at 600 ℃ for 5 h.

Some research discovered that manganese based metal oxides are easy to form alpha phase with the higher catalytic activity after 150 degree hot-heat treatments. Therefore, zinc manganese oxide (ZnMn₂O₄) with Zn and Mn molar ratio to 1:2 is also hot-heat treatment and as catalyst material used for air electrode of potassium-oxygen batteries.

2.2 Preparation of air electrode and experimental 2032 type button potassium-oxygen batteries assembly

Preparation of air electrode and experimental 2032 type button lithium-oxygen batteries assembly are the same as our previous researches [1]. The only differences are potassium as anode and 1M KPF₆ in ethylene carbonate and Diethyl carbonate mixed solvent (EC/DEC v:v=1:1) as the electrolyte in this experiment.

2.3 Physical characterization and electrochemical test

The physical properties of Zinc manganese oxide (ZnMn₂O₄) were confirmed by field emission scanning electron microscope (FE-SEM), X-ray diffraction (XRD) and Raman spectrum tests. FE-SEM was used S4800 type equipment produced by Hitachi Company. XRD test was conducted with a D Max-RD12 Kw diffractometer with Cu Kα radiation using Rigaku Ultima IV. The scan data were collected in the 2θ rang 10-80° at scan rate 2°min⁻¹. The Raman spectrum information was obtained by Labram HR Evolution type Raman Spectrometer produced by Horiba Company. The wavelength of the light source was 532 nm and the wave number range was from 50 to 1000 cm⁻1.

The electrochemical performances of Zinc manganese oxide (ZnMn₂O₄) as catalyst for air electrode of potassium-oxygen batteries were tested by contact current charge and discharge, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests. The contact current charge and discharge test was performed by Neware (CT-4008-5V10mA-164) charging and discharging test system at different current density from 1.0 to 4.5 V voltage ranges. CV and EIS tests were carried out by CHI604E electrochemical workstation with air electrode as work electrode and potassium as auxiliary and reference electrodes. The CV test voltage range was from 1.0 to 4.5 V at a scan rate of 0.1, 0.2 and 0.5 mV·s⁻¹. And the frequency range of EIS was from 100 KHz to 10 mHz with the 5 mV amplitude.

3. Results & Discussion

In order to explore the chemical composition and crystal structure of the samples with different molar ratios, XRD and Raman spectrum tests have been carried out, as shown in Fig.1. XRD patterns show that the samples with different molar ratios synthesized via a facile coprecipitation method are all constructed with zinc manganese structure (ZnMn₂O₄) correspond to standard PDF card (PDF#24-1133). And with the increase of the zinc-ion molar ratio, a large number of impurity peaks are discovered because some extra zinc-ion cannot enter into the lattice. Meanwhile, we also find that ZnMn₂O₄ with Zn and Mn molar ratio to 1:2 via 150 ℃ hot-heat treatment has the higher crystallinity and lower heterophase content. Raman spectrums display that an obvious Raman scattering peak at 644.89 cm⁻¹ corresponds to the Mn-O bond structure and ZnMn₂O₄ with Zn and Mn molar ratio to 1:2
via 150 °C hot-heat treatment material has the highest relative intensity. This means that hot treatment at 150 °C can effectively raise the surface crystallinity of the ZnMn$_2$O$_4$ material.

Fig.1 XRD patterns and Raman spectrums of ZnMn$_2$O$_4$ with different molar ratios

Fig.2 shows SEM images of ZnMn$_2$O$_4$ with different molar ratios. It can be observed the ball (Zn structure) and rod (Mn structure) coexistence micromorphology and as the increase of manganese molar ratio, rod structure has been obviously raised. However, after hot-heat treatment at 150 °C, ZnMn$_2$O$_4$ material with Zn and Mn molar ratio to 1:2 has uniform spherical morphology with loose arrangement and this can be beneficial to mass transfer and discharge products storage. And ZnMn$_2$O$_4$ material with uniform spherical can possess a stable property and will effectively inhibit Lattice distortion of manganese oxides (Jahn-Teller Effect).

In order to probe the electrochemical performances of air electrodes used ZnMn$_2$O$_4$ with different molar ratios as catalyst for potassium oxide batteries, cyclic voltammetry and electrochemical impedance spectroscopy tests have been performed, as shown in Fig.3. From CV curves (Fig.3 (a-d)), it shows that an obvious oxidation peak at about 4.0 represents K$_2$O conversion to K$_2$O$_2$. By comparison, it displays that air electrodes used ZnMn$_2$O$_4$ material with Zn and Mn molar ratio to 1:2 by hot treatment at 150 °C have almost similar oxidation peak at the sweep rate to 0.1, 0.2 and 0.5 mV.s$^{-1}$. This means that this air electrode has a relatively good reversibility. Nyquist plots (Fig.3 (d)) show that there is a circular arc corresponding to electron transfer in the high frequency region and a straight line corresponding to mass transfer in the low frequency region. Through detailed analysis, we can find that the circular arc shape is irregular and this is because that air electrode with the high active catalyst will form SEI (Solid Electrolyte Interface) film on the electrode surface. However, by comparison with air electrodes used ZnMn$_2$O$_4$ material in the different molar ratios, Nyquist plots in the high frequency region has the largest electron transfer rate for ZnMn$_2$O$_4$ catalyst in the different molar ratios to 1:2 by hot-heat treatment at 150 °C and in the low frequency region has almost the same linear slope in the different molar ratios. This implies that the change of catalyst mainly affects the electron transfer rate of air electrodes for potassium-oxygen batteries.
Fig. 3 Cyclic voltammetry curves and Nyquist plots of potassium oxygen battery used ZnMn$_2$O$_4$ with different molar ratios as catalyst.

Fig. 4 shows charge and discharge curves at different cycle of potassium oxygen battery used ZnMn$_2$O$_4$ as catalyst with different molar ratios. It shows that air electrodes used ZnMn$_2$O$_4$ with Zn and Mn to 1:2 after hot-heat treatment at 150 °C as catalyst can stably complete two charge and discharge cycles and the discharge voltage platform at the two cycles is very smooth. This means that the ZnMn$_2$O$_4$ catalyst can play an important role in the oxygen evolution of the gas electrode for the potassium-oxygen batteries. However, we feel that ZnMn$_2$O$_4$ catalyst still does not show ideal charge and discharge performance (only two charge and discharge cycles). Therefore, it is necessary to research some high performance carriers in order to raise their distribution state, crystal structure and catalytic activity.
4. Conclusions
In this paper, zinc manganese oxide (ZnMn₂O₄) has been synthesized via a facile coprecipitation method. When Zn and Mn molar ratio is 1:2 along with hot-heat treatment at 150 °C, ZnMn₂O₄ shows a higher crystallinity and lower heterophase content. Moreover, this ZnMn₂O₄ material shows uniform spherical morphology with loose arrangement, which can be beneficial to mass transfer and discharge products storage. As catalyst material, the air electrode can achieve rapid electron and ion transfer and successfully carry out the charge and discharge process in the potassium-oxygen battery system.

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