Preparation and Electrochemical Characterization of La Doping Co₃O₄ Super Capacitor Electrode Materials

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Abstract—An aqueous solution containing deionized water, cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O), ethylene glycol (EG) and urea (NH₂CONH₂) were reacted in an autoclave with hydrothermal reaction method at 180 °C for 20 h to generate precursors with 0.1%, 0.2%, 0.3%, 0.4% and 0.5% of La (NO3)3. Then the precursor was decomposed to cobalt oxide powders at 300-500 oC for 2h. The morphology and electrochemical properties of samples were characterized by powder X-ray diffraction (XRD), scanning electron microscope (SEM) and electrochemical analyzer. The results suggested that the average crystallite size and fine crystallinity of Co3O4 crystal lattices increased with the mass percentage of La (NO3)3. Ethylene glycol as a shaping agent may be the possible reasons of decrease in particle size at higher temperatures in the process of the formation of Co3O4 microspheres. The specific capacitance and the current density of the best sample are 5 ma/s, 372.7 F/g and 10 ma/s, 310.56 F/g respectively.

Keywords- Cobalt oxide; electrochemical performance; specific capacitance; Super Capacitor; Lanthanum

I. INTRODUCTION

Cobalt oxide is a transition metal oxide spinel, playing an important role in engineering technology, with excellent electrochemical properties, catalytic properties and magnetic properties [1-6]. There are hydrothermal method [2, 7-9], the thermal decomposition method [10-11], solid-phase precipitation [12], sol-gel method [3, 13-14] and chemical vapor deposition method [15-16] for preparing Co_3O_4 in laboratory. Generally using the thermal decomposition of cobalt salts to get Co_3O_4 is easy to operate in industry. However, sizes of the product are relatively large and distributed more widely, and their physical and chemical properties are difficult to achieve the requirements of the electronics industry.

Here, we prepare Co_3O_4 powders by the combination of hydrothermal synthesis and thermal decomposition at different temperatures. In addition, to modify the samples in structure and properties of Co_3O_4 powders rare metal cation La^{3+} as additive have taken apart in reaction while the precursors are manufacturing in an autoclave. Then, we test their electrochemical performance of modified Dandan Zhan Department of Materials chemistry Huzhou University Huzhou, China 2274077834 @qq.com

powders, such as cyclic voltammetry, constant current charge/discharge and AC impedance.

II. EXPERIMENTAL PROCEDURES AND CHARACTERIZATION

A. preparation

In a typical synthesis, cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O) (1.4550 g, 5 mmol) were first dissolved in deionizedwater (15 mL) and ethylene glycol (EG) (25 mL) to form a homogeneous solution under continuous magnetic stirring. The mixture was stirred for another 20 min to obtain a homogeneous solution, which was transferred into a Teflon-lined autoclave with a volume of 40 mL. The autoclave was heated in a temperature preset oven at 180 °C for 20h. After cooled down to room temperature naturally, the kettle solution was transferred into a centrifuge tube, and then placed in the rotational speed of 500 r/min 5 times. The precipitates were collected by centrifugation and rinsed with deionized water and ethanol for 3 times each, and dried in an oven at 80 °C for 12 h to get red powders of precursor. Finally, the samples were calcined in a muffle furnace at 300- 500 °C for 2 h in N₂ inert gas, and then cooled to room temperature. The resulting powders of the final products were Co₃O₄ powder.

B. characterizations

The phase composition of the final products were measured by powder X-ray diffraction (XRD) with an D/max 2550 V X-ray diffractometer (General Analysis Instruments, Beijing, China) with monochromatized Cu K_{α} incident radiation. The sizes and morphologies of the as prepared samples were analyzed with Scanning Electron Microscopy (SEM, SN3400).

C. Electrochemical properties

With the Co_3O_4 sample experimentally obtained as a positive electrode, polytetrafluoroethylene (PTFE) as a binder and acetylene black as a conductive agent, the electrode materials to construct working electrodes were composed of active materials (Co_3O_4 , 80 wt%, 1 mg/cm²), conductive material (acetylene carbon black, ATB, 10

wt%) and binder (polytetrafluoroethylene, PTFE, 10 wt%). After the mixture of electrode materials was ground,

it was coated onto the surfaces of nickel foam meshes(1×3 cm²) and pressed with a hammer. sheets with electrode materials were dried for experiment. Electrochemical studies were carried out in a three-electrode system. A piece of nickel foam mesh coated with freshly prepared Co₃O₄ architectures, a platinum electrode and a saturated calomel electrode (SCE) were used as the working electrode, counter electrode, and reference electrode, respectively. The electrolyte used in the system was an aqueous NaOH solution (2 mol L⁻¹). The constant current charge-discharge test was operating under the conditions of 5 mA / s and 10 mA / s current, while 10 mA / s currents were 1000 times charge-discharge cycles test. AC impedance test is conducted in 100 kHZ - 10 mHZ, relatively open next potential OV, under 5mV of disturbance.

III. RESULTS AND DISCUSSION

A. XRD

The XRD spectra of products are shown in Figure 1. In picture they have good crystallinity and can be indexed as Co₃O₄ (JCPDS Card No. 43-1003) with face-centered cubic structure. It can be found that all of the diffraction peaks in XRD profile of the product agree well with the standard spectrum of Co₃O₄. There is no any other peaks detected, which indicate its high purity. Miller index can be calculated by the analysis of Jade 5.0 software. Fig. 1 patterns of Co₃O₄ products of different XRD concentrations of La $(NO_3)_3$. With the accession to the increase La (NO₃)₃ concentration, peak gradually becomes higher, the peak has become increasingly acute. It also may be attributed to the fact that La cation had play on much fine crystallinity of the Co₃O₄ crystal lattices with an increase of concentrations of implanted on. The crystallite sizes of samples composition calculated by XRD data from (311) peak are listed in Table 1, samples a-e labeled 0.1%-0.5% La(NO₃)₃. The crystallite size of the powders can be evaluated from the highest peak with Scherrer's equation (1):

$$d = \frac{k\lambda}{\beta \times \cos\theta} \tag{1}$$

where *d* is crystallite size, λ is equal to 0.15406 nm, *k* is Scherrer constant, generally taken to be 0.89, θ is the Bragg diffraction angle, β is characteristic diffraction peaks corresponding to the full width at half maximum (FWHM) radians.



Figure 1. XRD patterns of Co_3O_4 sample with La (NO₃)₃ (a-e labeled 0.1%-0.5%)

 TABLE I.
 CRYSTALLITE SIZES OF SAMPLES COMPOSITION CALCULATED BY XRD DATA.

Samples	2θ(°)	FWHM(°)	Size /nm
а	36.88	0.289	28.65
b	36.94	0.280	29.58
с	37.04	0.272	30.45
d	36.92	0.184	45.01
e	36.98	0.222	37.31
Average	/	/	34.2





Figure 2. SEM of samples with different calcine temperature (a: no calcine; b: 300 °C; c: 400 °C; d: 500 °C)

B. SEM

Morphologies of the samples obtained by the analysis of scanning electron microscope are shown in Fig. 2 From these pictures, the morphologies in each figures are Co₃O₄ spheres with many folds and stripes constituted of EG or carbon calcined from EG at 300-500 °C. Obviously in the process of the formation of the spheres, similar to HMT [17], EG acts as a shaping agent coated surface of the samples to control their morphology [18]. EG not only induce to limit their structure and morphology but also help to enhance properties if EG burn and decompose into carbon. The presence of carbon having a conductive property may contribute to improve the electrochemical performance of the spheres. And particle size of Co₃O₄ spheres are affected by calcination effect from average 5 um to 1 um as the temperature increases up to 500 °C. As we all know, the crystallinity as well as size will increase with the temperature, so using too much EG is the maximum possible cause of this phenomenon. The higher the calcination temperature, the less EG consisted of the spheres surface, the smaller size of the spheres. Taking into account the specific surface area, we chose the smallest samples as the next experiment materials, mark as 500-Co₃O₄.

C. Electrochemical properties of $500-Co_3O_4$



Figure 3. Voltage characteristic curve of the sample Co₃O₄. (Scanning rate: 10 mv/s)



Figure 4. The charging curve of Co_3O_4 (Current density: 5mA/s, 10mA/s, 20mA/s)



Figure 5. 1000 cycles specific capacitance of $\rm Co_3O_4$ (Current density: 5mA/s)

Voltage characteristic curve of Co_3O_4 was show at scanning rates 10 mv/s in Fig. 3. From it, there are obvious oxidation peak and reduction peak. Two pairs of redox peaks are indexed as the oxidation-reduction reaction of $Co_3O_4/CoOOH$ and $CoOOH/CoO_2$. Their intrinsic reaction potential is different, resulting in two distinct redox reactions. The oxidation reaction equation:

$$Co_3O_4 + OH^- + H_2O \leftrightarrow 3CoOOH + e^-$$
(2)

$$CoOOH + OH^{-} \leftrightarrow CoO^{2^{-}} + H_2O + e^{-}$$
(3)

Its reduction reaction equation was the reverse process of oxidation reactions.

It is shown in Fig. 4 is discharge curve of Co_3O_4 electrode under the current density of 5 mA/s, 10 mA/s, 20 mA/s. The current increases while the same current corresponding to the charging time was significantly reduced during charging. It suggests that description of the electrode reaction in the electrolyte is almost reversible. Quality capacitance of electrode materials can be calculated according to formula (4):

$$C = \frac{I \cdot t}{m \times \Delta V} \tag{4}$$



Figure 6. AC impedance image of Co_3O_4 (when the low frequency is 1Hz)

Where C is quality capacitance (F/g), I is the current of the charge/discharge (A), t is discharging time(s), delta Vis the charge/discharge voltage range (V), m is the mass of the substance (g). By calculating quality capacitance at different current of the charge/discharge, we can know that when the current density is 5m/s and 10m/s quality capacitance is 372.7 F/g and 310.56 F/g, respectively. It suggests that quality capacitance has an apparent downward trend while the current of the charge/discharge increasing, resulting from the electrode material not being used effectively at a large current. The relation between quality capacitance and cycle time during Co₃O₄ electrode discharging is shown in Fig. 5, the current density is 5 mA/s. And the quality capacitance is around 372 F/g in the first charge-discharge process, and electrode capacitance decreases with cycle time increases. It shows that the electrochemical properties of the electrode material are in constant attenuation in this process. In AC impedance, Z ' as a real part, Z" is the imaginary part. In general, AC impedance curves of super capacitor are composed of a semicircle and a straight line. Semicircle at high frequency is related to Faraday reaction, and linear at low-frequency is indexed as Warburg impedance related to electrolyte diffusion electrode pores. Rs and Rct represents solution and charge-transfer resistances, respectively. Intersection is a contact resistance (Re) of electrode. Semicircle corresponds to the material charge transfer resistance (Rct) and a capacitor. What in Fig. 6 is AC impedance image of Co_3O_4 when the low frequency is 1Hz. Intersection coordinates (4, 0), where Re is 4 ohms.

IV. CONCLUSIONS

The average crystallite size and fine crystallinity of Co3O4 crystal lattices increased with the mass percentage of La(NO3)3. Ethylene glycol as a shaping agent may be the possible reasons of decrease in particle size at higher temperatures in the process of the formation of Co3O4 microspheres. The specific capacitance and the current density of the best sample are 5 mA/s, 372.7 F/g and 10 mA/s, 310.56 F/g respectively.

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