3 Analysis of economic effectiveness

962,800 Yuan of RMB was invested, with 275,800 Yuan for construction engineering, 484,500 Yuan for equipment and 200,000 Yuan for designing and others.

(1) Cost for agents: 20gPAM was needed for wastewater of 1m$^3$, at the price of 13,000 Yuan/t and 6kg carbide slag was needed at the price of 10 Yuan/t. And 0.4L industrial waste acid at the price of 10 Yuan/t was needed to balance the pH of supernatant liquid of about 40% separated from 1m$^3$ wastewater. Sum of these three items was:

$$20 \times 0.13 + 6 \times 0.01 + 0.4 \times 0.01 = 0.324 \text{ Yuan/m}^3$$

(2) Cost for workshop depreciation:

$$27.58 / 40 / 39 = 0.011 \text{ Yuan/m}^3$$

(3) Cost for equipment depreciation:

$$48.45 / 20 / 39 = 0.062 \text{ Yuan/m}^3$$

(4) Cost for workforce: Eight workers were needed with a salary of 500 Yuan per capita, so the cost was:

$$500 \times 8 \times 12 / 390000 = 0.123 \text{ Yuan/m}^3$$

(5) Cost for electricity: The service capacity of the equipments and installed capacity for illumination of this project were 32Kw, and the power fare in Tiefa City was 0.40 Yuan/degree, so the cost was:

$$0.40 \times 32 / 65 = 0.197 \text{ Yuan/m}^3$$

(6) Cost for maintain: 0.01 Yuan/m$^3$

The treated water can be used for coal washing and will do no damage to the water area around, also the coal slurry can be soled out. So the environmental and social benefits are both preferable.

Water rate can be saved due to the reuse of the treated water in coal washing:

$$0.40 \text{ Yuan/m}^3 \times (390,000 \text{ m}^3/\text{a} \times 40\%) = 62,400 \text{ Yuan}$$

20,000 ton of dried coal slurry can be reused every year and its price is 5 Yuan/t, the economic benefit of each year is:

$$20,000 \times 5 \times 100,000 = 100,000,000 \text{ Yuan}$$

The saved charges of water pollution every year:

$$800,000 \text{ Yuan}$$

Running cost of each year:

$$0.727 \text{ Yuan/m}^3 \times 390,000 \text{ m}^3 = 283,350 \text{ Yuan}$$

Therefore, the economic benefit of a year is:

$$800,000 + 100,000,000 + 283,350 = 673,350 \text{ Yuan}$$

All the investment can be paid off in half and a year.

4 Conclusions

(1) The coal washing wastewater is a stable colloid system, characterized by high concentration of suspended substance, small particles and negative potential on the surface of particles.

(2) The experiment results and the running effects of the application have both proved that the use of carbide slag and PAM and the process introduced in this paper are feasible to treat the wastewater produced in the washing of coal of not too long time. The quality of treated water can meet all the requirements of reuse and discharge standards. The recollected coal slurry can be reused as fuel.

(3) This treatment process is simple and effective, and the cost is low. All of these characters are reasonable according to the rules in wastewater treatment. The environmental and social benefits are also preferable so that this technology has a high promotional value.

References


Ordered Mesoporous Carbon/FeO(OH) Composites as the Electrode Material for Supercapacitors with High Capacitive Performance

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Abstract: Ordered mesoporous carbon/FeO(OH) composites were synthesized by hydrothermal incipient wetness impregnation method in an autoclave. The morphology and microstructure of the samples were examined by X-ray diffraction (XRD), transmission electron microscopy (TEM) and N\textsubscript{2} adsorption/desorption isotherms. Capacitor properties of the ordered mesoporous carbon/FeO(OH) composites were characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in 2 M KOH aqueous solutions. The XRD analysis shows that a new hydrated iron oxide was obtained but few reported before by the method, and FeO(OH) has advantages of low cost and environmental benignity for composite electrode. For the content of Ordered mesoporous carbon/FeO(OH) composites reaches 9.6wt%, the highest specific capacitance (486.27 F/g measured at 5 mV/s) was obtained, and good cycling stability and long cycle life. Additionally, for comparison, the capacitor properties of different content of FeO(OH) in the composite were also investigated in this work.

Keywords: iron oxide, hydrothermal incipient wetness impregnation, capacitor properties

1 Introduction

Electrochemical supercapacitors (ESs) have attracted increased interest due to their higher power density and long cycle life than batteries\textsuperscript{[6,7]}, so ESs are regarded as ideal energy storage devices to meet urgent needs in electric and electronic devices and can be deeply discharged without any deleterious effect on lifetime. For example, hybrid systems consisting of batteries and electrochemical supercapacitors are being pursued for electric vehicle propulsion. In such hybrid systems, electrochemical supercapacitors can provide the peak power during acceleration and therefore, the batteries can be optimized primarily for higher energy density and better cycle life. ESs are also attractive for other applications such as backup energy sources, since they have high power density and long cycle life. The capacitor properties of the ESs are closely related with the electrode and electrolyte\textsuperscript{[8,9]}, so it is indispensable to develop an advanced supercapacitor device. Ordered mesoporous carbons (OMC) not only have attracted much attention as a promising candidate for catalyst supports, absorbents, hydrogen storage media\textsuperscript{[10-12]}, they can but also used as the electrodes in ESs, due to their chemical stability, high conductivity, large specific surface area, etc. To further improve capacitor properties of ESs, the metal oxides, such as NiO\textsuperscript{[10-12]}, have been introduced into OMC electrodes. However, carbon/metal oxide composites have gained much interest owing to their potential applications in supercapacitors requiring both high capacitance and long cycle life. Currently much interest has been focused on Goethite (FeO(OH)), However, though iron oxide be used in various areas\textsuperscript{[13-15]}, the potential application of iron oxide combined with OMC as the electrode materials in ESs is seldom discussed\textsuperscript{[16]}.

In this paper, FeO(OH)-OMC composites as the electrodes were prepared as a promising candidate for use in capacitors. The effect of the introduction of FeO(OH) on the main physicochemical properties and electrochemical performance of FeO(OH)-based electrode in 2M KOH solution were analyzed.

2 Experimental

2.1 Preparation of OMC/FeO(OH) composites

Analytically pure chemicals were obtained commercially and used without further purification unless...
The SBA-15 silica mould was chosen as a hard template. The synthesis of SBA-15 was performed according to the procedure reported by Zhao et al. by using a tri-block copolymer poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), EO$_{20}$PO$_{70}$EO$_{20}$ (Pluronic 123,BASF) as structure-directing agent and Tetraethyl orthosilicate (TEOS, AR) as silica source in acid condition.

1 g of calcined SBA-15 was impregnated in 100 ml of an ethanol solution containing 1 g of AlCl$_3$ under vigorous stirring for 14 h. The resulting Al-SBA-15 was filtered and washed with ethanol to remove aluminum from the outer surface. Afterwards, Al-SBA-15 was generated by calcination at 550 °C for 5 h in air. The mesoporous carbon was synthesized by using Al-SBA-15 as template and furfuryl alcohol as carbon source by incipient wetness impregnation method. 1.6 g of Furfuryl alcohol dissolved in 5.4 mL ethanol was used as carbon precursor. The furfuryl alcohol solution was infiltrated in Al-SBA-15 by incipient wetness impregnation at room temperature, followed by polymerization at 90 °C for 5 h and then 150 °C for 2 h, respectively under air. Afterwards, the composite was heated at 150 °C under vacuum for 3 h for removal of the unpolymerized furfuryl alcohol. Finally the temperature of the composite was increased to 900 °C with a heating rate of 5 °C min$^{-1}$ and maintained at that temperature for 3 h under nitrogen atmosphere to complete the carbonization, and then the resulting mesoporous carbons are obtained and denoted as CMK-3.

2.2 Physical characterization of the composites

The structures of the samples were characterized by X-ray diffraction. XRD data were collected using a Rigaku D/MAX2550 diffractometer with Cu Ka radiation ($\lambda$=0.15406 nm), Transmission electron micrographs (TEM) were taken on a JEOL-2010 microscope at an accelerating voltage of 200 kV.

2.3 Electrochemical characterization

In order to prepare the EC electrode, a mixture of the composite, BP2000 and poly tetrafluoroethylene (PTFE) binder with the weight percent ratio of 75:20:5 was dispersed in alcohol and coated on a piece of nickel foam substrate (1×1 cm), which was pressed and dried at 35 K for 1 h. The mass of activated substance in each electrode ranged from 3 to 4 mg. The electrochemical performance of the composites was analyzed using a three-electrode configuration in aqueous 2.0 M KOH electrolyte. The Pt flag and saturated calomel electrode were used as the counter and reference electrodes, respectively. Cyclic voltammetry was performed on a CHI660C electrochemical workstation in the potential range of -0.1-0.5 V (vs SCE) with a scan rate from 5 to 200 mV s$^{-1}$. The specific capacitance (SC) at a given scan rate, was calculated from voltammetric response using the following equation.

$$C_s = \frac{1}{mv(V_f - V_i)} \int_{V_i}^{V_f} I(V) dV$$

(1)

Where m is the mass of the activated substance,
Vf and Vi are the two integration limits of the voltammetric curve, and \( I(V) \) is the voltammetric current \([9]\).

3 Results and discussion

Fig. 1 shows the typical XRD patterns of the as-prepared OMC/FeO(OH) composites with different loading amount. The wide-angle XRD patterns exhibit three broad peaks at 2\( \theta \) around 21.6°, 33.6° and 36.9° and are marked with their indices as shown in Fig. 1.

![Fig. 1. Typical XRD patterns of the as-prepared OMC/FeO(OH) composites](image)

The position and intensity of all the peaks agree with the diffraction files. XRD analysis confirms it can be indexed to Goethite. There are diffraction peaks of the different content of Ordered mesoporous carbon/FeO(OH) composites, showing that all of the nanocrystallites can be indexed to Goethite.

The nitrogen adsorption/desorption isotherms are shown in Fig. 2a and the textural properties are listed in Table 2. All samples are type IV isotherm with a marked increase in the adsorption curves at relative pressure \( P/P_0 \) of 0.5, which is typical for mesoporous solid. The specific surface area is found to decrease gradually from 789.9 m\(^2\)/g to 264.1 m\(^2\)/g with different loading from 5% to 29.86% and correspondingly the pore volumes decreased from 0.93 cm\(^3\)/g to 0.26 cm\(^3\)/g (Table 2).

![Fig. 2. The N2 adsorption-desorption isotherms (a) and pore size distributions (b) of OMC-FeO(OH) with different content](image)

Table 2. Pore characteristics of OMC, FeO(OH), LODI-\( x \) (\( x=1; 2; 3; 4 \))

<table>
<thead>
<tr>
<th>Samples</th>
<th>( S_{BET} ) (m(^2)/g)</th>
<th>( V_\text{t} ) (cm(^3)/g)</th>
<th>Mean pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LODI-1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LODI-2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LODI-3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LODI-4</td>
<td></td>
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</tbody>
</table>

which is presumably related to the micropores in carbon framework, which is in good agreement with that deduced from adsorption and desorption isotherms, and the peaks of pore size of LODI-\( x \) (\( x=1-4 \)) tend to disappear with the increase of the amount of FeO(OH) loading amount.
TEM images of the ordered mesoporous carbon and the LODI-2, it is shown in figure (a), a image of the structural of the ordered mesoporous carbon was preserved. It can clearly be seen, that the structure of LODI-2 become somewhat unclear relative to the image of the structural of the ordered mesoporous carbon. There is much darker dots on the image of the (b). They may be the FeO(OH) nanocrystallites. The dark dots on the image are very clear. It is obvious that the TEM image of the LODI-2 is different from the ordered mesoporous carbon and the state of the ordered mesoporous carbon is changed after loaded FeO(OH).

Fig. 3 shows transmission electron micrograph

Fig. 3 shows transmission electron micrograph of the ordered mesoporous carbon and the LODI-2, it is shown in figure (a), a image of the structural of the ordered mesoporous carbon was preserved. It can clearly be seen, that the structure of LODI-2 become somewhat unclear relative to the image of the structural of the ordered mesoporous carbon. There is much darker dots on the image of the (b). They may be the FeO(OH) nanocrystallites. The dark dots on the image are very clear. It is obvious that the TEM image of the LODI-2 is different from the ordered mesoporous carbon and the state of the ordered mesoporous carbon is changed after loaded FeO(OH).

Fig. 4 shows the CV curves tested at the scan rates of 5, 10, 20, 50, 100, 200 and 500 mV s⁻¹ in 2M KOH solution and the corresponding specific capacitance is calculated to be 486, 316, 212, 133, 97 and 69 F/g from -0.1 to 0.5 V. Redox peak behaviors were observed in the range of voltage. At different voltage scan rate, redox current not almost kept constant, as the scan rate was increased from -0.1 V to 0.5 V, the specific capacitance dropped. The curve reflects the same results that there are obvious peaks of reduction current were observed. It can also be observed that CV curves of LODI-4 are relatively Triangle shape even at the scan rate of 200 mV s⁻¹. The rectangular characteristic of CV curves indicates a very rapid current response on volt-
age reversal at each end potential.

![Graph showing specific capacitance vs. scan rate for OMC/FeO(OH) composites at different scan rates.](image1)

**Fig. 5.** Specific capacitance of OMC/FeO(OH) composites at different scan rates

The variation in the specific capacitance of OMC/FeO(OH) composites as a function of the scan rates is plotted in Fig. 5. As shown, the specific capacitance increases with the increasing amount of Fe(NO₃)₃ at the same scan rate from LODI-1 to LODI-2, and the specific capacitance decreases with the increasing amount of Fe(NO₃)₃ at the same scan rate from LODI-2 to LODI-4. For the LODI-2 sample, the initial specific capacitance based on FeO(OH) is 486 F/g at the lowest scan rate of 5 mV s⁻¹, which is much higher than that of other three samples, so high content of OMC in the composites will increase the effective contact area between FeO(OH) and OMC, which results in high electrochemical utilization of FeO(OH) in the OMC/FeO(OH) composites. This result could be anticipated as some pores are likely to be filled by Goethite. This is illustrated by the data listed in Table 1 showing the variation in surface area. At the same time, OMC provide a direct conductive path for FeO(OH) particles due to their high electric conductivity, thus reducing the internal resistance within the composite itself. The reason that the amount of 9.6% Goethite in the Goethite/OMC composites exhibits better specific capacitance than the other loading of Goethite could be related to the best content of Goethite, it is not the highest content or the lowest content, only the 9.6% content in the composites is the best.

![Nyquist plots for OMC, LODI-1, LODI-2, LODI-3 and LODI-4.](image2)

**Fig. 6.** Nyquist plots obtained for the OMC, LODI-1, LODI-2, LODI-3 and LODI-4 in 2 M KOH solution.

Fig. 6 represents the complex plane impedance (Nyquist) plots for the LODI-1, LODI-2, LODI-3 and LODI-4. Nyquist plots are generally composed of a semicircle and an inclined straight line. The high frequency semicircle represents the charge transfer process at electrode/electrolyte interface, while the inclined straight line at low electrochemical processes. Therefore, the high impedance (Z') value of the system corresponds to high internal resistance as well as diffusion limitation. The impedance behavior of LODI-1 electrode is close to an ideal EDLC, and shows low charge transfer resistance with a vertical line shape towards lower frequency indicating DLC storage. LODI-2 decreases the charge transfer resistance. The Nyquist plots for LODI-2 nano-composite show that the electrode impedance internal is close to that of the OMC electrode with even lower internal resistance, this is due to the effect of LODI-2 on the nano-composite electrode is clearly presented by significant decrease in the impedance and internal resistance of the electrode. The effect of FeO(OH) on the OMC electrode is clearly presented by significant decrease in the impedance and internal resistance of electrode.

Fig. 7 shows the variations of specific capacitance with charge-discharge cycle number of LODI-2 composite electrode prepared by incipient wetness impreg-
nation method described above. As revealed in this Fig 7. The electrode is found to exhibit excellent stability over the entire cycle numbers. The specific capacitance of the composite electrode decreases only 8.9% by repeating the CV test between -0.1 and 0.5V (vs. SCE) at a scan rate of 5mV s⁻¹ for 500 cycles.

4 Conclusions

In summary, FeO(OH)/OMC composites have been synthesized by using the incipient wetness impregnation method, an ordered mesoporous nanocomposite was successfully synthesized. The FeO(OH) nanocrystallites were encapsulated in the carbon channels. For LODI-2 composite, the specific capacitance is 486.27 at 5 mV s⁻¹, respectively. The composites also show excellent cycle stability, and the capacitance decreases only 5.4% after 500 cycles. The excellent capacitance performance is primarily attributed to high electrical conductivity of the composites and homogeneous dispersion of FeO(OH) on the surfaces of OMC, facilitating the rapid transport of the electrolyte ions and increasing the electrochemical utilization of FeO(OH). Therefore, the FeO(OH)/OMC composites prepared by incipient wetness impregnation method are very suitable and promising electrode materials for supercapacitors with power and low price.

Acknowledgements

The authors are grateful for project supported by Songjiang economic committee of Shanghai.

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