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Short communication

Nickel hydroxide/activated carbon composite electrodes for electrochemical capacitors

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Abstract

In this paper, a nickel hydroxide/activated carbon (AC) composite electrode for use in an electrochemical capacitor was prepared by a simple chemical precipitation method. The structure and morphology of nickel hydroxide/AC were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results showed that nano-sized nickel hydroxide was loading on the surface of activated carbon. Electrochemical performance of the composite electrodes with different loading amount was studied by cyclic voltammetry and galvanostatic charge/discharge measurements. It was demonstrated that the introduction of a small amount of nickel hydroxide to activated carbon could promote the specific capacitance of a composite electrode. The composite electrodes have good electrochemical performance and high charge–discharge properties. Moreover, when the loading amount of nickel hydroxide was 6 wt.%, the composite electrode showed a high specific capacitance of 314.5 F g^{-1}, which is 23.3% higher than pure activated carbon (255.1 F g^{-1}). Also, the composite electrochemical capacitor exhibits a stable cyclic life in the potential range of 0–1.0 V.

Keywords: Electrochemical capacitor; Composite electrode; Nickel hydroxide/AC; Specific capacitance

1. Introduction

Electrochemical capacitors (ECs) attract great interest as energy storage devices due to their high power capability and long cycle life. In these ECs, two basic types can be realized using different charge-storage mechanisms [1,2]: (i) electrical double-layer capacitors (EDLCs), mainly focusing on carbon materials [3,4], which utilize the capacitance arising from charge separation at an electrode/electrolyte interface, and (ii) redox electrochemical capacitors, mainly focusing on transition metal oxides [5–7], which utilize the charge-transfer pseudo-capacitance arising from reversible Faradaic reactions.

To take full advantage of the double-layer capacitance and pseudo-capacitance, many metal oxide/carbon composite electrodes have been investigated for ECs [8–12]. Based on electrical double-layer capacitance, activated carbon is very suitable for ECs, and has good conductivity, high surface area, excellent temperature stability and a relatively low cost [3,13]. On the other hand, noble metal-oxide based materials, e.g. RuO_2, exhibiting Faradaic pseudo-capacitance, have also been identified as the ideal electrode materials for ECs. However, the high cost of such metal oxides has stimulated research to identify other cheap materials that exhibit similar behavior, e.g. MnO_2, NiO [14–20]. Thus, recent efforts are aiming at making activated carbon-inexpensive metal oxide composites as electrode materials. Nickel-based compound/activated carbon composites are one of the most commonly used candidates for electrochemical capacitors, such as NiOOH/carbon, NiO/activated carbon [9,21,22]. However, the instability of NiOOH in alkaline electrolyte and the high resistance of NiO limit their practical applications. Recently, nickel hydroxide/activated carbon composite electrode has been extensively studied due to its better electrochemical reversibility and high proton diffusion rate and a better discharge property [23–26].

An analysis of the previous studies showed that fairly high specific capacitances were obtained particularly when a small amount of metal oxide (less than a few tenths of a wt.%) were dispersed on the carbon materials with a very high surface

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area [8,11,14,21,22]. Tai and Teng reported that the specific capacitance of impregnated nickel oxide on porous carbon (1 wt.% nickel oxide) was $220\,F\,g^{-1}$ [21]. Yuan et al. [22] reported electrochemical behavior of activated carbon loaded with nickel oxide and its specific capacitance increase by 10.84% ($175.40 \rightarrow 194.01\,F\,g^{-1}$). In our work, nickel hydroxide/activated carbon composites were prepared by a simple chemical precipitation method. In order to study the increase in capacitance of the composite, we report the enhancement in the specific capacitance of porous carbon loading with small quantity nickel hydroxide. Moreover, we studied the optimal loading amount of $Ni(OH)_2$ and the electrochemical performances of composite electrode when used in electrochemical capacitor.

2. Experimental

2.1. Preparation of nickel hydroxide/AC composite electrode

The porous activated carbon (AC) is supplied by the Activated Carbon Company of Huaxian County in Henan Province, China. Firstly, activated carbon was treated in 2 M H_2SO_4 and HNO_3 solution for 4 h, respectively, and was filtrated and washed with distilled water till the pH value of the filtrate reached 7, then dried at 140°C before the next experimental was done.

The amount of nickel hydroxide loadings were 0–10 wt.%. Nickel hydroxide was loaded by chemical precipitation. Predetermined amounts of activated carbon were added to the $Ni(NO_3)_2$ solution before nickel hydroxide precipitation. Subsequently, NaOH solution was slowly dropped into the above mixed solution, the $Ni(NO_3)_2$/NaOH molar ratio was 1:2. Then, the mixed solution was stirred for 12 h. The precipitated materials were washed with distilled water till the pH value of the filtrate reached 8, they were then dried at a temperature of 140 °C for 8 h under vacuum condition. Then nickel hydroxide/AC composites were obtained.

2.2. Measurement techniques of structural characterization

(1) X-ray diffraction (XRD) of samples was performed on a diffractometer (D/MAX-3C) with Cu Kα radiation ($\lambda = 1.5406$ Å) and a graphite monochromator at 40 kV, 300 mA.
(2) The scanning electron microscopy (SEM) of the samples was performed with a JSM-5600LV (JEOL Microscope).

2.3. Evaluation of electrochemical properties

The mass ratio of activated materials/graphite was 8:1, the powder mixture was mixed with 10 wt.% of polytetrafluoroethylene (PTFE) aqueous suspension (60%) as a binder and mixed well to obtain a paste. The paste was then pressed into the nickel foam substrate using a spatula. After drying under vacuum at 140 °C for 12 h, the electrode was pressed at 20 MPa for 2 min assure a good electronic contact and formed a tablet 20 mm × 15 mm × 0.8 mm in size.

A typical three-electrode test cell in electrolytes at room temperature was used for all electrochemical measurements. The electrolyte was 6 M KOH solution. Nickel hydroxide/AC composites as electrode materials in electrochemical capacitors were characterized using cyclic voltammetry and a galvanostatic charge/discharge test. The cyclic voltammetric behavior of the electrodes was measured by means of electrochemical analyzer systems, CHI660 (CH Instruments, USA). The charge/discharge measurements at constant current were carried out by potentiostat/galvanostat (BS-9300SM, Qingtian Electric Coop., Guangdong, China) on unit cell capacitors, which were constructed with an electrolyte impregnated micro-porous polypropylene film sandwiched between the cathode and anode.

All potentials in this paper are referred to Hg/HgO reference electrode immersed in 6 M KOH electrolyte.

3. Results and discussion

3.1. Material characterization

Fig. 1(a) shows porous surface morphology of nickel hydroxide prepared by chemical precipitation. Particles with diameters ranging from 10 to 100 nm were observed. It can be inferred that nano-sized $Ni(OH)_2$ particles with a highly porous struc-

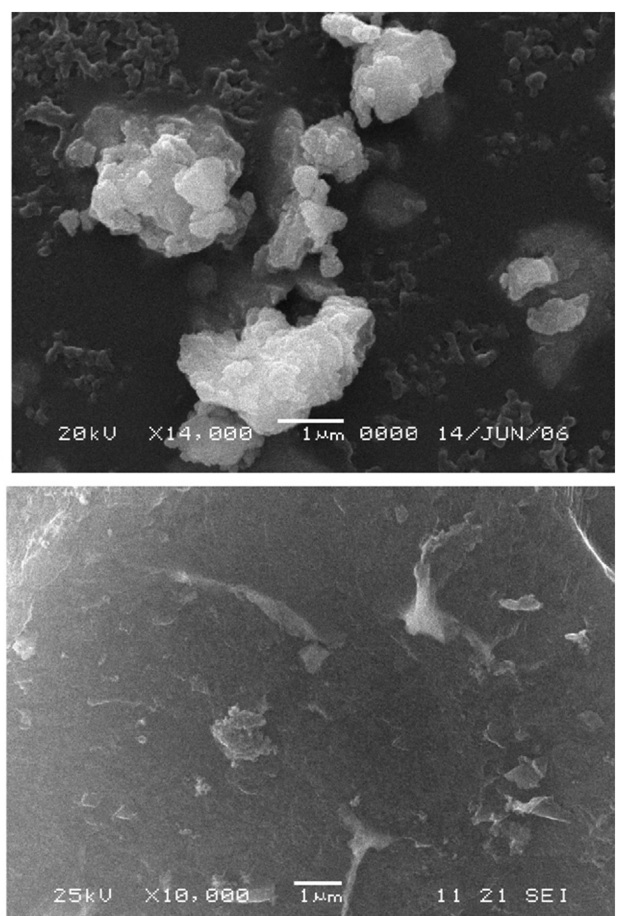
(a)
(b)


Fig. 1. SEM photographs of $Ni(OH)_2$ (a) and AC loading with 6 wt.% $Ni(OH)_2$ (b).

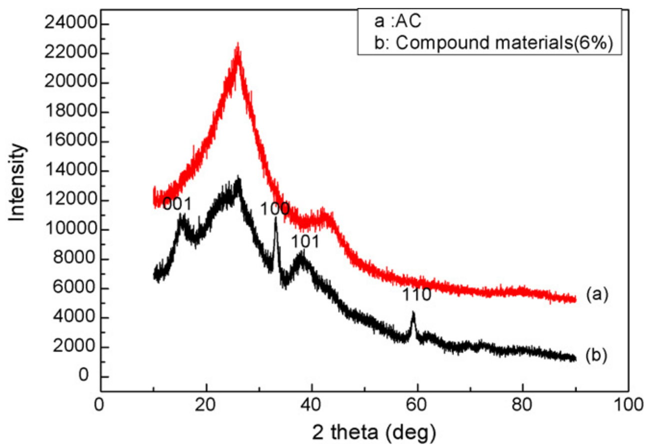


Fig. 2. XRD patterns for AC and nickel hydroxide/AC composite.

ture could deposited onto the surface of activated carbon and some particles would fill the inner big pores of activated carbon, which is confirmed in Fig. 1(b). Although nickel hydroxide is a low conductivity semi-conductor material, the utilization of activated materials can be greatly increased by loading small amount of nickel hydroxide due to good conductivity of activated carbon, thus high specific capacitance value would be obtained.

The XRD patterns of carbon and nickel hydroxide/AC composites were compared in Fig. 2. As the loading amount of $Ni(OH)_2$ in nickel hydroxide/AC composites was very small, only weak diffraction peaks of nickel hydroxide were obtained, which appeared at 18.8, 33.02, 38.2 and 59.87° of 2θ. The result confirms that nickel hydroxide loaded onto the activated carbon is β-$Ni(OH)_2$ [22].

3.2. Electrochemical characterization

CVs for the nickel hydroxide/AC composite electrodes at a scan rate of $2\,mV^{-1}$ are presented in Fig. 3. It can be seen that the CV of activated carbon is nearly symmetrical and shows no redox peaks, indicating that the composite has excellent electrochemical behavior in the application of electrochemical capacitor. Moreover, the CVs of composite electrodes show nearly rectangular shape, which means that the electrodes are charged and discharged at a constant rate over the complete cycle. Note that the CVs of nickel hydroxide/AC composite electrodes have bigger current response and larger surface area of rectangle than those of activated carbon, which suggests that the specific capacitance of composite is higher.

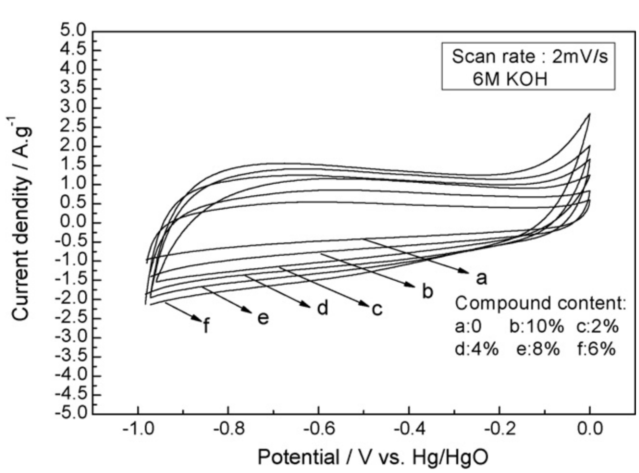


Fig. 3. Cyclic voltammograms of nickel hydroxide/AC electrodes with different $Ni(OH)_2$ content, scan rate: $2\,mV\,s^{-1}$.

Table 1
Capacitances of nickel hydroxide/AC composite with different contents

$Ni(OH)_2$ content (%)	Capacitances of composite electrodes at different scan rates ($F\,g^{-1}$)		
	$2\,mV\,s^{-1}$	$5\,mV\,s^{-1}$	$8\,mV\,s^{-1}$
0	255.1	234.1	213.9
2	292.4	275.2	246.1
4	300.5	289.2	258.1
6	314.5	297.2	272.3
8	302.4	276.2	253.8
10	260.9	237.5	224.6

The specific capacitance of composite electrodes were estimated from the following equation [7,12]:

$$C_{s.t} = \frac{I_a + |I_c|}{2W(dV/dt)} \quad (1)$$

where I_a and I_c are the current of anodic and cathodic voltammetric curves on positive and negative (A), respectively, W the mass of the composites (g), and dV/dt is the scan rate ($V\,s^{-1}$).

Table 1 tabulates the specific capacitances of composites materials with different mass loading, which were measured in 6 M KOH solution and calculated according to Eq. (1). Note that the increase in the specific capacitance was observed up to a small mass loading. The increase of specific capacitance for a composite electrode loading of 2 wt.% $Ni(OH)_2$ was 14.6% ($255.1 \rightarrow 292.4\,F\,g^{-1}$) at a scan rate of $2\,mV\,s^{-1}$. When the mass loading increased to 6 wt.%, the average increase rate in capacitance was 23.3% ($255.1 \rightarrow 314.5\,F\,g^{-1}$) which is better than the results reported by Yuan et al. [22]. Moreover, when the loading amount increased to 10 wt.%, the specific capacitance nearly unchanged compared with pure activated carbon. This can be attributed to the loss of the double-layer capacitance of carbon, increase in particle size of $Ni(OH)_2$, aggregation of $Ni(OH)_2$, etc. [11,12] and decrease of the path of ions.

The introduction of nickel hydroxide can produce the Faradaic pseudo-capacitance; at the same time, activated carbon with a high specific area can provide both a large double-layer capacitance and an excellent conductivity, thus the specific capacitance of composite electrode, which was a combination of double-layer capacitance and Faradaic pseudo-capacitance, can be promoted greatly [8,14,16].

The relationship between potential scanning rate and the specific capacitance of composite electrodes are presented in Fig. 4. It exhibits that the specific capacitance decreases with the increasing scan rate, which may be caused by an effective ions transport into the pores of active materials and small concentration polarization at the low scan rate; while at a higher scan

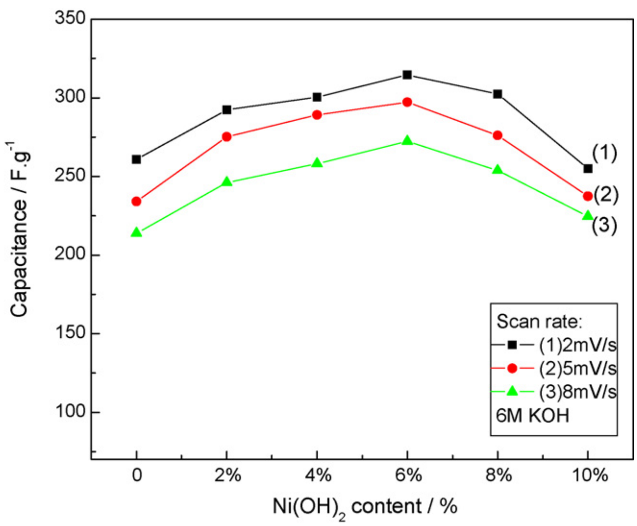


Fig. 4. Effects of CV scan rate on the specific capacitances of electrodes with different $Ni(OH)_2$ content in 6 M KOH electrolyte.

rate, some active surface areas are inaccessible for charge storage [12,25] and big concentration polarization easily appeared. Moreover, it can be seen more clearly that optimal loading amount of $Ni(OH)_2$ was about 6 wt.%.

Charge/discharge behaviors of the AC and nickel hydroxide/AC electrodes in the potential range between 0 and 1.0 V in 6 M KOH solution at 2 mA are given in Fig. 5. It can be found from the curves that the capacitor voltage varies nearly linearly with time, which indicates good capacitive behavior. The average specific capacitance of AC and nickel hydroxide/AC can be calculated on the basis of Eq. (2) [12,25]:

$$C = \frac{2Q}{mV} = \frac{2 \times 3600 \times 0.001C^*}{mV} = \frac{7.2C^*}{mV} \qquad (2)$$

where C is the specific capacitance of the electrochemical capacitor ($F\,g^{-1}$), Q the electric quantity (C), C^* the capacitance measured (mA h), m the weight of single electrode (g), and V is the range of the charge/discharge (V).

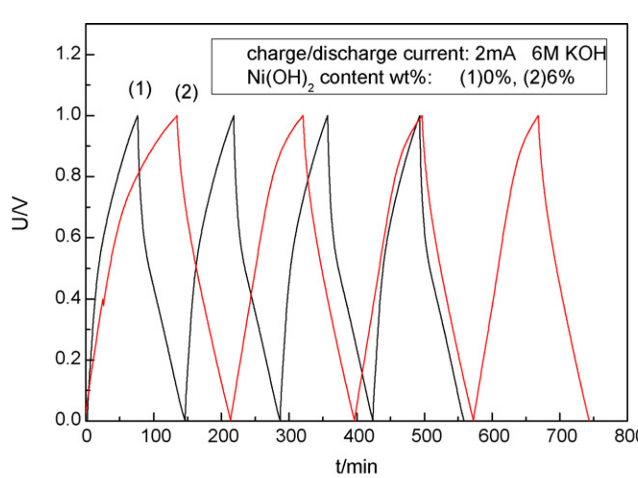


Fig. 5. Charge/discharge curves of AC and nickel hydroxide/AC electrochemical capacitors.

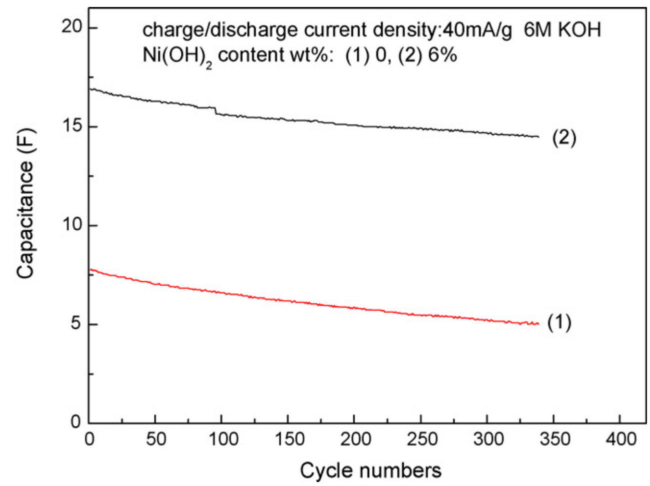


Fig. 6. Discharge capacitance as a function of cycle number for AC and nickel hydroxide/AC electrochemical capacitors.

The average specific capacitance of activated carbon loading with 6 wt.% $Ni(OH)_2$ obtained from the charge/discharge curves on the basis of Eq. (2) is 309.1 $F\,g^{-1}$, which is increased by 25.9% than pure activated carbon (245.6 $F\,g^{-1}$). The result is identical with the results estimated from the CV curves. It is most likely that there is a significant increase in the capacitance due to a pseudo-capacitance of $Ni(OH)_2$.

The stability of the prepared capacitors can be examined by repeated charge–discharge cycling. Capacitors were charged and discharged between 0 and 1.0 V at 40 $mA\,g^{-1}$ in 6 M KOH solution to confirm the stability. The variations of the discharge capacitance with cycle number are illustrated in Fig. 6. The results exhibit that the capacitor of nickel hydroxide/AC composite has a higher specific capacitance than activated carbon.

Based on the above results, the introduction of 6 wt.% nickel hydroxide into activated carbon can promote both the capacitance of electrode and its cycle life. Hence, this material is a suitable electro-active material for application to electrochemical capacitors.

4. Conclusions

In this paper, nickel hydroxide/activated carbon composite electrodes were prepared by a simple chemical precipitation method and characterized for application to electrochemical capacitors. The XRD pattern and SEM images indicated that some nanometer-scale amorphous particles of nickel hydroxide were loaded onto activated carbon. The results suggest that small amounts of nickel hydroxide could also promote the specific capacitance of composites when loading onto activated carbon. They also showed that the optimal loading amount of nickel hydroxide is about 6 wt.%, for an increase of 23.3% in capacitance (255.1 → 314.5 $F\,g^{-1}$). Moreover, the nickel hydroxide/AC electrochemical capacitor has stable electrochemical properties and a long cycle life, which indicates that it is a promising material for electrochemical capacitors.

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