Preparation and properties of coke powder activated carbon/ α -Co(OH) $_2$ composite electrode materials

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Abstract Coke powder activated carbon (CPAC) was prepared by dipping-calcined KOH activation method. Using CPAC as the raw material a series of composite electrode materials of CPAC/ α -Co(OH) $_2$ with different mass fractions of cobalt were synthesized by the Sol–gel method. The physical properties of the resulting samples were characterized by the field emission scanning electron microscopy and the X-ray diffraction. The results show that composite materials, CPAC/ α -Co(OH) $_2$, have a flower-like structure. The results of electrochemical performances show that the composite material has a good electrochemical capacity of 472.3 F g $^{-1}$ with a cobalt doping amount of 30 wt %. By the cyclic voltammetry testing, we found that the anodic peak potential of the redox peaks in composite electrode materials shifted positively when the scan rate increased, while the cathodic peak potential shifted negatively, and that would cause a gradual increase of the peak potential difference of redox peaks. In contrast, the lower of the scan rate, the smaller of the peak potential difference and the better of the reversibility of composite material. The results of impedance testing show that CPAC/ α -Co(OH) $_2$ has a lower electrochemical impedance than that of CPAC.

1 Introduction

Recently, as a kind of new energy store and conversion equipment, electrochemical supercapacitors (ECs) have generated great interests due to their large capacitance, long cycle life and quick charge/discharge performance, etc. [1–4]. Based on the energy store mechanism, electrochemical supercapacitors can be separated into two different categories: electric double layer capacitors (EDLCs) and redox pseudocapacitors [5–7]. The electrode materials have an extremely high influence on the property of the ECs and an appropriate electrode material plays an important role in enhancing the energy density and the range of working potential windows [8–10]. So far, several kinds of porous carbon materials [11–15] have been widely applied in the electrochemical double-layer capacitors (EDLCs), owing to characteristics of abundant raw materials, low production cost, high special surface area, higher electrochemical stability, better electrical conductivity, and so on. But the specific capacitance of the porous carbon materials is lower, so it is necessary to improve the specific capacitance by depositing the metal oxides and metal hydroxides on their surface. Therefore, one can build the electrochemical supercapacitors, which have the advantages of both of electric double layer capacitors (EDLCs) and redox pseudocapacitors [16, 17]. Considering the low cost and excellent capacitance, the cobalt compounds have been widely used as electrode materials [18, 19]. And as we know, α -Co(OH) $_2$ and β -Co(OH) $_2$ are two different crystal structures of Co(OH) $_2$ compounds, and the former has attracted much attention for its outstanding electrochemical performance [18, 20, 21].

Coke powder is generally known as the coke particles with an average diameter of less than 5 mm produced in the breaking process of coke, and treated as a waste

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because of its small particle size. Nowadays, the reuse of coke powder is mainly focused on the treatment of waste water after being activated by alkaline compounds [22]. However, the coke powder has been rarely employed as electrode material. In this study, coke powder activated carbons (CPAC) were prepared by dipping-calcined activation method with the modifier of KOH using coke powder as the raw material [23], and the composite electrode materials, CPAC/ α -Co(OH)₂, were synthesized by the Sol-gel method. Moreover, the physics and electrochemical performances of the composite electrode materials were systematically investigated.

2 Experimental

2.1 Preparation of CPAC/ α -Co(OH)₂ composite materials

CPAC were prepared according to our previous study [23]. Dissolved certain quality of CoCl₂·6H₂O into 50 mL distilled water and stirred for 30 min at room temperature. Then CPAC were added with a little of alcohol, and made sure the mass ratio of cobalt respectively was 5, 10, 20, 30, 50 wt %. After subsequent stirring for 30 min, aqueous ammonia (10 wt %) was added into each of samples and the pH value was adjusted to between 9 and 10. And after stirring for 6 h and standing for 4 h, each of the precipitates was collected by filtration under reduced pressure. Finally, each of the samples was washed to pH value is 7 with distilled water and dried for 24 h at 80 °C. Cooling in the normal temperature, samples were fully grinded in the agate mortar, respectively.

2.2 Preparation of CPAC/ α -Co(OH)₂ electrode

CPAC/ α -Co(OH)₂ electrode was composed of composite materials, acetylene black and polytetrafluoroethylene (PTFE) emulsion with a mass ratio of 8:1:1 and drops of anhydrous ethanol were added to get paste sample. Then the paste sample was filled into a foam nickel with an apparent area of 10 × 10 mm², dried at 80 °C for 2 h under vacuum and pressed to a sheet at the pressure of 10 MPa for 1–2 min to assure a good electronic contact and to form an effective quadrate coating, next drying at 80 °C for 4 h.

2.3 Characterization and electrochemical measurement

Morphology observation of the composite materials was performed on a FE-SEM (JSM-6701F, Japan) and a XRD (D/Max-2400, Rigaku, Japan) technique. The electrochemical measurement of electrodes were carried out using

an electrochemical working station (CHI660B, Shanghai, China) in a three electrode cell at room temperature. In the normal three electrode system, CPAC/ α -Co(OH)₂ composite electrode was used as working electrode. Furthermore, a platinum gauze electrode and a saturated calomel electrode (SCE) were served as the counter electrode and the reference electrode, respectively, and KOH solution (2 mol L⁻¹) was used as the electrolyte.

3 Results and discussion

3.1 FE-SEM analysis

The FE-SEM images of CPAC and CPAC/ α -Co(OH)₂ composite materials are shown in Fig. 1. FE-SEM image of Fig. 1b indicates that the composite materials have a flower-like structure prepared by sol-gel method, which is similar to the morphology of CPAC, as shown in Fig. 1a. This particular structure not only increased the special surface area of composite materials but made it easier to have a contact between the α -Co(OH)₂ active materials and electrolyte ions. The transfer of H⁺ and OH⁻ ions out of the inner pore rapidly, which would benefit to enhance the utilization ratio of α -Co(OH)₂ in composite materials.

3.2 XRD analysis

The XRD patterns of pristine CPAC and CPAC/ α -Co(OH)₂ composites are shown in Fig. 2. From Fig. 2, it could be seen that diffraction peaks were observed when 2 θ is 23° and 44.5°, corresponding to the C(002) and C(101) typical peaks of graphite. The obvious diffraction peaks of CPAC/ α -Co(OH)₂ occurred at 11.2°, 22.8°, 34.4° and 60.04°, which can be assigned to the (003), (006), (012) and (110) planes respectively. Contrast to the Ref. [24], we can know these diffraction peaks are indexed to the characteristic peaks of α -Co(OH)₂. Besides, the intensity of (003) plane is stronger than any of the others, it indicates that the growth of α -Co(OH)₂ has a preferential orientation along the c-axis. Based on these results, we could confirm that the cobalt has been successfully incorporated into CPAC to form composite electrode materials through the sol-gel method.

3.3 The electrochemical characterizations of CPAC/ α -Co(OH)₂

3.3.1 Chronopotentiometry

The specific capacitance of CPAC was evaluated from the charge/discharge test together with the following equation [25]:

Fig. 1 The FESEM of CPAC (a) and CPAC/ α -Co(OH) $_2$ composite material (b)

Fig. 2 The XRD patterns of **a** CPAC and **b** CPAC/ α -Co(OH) $_2$ composite material

$$C = I / [(dE/dt) \times m] \approx I / [(\Delta E / \Delta t) \times m]$$

$$= \frac{I \times \Delta t}{\Delta E \times m} (\text{Fg}^{-1})$$

where C is the specific capacitance; I is the constant discharging current; Δt is the time period for the potential change ΔE ; and m is the mass of the CPAC/ α -Co(OH) $_2$ composite materials measured.

The constant current charge/discharge curves of composite materials in the different cobalt contents were investigated at a current density of 5 mA cm^{-2} over the potential range of -0.2 – 0.45 V (vs SCE), as shown in Fig. 3. It could be seen from Fig. 3 that the constant current discharge time prolonged with the increase of the complex quality of cobalt. The result indicates that cobalt has a positive influence on the electrochemical performance of the composites. The highest specific capacitance was

obtained about 472.3 F g^{-1} when the composite amount of cobalt was 30 wt %. However, the discharge time and the specific capacitance became shorter and lower inversely with further increase of the percentage of cobalt. The fading of the specific capacitance and the discharge time may come from two reasons. First, the production of α -Co(OH) $_2$ increased continuously and occurred mass accumulation and agglomeration on surface of CPAC lead to enlarge the difficulty to transfer electrolyte ions to their inner pores of the composites. Especially, deficiently contact between active materials and electrolyte ions caused oxidation–reduction reaction, which would weaken the Faradaic pseudo-capacitive nature of the active materials and declined specific capacitance. Second, because of the accumulation and agglomeration of mass α -Co(OH) $_2$ active particles, the special surface area decreased and double layer capacitor effect declined so as to reduce of specific capacitance of CPAC. From Fig. 3, there are two discharge plateaus in the curve of each composite material due to an oxidation–reduction reaction between Co(II)(OH) $_2$ active material and OH $^-$ anions in the electrolyte. The resulting Co(III)OOH could keep reacting with OH $^-$ anions to get the production of Co(IV)O $_2$ with Faraday effect. The chemical equations were described as follows:

The specific capacitance of composite electron materials with different cobalt contents were investigated with a current density of 5 mA cm^{-2} , as shown in Fig. 4. It could be seen from Fig. 4, the specific capacitance increased firstly and then decreased with further increase of the percentage composition of cobalt. When the cobalt contents are 5, 10, 20 and 30 wt %, the corresponding specific capacitance of the electrode materials are 112.4, 172.3, 289.3 and 472.3 F g^{-1} , respectively. When the cobalt content was increased continuously to 50 wt %, the

specific capacitance value would reduce to 353.1 F g^{-1} , which is consistent with the results getting from Fig. 3. The results indicate that CPAC/ α -Co(OH) $_2$ composite electrode materials show the best electrochemical performance when the composite quality of cobalt reaches 30 wt %. This conclusion has been confirmed by the testing of constant current charge/discharge previously.

3.3.2 Cyclic voltammetry

The cyclic voltammograms of the electrode materials with different cobalt contents are shown in Fig. 5, the materials were tested in 2 mol L^{-1} KOH electrolyte at a scan rate of

Fig. 3 The constant current charge/discharge curves of composite materials prepared in the different cobalt contents at a current density of 5 mA cm^{-2}

Fig. 4 The specific capacitance of composite materials prepared in the different cobalt contents at a current density of 5 mA cm^{-2}

5 mV s^{-1} over the potential range of -0.2 – 0.5 V . The oxidation peaks were remarked as p_1 and p_3 but the reduction peaks were noted as p_2 and p_4 . It is observed obviously from Fig. 5 that in each cyclic voltammetry curve, two pairs of REDOX peaks presents good mirror symmetry characteristic. The p_1 oxidation peak corresponds to the oxidation process that Co(II)(OH) $_2$ changed into Co(III)OOH and p_3 oxidation peak corresponds to the oxidation process which Co(III)OOH transform into Co(IV)O $_2$, while p_2 and p_4 reduction peaks are related to the high valence compounds reduced to low quantivalence in chemical Eqs. 1 and 2.

It can be also seen from Fig. 5 that, the current response for the electrode is quite higher than others when the cobalt content is 30 wt %. This verdict is consistent with that of shown in Figs. 3 and 4. Besides, it is obvious that the peak potential absolute value of the reduction is equal to that of the oxidation, showing an approximate ideal symmetry. Undoubtedly, we conclude that the composite electrode materials exhibit a good reversibility characteristic.

The cyclic voltammograms of composite materials with 30 wt % cobalt content at various scan rates are shown in Fig. 6. The anodic peak potential shifts to higher value when the scan rate continuously increased while the cathodic peak potential shifts to lower value, and large potential windows between the anodic peak and the cathodic peak can be detected. The lower scan rate, the narrower potential window, e.g., the electrode exhibits a narrowest window at a smallest scan rate of 2.5 mV s^{-1} . However, when the scan rate was set over 50 mV s^{-1} , the mirror symmetrical feature of the CV curve disappeared over the same potential range of -0.2 – 0.5 V . Greater scan rate leads to irreversibility reaction and polarized behavior

Fig. 5 The cyclic voltammograms of composite materials prepared in the different cobalt contents at a scan rate of 5 mV s^{-1}

Fig. 6 The cyclic voltammograms of composite materials prepared in 30 % of cobalt content at various scan rates

of the electrode material, then the decrease of specific capacitance was inevitable.

3.3.3 AC impedance

The AC impedance spectra of CPAC and CPAC/ α -Co(OH) $_2$ were measured in the frequency range of 10^{-2} – 10^5 Hz, and the images are described in Fig. 7. The images reveal that all the Nyquist plots are formed by a semicircle in high frequency area and an incline straight in low frequency area, but with different impedance characteristics. The high frequency region corresponds to the contact resistance at the interface between electrode material and electrolyte is inconspicuous, which implies the low contact resistance. At the middle and low frequency regions, the oblique line is closer to the vertical axis, which illustrates that the composites exhibit an excellent capacitance characteristic. The capacitive behavior of composites is better than that of the CPAC owing to the special petal-like or flower-like appearance of composite materials. It is easy to transfer the electrolyte ions among the channels and has an excellent contact between electrolyte ions and active materials, which is favorable to decrease the transport resistance and attain charge saturation status rapidly [26]. Moreover, the composite materials with 30 % cobalt have a lower impedance than that of pure CPAC according to the Fig. 7. And the equivalent series resistances (ESR), corresponding to the intercept of Z' axis, were measured to be 0.953 and 1.009 Ω , respectively.

4 Conclusions

A series of CPAC/ α -Co(OH) $_2$ composite electrode materials with different cobalt contents were prepared by the

Fig. 7 The AC impedance spectra of CPAC and CPAC/ α -Co(OH) $_2$ composite material

sol-gel method. The results obtained from electrochemical testing show that, with cobalt contents of 30 wt %, the optimal specific capacitance of the as-prepared composite electrode reaches up to 472.3 F g^{-1} . The cyclic voltammetry curves reveal that active substances have a wider current window and an optimum electrochemical property at a scan rate of 5 mV s^{-1} . The electrochemical impedance spectroscopy results indicate that CPAC/ α -Co(OH) $_2$ composite electrode materials exhibit an outstanding conductivity and a lower impedance compared with that of CPAC.

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