原位电化学合成铁基电极材料及其超级电容器性能

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摘要:采用胶体纳米粒子为模型进行研究。假设活性阳离子均匀分布在导电碳与粘结剂中,电解液离子的渗入可以原位形成 活性胶体团簇。通过原位电化学方法合成了不同组成的铁基超级电容器电极材料。在不同的阳离子电解液中,铁胶体离子电 极的电容不同,其中在KOH、NaOH、LiOH电解液中分别为1113、927、755 F·g⁻¹。通过胶体的介尺度结构构筑,实现离子到材 料性能的跨尺度可控调节。通过对胶体模型的拓展,提供了原位组成调节到材料性能跨尺度调控的新方法。

关键词:电化学;合成设计;铁氧化物;电极材料;超级电容器
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In Situ Electrochemical Synthesis of Fe-Based Electrode for Supercapacitors

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Abstract: This work adopts the colloidal nanoparticles as a model for research due to the prominent specific surface area of colloidal nanoparticles. There was a hypothesis that cations uniformly distributed in the conductive carbon and binder. Electrolyte ion can interact with cations to form reactive colloidal clusters *in situ*. Herein, the electrochemical method was adapted to synthesize different iron based electrode materials by the changes of electrolyte. Febased electrodes exhibited specific capacitances of 1 113, 927 and 755 $F \cdot g^{-1}$ in KOH, NaOH and LiOH aqueous electrolyte, respectively. A novel type of colloid systems with adjustable structure was built, achieving multiscale controllable regulation of colloid structure and material performance. By extending the colloid model, a novel method of in situ composition adjustment to cross-scale control of material properties was provided.

Keywords: electrochemistry; synthesis design; iron oxide; electrode materials; supercapacitor

0 Introduction

With the development of society, energy demand is increasing recently. Safe, clean and sustainable energy storage devices are necessary to satisfy the need for electrical energy storage^[1-5]. Electrochemical capacitors, also called supercapacitors, store energy in two closely spaced layers with opposing charges or electrodes with redox reactions near surface^[6-8], which offer high power densities and ideal cycling ability. However, supercapacitors are still limited by low energy densities^[9]. A large variety of materials such as gra-

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phene^[10-13], nanotube^[14-16], MXene^[17-20] and transition metal oxides/hydroxides have been explored in supercapacitors recently^[21-24].

Iron oxides have a broad working window in negative range and high theoretical specific capacitances^[25]. Therefore, various iron oxides have received increasing interests in the field of supercapacitors. At present, the specific capacitance of most iron oxides is far from their theoretical value mainly due to relatively large particle size and poor conductivity. Porous Fe₂O₃ nanoparticles on graphene delivered a specific capacitance of 357 F·g⁻¹ at 10 mV·s⁻¹. Graphene improved the conductivity of the electrode and porous structure provided rich surface for redox reaction^[26]. A hydrothermal method was used to synthesize reduced graphene oxide (rGO)/Fe₂O₃ aerogel. A specific capacitance over 700 $\mathbf{F} \cdot \mathbf{g}^{-1}$ was achieved due to the synergetic effect of the higher conductivity of rGO, and the mesoporous structure of Fe₂O₃ nanoparticles^[27]. Carbon fabric (CF), vertically aligned graphene nanosheets (VAGN) and FeOOH nanorods were incorporated into an electrode. This CF/VAGN/FeOOH electrode can charge/discharge at a low potential window (0 to -1.1 V vs Hg/ HgO), and exhibited a high specific capacitance of 909 $\mathbf{F} \cdot \mathbf{g}^{-1}$ aided by the unique structure of VAGN^[28]. $\mathbf{Fe}_3\mathbf{O}_4$ nanospheres were in situ decorated in graphene to form a nanocomposite, which exhibited a notably enhanced specific capacity of 268 $F \cdot g^{-1}$ at 2 mV $\cdot s^{-1}$. The unique structure of the graphene/Fe₃O₄ could provide more pathways for rapid transfer of electrons and transport or diffusion of electrolyte ions during fast charge/discharge processes^[29].

Interface plays a key role in electrochemical reactions in supercapacitors. Interface consists of electrode materials and electrolyte in supercapacitors^[30]. In order to construct suitable interface, we can tune various electrolytes to construct different interface^[31]. Herein, we choose FeCl₃·6H₂O served as a precursor to synthesize electrode materials in different kinds of electrolytes. The electrode exhibited a specific capacitance of 1 113 F·g⁻¹ at a current density of 3 A·g⁻¹ in 2 mol·L⁻¹ KOH solution. The electrode exhibited specific capacitances of 927 and 755 F·g⁻¹ at a current density of 3 A· g^{-1} in 1.5 mol·L⁻¹ NaOH and 1.5 mol·L⁻¹ LiOH electrolyte, respectively.

1 Experimental

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1.1 Synthesis of Fe-based electrode

FeCl₃·6H₂O was purchased from Tianjin Huadong Reagent Factory and was used without further purification. FeCl₃·6H₂O salt was mixed with conductive carbon and polyvinylidene fluoride (PVDF) with a weight ratio of 6:3:1, then proper NMP was dropped into the mixture to form homogenous mixture. Then the mixture was incorporated onto nickel foams and put into the oven at 55 °C for 7 hours. The nickel foam with paste was pressed at 15 MPa for 5 s. The geometrical area of working electrode was 1 cm×1 cm. The mass loading of FeCl₃·6H₂O in the electrode was 1.55 to 2.71 mg. The working electrode was put in electrolyte and carried out electrochemical reaction to form active Fe - based electrode.

1.2 Characterizations

The structural investigation of Fe - based electrodes was detected using a scanning electron microscope (SEM, Hitachi, S-4800 field emission scanning electron microscope, 10 kV). All electrochemical measurements were carried out using electrochemical workstation (CHI 660e) in room temperature.

1.3 Electrochemical measurements

LiOH · H₂O was purchased from Tianjin Huadong Reagent Factory. KOH and NaOH were purchased from Beijing Chemical Works. Then they were mixed with deionized water to form different concentrations of electrolyte for electrochemical reaction. Electrochemical measurements were carried out in a three-electrode cell. The counter electrode and reference electrode were Pt wire and saturated calomel electrode (SCE), respectively. The electrolytes were different concentrations of KOH, NaOH and LiOH aqueous solution. Cyclic voltammograms (CV) were carried out at scan rates of 2, 5, 10, 25, and 50 mV·s⁻¹, respectively. Galvanostatic charge and discharge (GCD) measurement was carried out at current densities of 3, 5, 10, 15, and 30 $A \cdot g^{-1}$, respectively. The specific capacitance of Fe based electrode was calculated from GCD curves according to equation^[32]:

$$C = \frac{I\Delta t}{m\Delta V}$$

where I is the current (A), m is the mass of active ions loaded in electrode (g), Δt is the discharge time (s) and ΔV is the potential window (V).

2 Results and discussion

2.1 Material synthesis and morphology characterization

In a typical synthesis process, FeCl₃•6H₂O salt was mixed with conductive carbon and PVDF to load on nickel foam, forming working electrode. The electrode was put in electrolyte, in which pristine salts were distributed in conductive matrix. CV measurement was used for the working electrode at 1 mV \cdot s⁻¹ about 10 cycles in a three-electrode cell to obtain active Fe-based electrode. Salts dissolve into ions and ions interact with OH⁻ instantly to form colloids, which was shown in Scheme 1. By tuning the kind of electrolytes, we can obtain various colloids with different compositions. The morphologies of the Fe-based electrode were investigated by SEM. Pristine salts, conductive carbon and PVDF were pasted on nickel foam (Fig.1a). The sample showed rough after experiencing cyclic voltammetry measurement. It seemed that active mate-



Compositions can be tuned by various electrolytes including LiOH, NaOH and KOH, respectively; Salts dissolve into ions, then form colloids withvarious composition by electrochemical reaction *in situ*



Scheme 1 Schematic fabrication of Fe-based electrodes with various compositions

Fig.1 SEM images of FeCl₃•6H₂O electrodes: (a) Salts in carbon and PVDF matrix; (b) Electrode materials react with KOH electrolyte after CV cycles; (c, d) Electrode materials after GCD

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rials had been formed in Fig. 1b. After GCD measurement, there were so many particles ensuring enough surface areas for electrochemical reaction, which could lead to superior specific capacitances (Fig.1c and 1d).

2.2 Electrochemical characterizations

In order to compare the electrochemical characteristics of Fe - based electrode with different compositions, the electrochemical measurements were carried out using a three-electrode cell in different concentrations of various kinds of electrolytes. The detailed values were shown in Table S1. It can be found that the specific capacitance could be effectively tuned by changing the kind of electrolytes. Fig.2 showed electrochemical performance of Fe-based electrode materials in various aqueous electrolytes. In KOH electrolyte, the synthesized electrode exhibited a highest specific capacitance of 1 113 $\mathbf{F} \cdot \mathbf{g}^{-1}$ at a current density of 3 A. g^{-1} in 2 mol·L⁻¹ aqueous solution. The value was higher than data reported in relatively literatures (Table S2)^[28-29,33-38]. Moreover, the Fe-based electrode synthesized in KOH solution showed relatively high capacitances in 1.5 mol·L⁻¹ (Fig. 2a). Fe - based electrode showed a capacitance of 927 $F \cdot g^{-1}$ at a current density of 3 $A \cdot g^{-1}$ in 1.5 mol·L⁻¹ NaOH (Fig. 2b). In LiOH aqueous solution, Fe-based electrode showed the highest value of 766 $F \cdot g^{-1}$ in 2 mol·L⁻¹ LiOH. Fig. 2d showed CV curves of Fe-based electrodes in 1.5 mol· L^{-1} electrolyte, where E_{pa} was anodic peak potential and $E_{\rm pc}$ was cathodic peak potential. The difference between anode peak potential and cathode peak potential indicates the reversible degree of the reaction. A pair of redox peak was obtained over a 1.2 V potential window at a scan rate of 2 mV \cdot s⁻¹. Fig.2e showed specific capacitances of Fe-based electrodes at various current densities in different electrolytes. It can be seen that Fe -based electrode synthesized in KOH electrolyte exhibited the highest values under the same concentration. Under the same concentration of 1.5 mol· L^{-1} , the capacitance calculated from GCD curves was determined to be 982, 927 and 755 F·g⁻¹ in KOH, NaOH and LiOH, respectively (Fig.2f).

To further evaluate the electrochemical behavior of the Fe-based electrode materials in KOH electrolyte, a series of electrochemical results were shown in Fig.3. CV curves at different scan rates from 2 to 50 mV \cdot s⁻¹ were shown in Fig.3a. One pair of redox peaks at vari-



Fig.2 Electrochemical performance of FeCl₃·6H₂O based electrode materials in various aqueous electrolytes: (a~c) Specific capacitances of Fe-based electrodes; (d) Comparison of the CV curves at 2 mV·s⁻¹;
(e) Specific capacitances of Fe-based electrodes; (f) GCD curves at a current density of 3 A·g⁻¹



Fig.3 Electrochemical performance of FeCl₃ electrode in 2 mol·L⁻¹ KOH: (a) CV curves at scan rates from 2 to 50 mV·s⁻¹;
(b) GCD curves tested at various current densities from 3 to 30 A·g⁻¹; (c) Nyquist plots of Fe-based electrode; Insert shows the high frequency region of the plots; (d) Relationship between peak current and sweep rate

ous scan rates was clearly observed. The linear slopes and presence of triangular with respect to the charge and discharge demonstrated that the capacitive characteristic of redox reaction in the electrodes (Fig.3b). The specific capacitances were calculated according to galvanostatic charge and discharge curves. The capacitances were 1 113, 731, 641, 592 and 535 F • g⁻¹ at current densities of 3, 5, 10, 15 and 30 $A \cdot g^{-1}$, respectively. Electrochemical impedance spectroscopy was collected with a frequency ranging from 0.01 to 100 000 Hz at 0 V. Nyquist plots were exhibited in Fig.3c. The insert was the local enlargement in high frequency region, which showed a semicircle. And the intercept on the x-axis was equivalent series resistance with a value of about 0.7 Ω , which was attributed to intrinsic resistance of ionic resistance of electrolyte, and contact resistance with current collector. The b-value was calculated according to CV curves at different scan rates, which was between 0.5 and 1. Diffusion process played a key role in redox reaction. Cycling stability was shown in Fig. S1. Capacitance was maintained 87.4% after 50 cycles.

Electrochemical behavior of the Fe-based electrode materials in 1.5 mol·L⁻¹ NaOH electrolyte were shown in Fig.4. CV curves were measured at the scan rates from 2 to 50 mV \cdot s⁻¹. Galvanostatic charge and discharge measurements were conducted at current densities ranging from 3 to 30 $A \cdot g^{-1}$ (Fig. 4b). The charge and discharge curves were close to ideal capacitive behaviour. The specific capacitance was 927 $F \cdot g^{-1}$ at a current density of 3 $A \cdot g^{-1}$. The value still maintained 622 F·g⁻¹ at 30 A·g⁻¹. Equivalent series resistance was about 0.85 Ω (Fig. 4c), which was higher than that in KOH aqueous solution. In anodic process, the *b*-value was about 0.596. In cathodic process, the *b*value was 0.752, which was higher than that in anodic process. It demonstrated that anodic process could be controlled by diffusion process.

Electrochemical behavior of the Fe - based electrode materials in 2 mol·L⁻¹ LiOH electrolyte were shown in Fig. 5. A pair of redox peak at different scan rates was shown in CV curves (Fig. 5a). Galvanostatic charge and discharge measurements were conducted at current densities ranging from 3 to 30 A·g⁻¹ (Fig. 5b). The specific capacitances were 766, 620 and 540 $\text{F} \cdot \text{g}^{-1}$ at current densities of 3, 5 and 10 $\text{A} \cdot \text{g}^{-1}$, respectively.

Equivalent series resistance was about 1 Ω (Fig. 5c), which was higher than that in KOH and NaOH aqueous



Fig.4 Electrochemical performance of FeCl₃ electrode in 1.5 mol·L⁻¹ NaOH: (a) CV curves at scan rates from 2 to 50 mV·s⁻¹;
(b) GCD curves tested at various current densities from 3 to 30 A·g⁻¹; (c) Nyquist plots of Fe-based electrode; Insert shows the high frequency region of the plots; (d) Relationship between peak current and sweep rate



Fig.5 Electrochemical performance of FeCl₃ electrode in 2 mol·L⁻¹ LiOH: (a) CV curves at scan rates from 2 to 50 mV·s⁻¹;
(b) GCD curves tested at various current densities from 3 to 30 A·g⁻¹; (c) Nyquist plots of Fe-based electrode;
Insert shows the high frequency region of the plots; (d) Relationship between peak current and sweep rate

solution. In anodic process, the *b*-value was about 0.600. In cathodic process, the *b*-value was 0.690, which was similar to that in anodic process.

3 Conclusions

In conclusion, electrochemical interface could be tuned by various electrolytes with kinds of cations to achieve favourable specific capacitances. Fe³⁺ colloidal systems showed the highest specific capacitance of 1 113 $\mathbf{F} \cdot \mathbf{g}^{-1}$ at 3 $\mathbf{A} \cdot \mathbf{g}^{-1}$ in 2 mol·L⁻¹ KOH aqueous electrolyte. The results demonstrated that tuning the kind of electrolytes may tune compositions of Fe-based electrodes to improve electrochemical performance. The active materials were synthesized in a three - electrode cell by in situ reaction, which exhibited superior reactive ability in the measurement conditions. Furthermore, by extending the colloid model, a novel method of in situ composition adjustment to cross-scale control of material properties is provided. This novel method may be applied in synthesizing other electrode materials with high specific capacitance.

Supporting information is available at http://www.wjhxxb.cn

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