

Short communication

A new type of $\text{MnO}_2 \cdot x\text{H}_2\text{O}/\text{CRF}$ composite electrode for supercapacitors

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Abstract

In this paper, $\text{MnO}_2 \cdot x\text{H}_2\text{O}/\text{carbon aerogel (CRF)}$ composite electrode materials were prepared by a chemical co-precipitation method. The structure and morphology of $\text{MnO}_2 \cdot x\text{H}_2\text{O}/\text{CRF}$ were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results showed that carbon aerogel was an amorphous material with a pearly network structure, the $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ powders possessed, a nanoscaled structure, and thus the $\text{MnO}_2 \cdot x\text{H}_2\text{O}/\text{CRF}$ composite materials were nano-sized particles with a relatively high specific surface area. Electrochemical performance of the composite electrodes with different ratio's was studied by cyclic voltammetry and galvanostatic charge/discharge measurements. The results indicated that $\text{MnO}_2 \cdot x\text{H}_2\text{O}/\text{CRF}$ composite electrodes had good electrochemical performance, high reversibility and high charge–discharge properties. Moreover, when the loading amount of $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ was 60%, the composite material has a high specific capacitance of 226.3 F g^{-1} , while the capacitance of carbon aerogel electrode alone was 112 F g^{-1} . Besides, $\text{MnO}_2 \cdot x\text{H}_2\text{O}/\text{CRF}$ composite supercapacitors showed a stable cycle life in the potential range of 0–1.0 V and retained 90% of initial capacitance over 400 cycles.

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Keywords: Supercapacitor; Electrode material; Carbon aerogel; $\text{MnO}_2 \cdot x\text{H}_2\text{O}$; $\text{MnO}_2 \cdot x\text{H}_2\text{O}/\text{CRF}$ composite material; Specific capacitance

1. Introduction

Supercapacitors, or electric double-layer capacitors, or electrochemical capacitors, have a much lower energy density, a higher power density, and a much longer shelf and cycle life than batteries [1]. Due to these properties, supercapacitors have potential applications in various power and energy applications, such as hybrid vehicles, portable computers, nano-electronics, burst power generation, and memory back-up devices. In supercapacitors, energy is stored in terms of both double-layer and pseudo-capacitance. Carbon materials with a high surface area are widely used for double layer capacitors, which utilize the capacitance arising from charge separation at an electrode/electrolyte interface, but this type supercapacitor has limited energy capacity and power output. Redox supercapacitors utilize the charge-transfer pseudocapacitance arising from reversible Faradaic reactions occurring at the electrode surface. Subsequently, carbon materials and transition metal oxides, such as hydrous RuO_2 , NiO , and MnO_2 have been identified as pos-

sible electrode materials for a high power and higher energy density supercapacitor. Recently, composite materials for supercapacitors have been developed, which are based on a combination of double layer capacitance and Faradaic pseudocapacitance [2–5].

Carbon aerogels, which are highly porous materials, represent promising and innovative materials because of their attractive properties such as a high electrical conductivity ($25\text{--}100 \text{ S cm}^{-1}$), a high porosity (80–98%), controllable pore structure and high surface area (up to $1100 \text{ m}^2 \text{ g}^{-1}$) for double-layer formation, are very suitable for supercapacitors and rechargeable batteries [6–8]. MnO_2 is a promising supercapacitor material due to low cost of the raw material, high specific capacitance, good electrochemical performance and environmentally friendly nature. There have been a lot of reports on MnO_2 preparation technologies, such as a co-precipitation method, a thermal decomposition method, a sol–gel method and so on [9–12].

In this paper, $\text{MnO}_2 \cdot x\text{H}_2\text{O}/\text{CRF}$ composite electrode materials were prepared by a chemical co-precipitation method. The electrochemical performances of $\text{MnO}_2 \cdot x\text{H}_2\text{O}$, CRF and $\text{MnO}_2 \cdot x\text{H}_2\text{O}/\text{CRF}$ composite electrode for supercapacitors were investigated. The composite electrode materials are expected to

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greatly improve the performance of the supercapacitors, which enable supercapacitors to provide both high energy and high power capability for various applications.

2. Experimental

2.1. Preparation of $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ /CRF composite electrode

The carbon aerogel was derived from pyrolysis of a resorcinol–formaldehyde (RF) gel. The molar ratio of formaldehyde to resorcinol was held at a constant value of 2, Na_2CO_3 was used as the catalyst [12]. It was dissolved in distilled water, the mass percentage of the reactants in solution was set at $\text{RF} = 40\%$, and the molar ratio of resorcinol (R) to catalyst (C) was set at $\text{R/C} = 1500$. Sol–gel polymerization of the mixture was carried out in a sealed glass cylinder by holding the mixture at 298 K for 24 h, at 333 K for 72 h, and at 353 K for 48 h. The wet gels were held at 323 K for 6 days, and then RF gels were dried under ambient conditions for 3 days. After the drying process, the carbon aerogels were obtained by carbonization at 1073 K for 3 h under a flow of pure Ar gas.

$\text{MnO}_2 \cdot x\text{H}_2\text{O}$ was prepared by chemical co-precipitation. Predetermined amounts of carbon aerogel (0, 20, 40, 60, 80, 100 wt.%) were added to the KMnO_4 solution before MnO_2 precipitation. Subsequently, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was dropped into the above mixed solution, the $\text{KMnO}_4/\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ molar ratio was 2:3. Then, the mixed solution was stirred for 4 h using ultrasonic waves. The precipitated materials were washed with distilled water till the pH value of the filtrate reached 7, they were then dried at a temperature of 353 K for 12 h. Then $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ /CRF composite materials 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 $\text{K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) and a graphite monochromator at 50 kV, 100 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 9:1, the powder mixture was mixed with 5 wt.% polytetrafluoroethylene (PTFE) (60%) used as a binder and kneaded to obtain a paste, the paste was pressed into the nickel foam substrate using a spatula, dried at 353 K for 12 h, and then pressed at 15 MPa for 1 min in order to assure a good electrical contact. A typical three-electrode test cell in electrolytes at room temperature was used for all electrochemical measurements. The electrolyte was 6 M KOH. $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ /CRF composite materials as electrode materials in supercapacitors were characterized using cyclic voltammetry and a galvanostatic charge–discharge test. Galvanostatic charge/discharge behavior was performed under the application of a constant current in the voltage range

of 0–1.0 V. All the measurements were carried out at room temperature.

3. Results and discussion

The energy storage of supercapacitors is the accumulation of ionic charges which occur in the double-layer at the electrode/electrolyte interface, the high surface area and the porosity of the carbon aerogels are the basic requirements to achieve formation of a double-layer. Besides carbon aerogels are novel mesoporous carbon materials with an electrically conductive carbon network, a low density, and other interesting properties [13–16], but it only possesses a double layer capacitance. In order to further enhance the specific capacitance of carbon-based capacitors, much attention has been placed on composite electrode materials which consist of metal oxide for electrochemical capacitors [3–5]. $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ is often used as the electrode material of a supercapacitor, however $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ is a semi-conducting material and has a low electronic conductivity. To improve the conductivity of $\text{MnO}_2 \cdot x\text{H}_2\text{O}$, nano- $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ was deposited in carbon aerogels in this study. The carbon aerogel possess an open porous network, which facilitates contact between the electrolyte and the active mass of the nanocomposite, allowing more energy to be extracted from $\text{MnO}_2 \cdot x\text{H}_2\text{O}$. Therefore, a $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ /CRF composite consisting of redox species and carbon aerogels with high electrical conductivity are considered to be a promising electrode material for a supercapacitor.

The carbon aerogels, $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ particles and composite materials prepared in this work were examined using SEM photographs and these typical results are shown in Fig. 1. As can be seen in the Fig. 1a, the hydrated MnO_2 is composed of many nanoparticles of 50–80 nm with the network structure. In Fig. 1b, it was found that the structure of the aerogel obtained by ambient drying of wet RF gels is the same as the aerogel prepared by conventional supercritical drying. The carbon aerogels consisted of a three-dimensional network of interconnected carbon particles with a larger percentage of big pores, it is an amorphous material with a pearly network structure, and a controllable pore structure and a highly useable surface area which makes carbon aerogels very suitable for supercapacitors. Fig. 1c is the SEM photograph of a $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ /CRF composite material with content of 60% $\text{MnO}_2 \cdot x\text{H}_2\text{O}$. It is seen that nanosized $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ particles were uniformly deposited onto the surface of porous carbon aerogels and filled the inner big pores of the CRF. Due to high conductivity of the porous carbon aerogels, the utilization of activated materials can be greatly increased, thus the specific capacitance of this composite material would be highly increased. This improves homogeneity is attributed to the pearly network structure of CRF, which improves the connectivity of the MnO_2 particles.

Typical XRD patterns for CRF, $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ and $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ /CRF are shown in Fig. 2. In Fig. 2a, the XRD measurement shows the structure of carbon aerogel, it provides strong C (002) and weak C (101) diffraction lines at 2θ (Cu $\text{K}\alpha$) of 23.5° and 43.8° , respectively. The carbon aerogel can be regarded as partly graphitized carbon, though

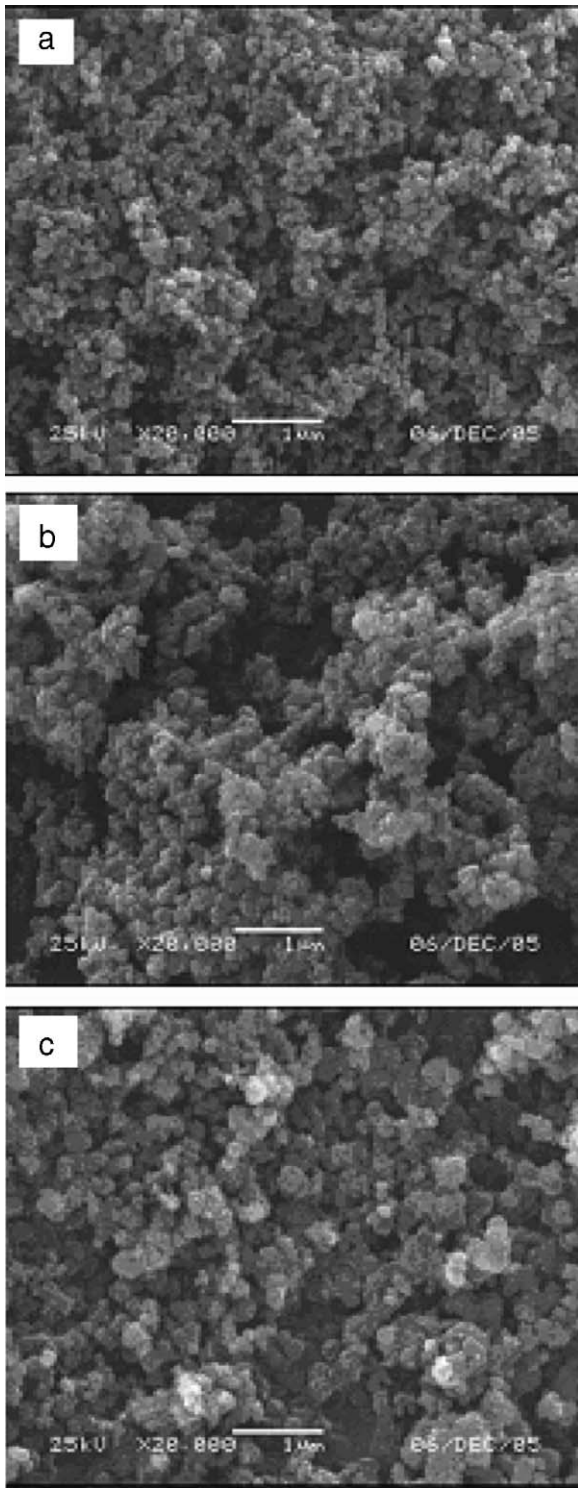


Fig. 1. SEM photographs of MnO₂·xH₂O(a), CRF(b) and MnO₂·xH₂O/CRF(c).

it differs from graphite. Hence, carbon aerogels have high electrical conductivity. The XRD patterns for MnO₂·xH₂O are seen from Fig. 2c. All patterns demonstrate that the prepared MnO₂·xH₂O has a poor crystalline structure, the intensities of the broad diffraction peaks corresponding to MnO₂·xH₂O, 12.3°, 24.7°, 38.6° and 65.6°, are very low. Comparing with the diffraction peak positions of MnO₂·xH₂O, the diffraction

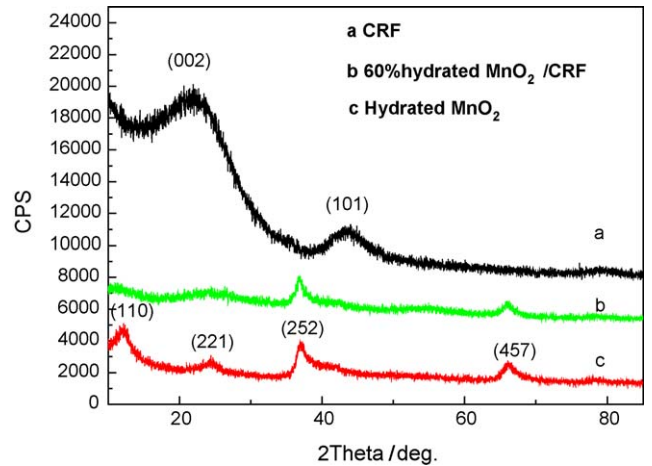


Fig. 2. XRD patterns of CRF, MnO₂·xH₂O and MnO₂·xH₂O/CRF.

peak positions of the MnO₂·xH₂O/CRF composite (Fig. 2b) are not apparently shifted. The results suggest that MnO₂·xH₂O is loaded on carbon aerogels and the structure of hydrated MnO₂ is not significantly influenced due to the presence of carbon aerogels.

Cyclic voltammograms for the MnO₂·xH₂O/CRF composite electrodes (versus Hg/HgO) at a scan rate of 5 mV s⁻¹ are shown in Fig. 3. The carbon aerogel electrode exhibited excellent electrochemical behavior, it is very symmetrical, while the CV curve of MnO₂·xH₂O electrode is distorted, and it is suggested that the reversibility of the MnO₂·xH₂O electrode is not good in this potential range. But the charging/discharging process of the MnO₂·xH₂O/CRF composite electrode is more reversible than that of MnO₂·xH₂O electrode, the profiles of the three electrodes have rectangular-like shapes. As the content of MnO₂·xH₂O increases, the profiles become gradually depressed, the CV curves of composite electrodes become distorted from mirror image symmetry. From the CV curves, the capacitances of MnO₂·xH₂O/CRF composite electrodes are larger than that of the carbon aerogel electrode based on double layer capacitance

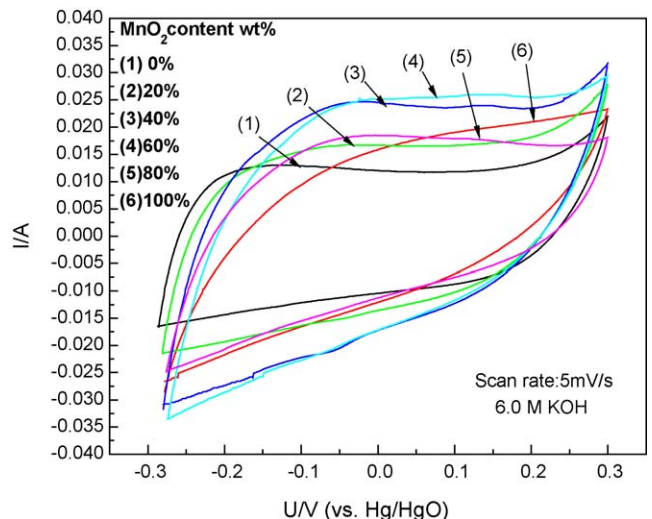


Fig. 3. CV curves of MnO₂·xH₂O/CRF electrodes with different MnO₂·xH₂O content, scan rate: 5 mV s⁻¹.

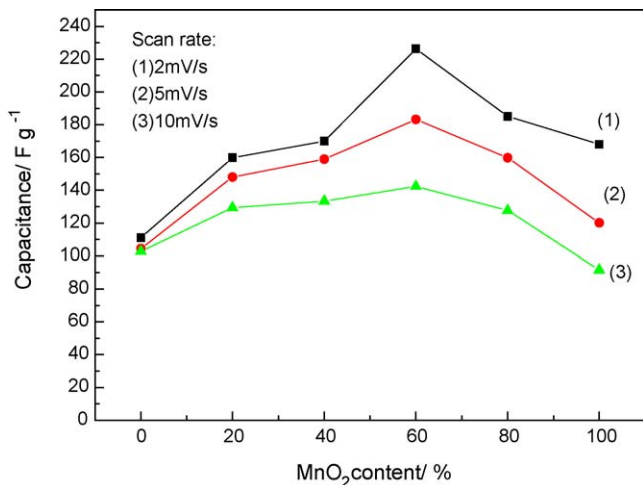
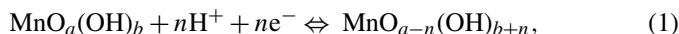


Fig. 4. Specific capacitances of electrodes with different MnO₂ content in various scan rates.

and the MnO₂·xH₂O electrode. It is well-known that the capacitance of carbon aerogels is based on the adsorbed charges on the electrode/electrolyte interface; this type of supercapacitor has limited energy capacity. However, CV curves of MnO₂·xH₂O or MnO₂·xH₂O/CRF composite are different from that of carbon aerogels, due to a Faradic reaction of MnO₂·xH₂O, as follows [17]:



where MnO_a(OH)_b and MnO_{a-n}(OH)_{b+n} indicate interfacial MnO₂·xH₂O at high and low oxidation states, respectively.

To analyze the variation of capacitance with the scan rate, the CV curves were measured in KOH electrolyte. The specific capacitance of the electrodes can be estimated from the following equation [18]:

$$C_{\text{st}} = \frac{I_a + |I_c|}{2W(dV/dt)}, \quad (2)$$

where I_a , I_c , W and dV/dt are the current of anodic and cathodic voltammetric curves on positive and negative sweeps, mass of the composite, and the sweep rate, respectively.

Specific capacitances of composite electrodes with different scan rates are given in Fig. 4. It can be seen that as the scan rate increases, the specific capacitance of composite electrode is gradually increased. There is an initial increase in the values of specific capacitance with an increase in amount of MnO₂·xH₂O. When the loading mass of MnO₂·xH₂O was 60%, the specific capacitance of MnO₂·xH₂O/CRF reached 226.3 F g⁻¹, while the capacitance of carbon aerogel electrode was only 112 F g⁻¹; when MnO₂·xH₂O loadings are over 60 wt.%, the specific capacitance of the composite material decreases. It was suggested that amount of MnO₂·xH₂O/CRF a optima was about 60%.

Carbon aerogels are highly porous materials, MnO₂·xH₂O are deposited on the surface or pores of the carbon aerogel, the introduction of MnO₂·xH₂O in carbon aerogels can promote the conductivity of MnO₂·xH₂O. On the other hand, the composite electrodes are based on a combination of double

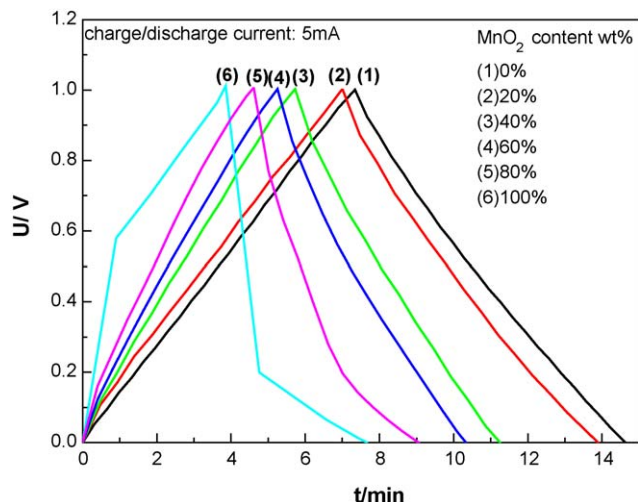


Fig. 5. Charge/discharge curves of carbon aerogel, MnO₂·xH₂O and MnO₂·xH₂O/CRF supercapacitors.

layer capacitance and Faradaic pseudocapacitance, so the specific capacitance can markedly increased.

In order to gain a further understanding on the electrochemical performance of MnO₂·xH₂O/CRF composite materials, the charge/discharge curves of composite electrodes measured in 6 M KOH at 5 mA are shown in Fig. 5, respectively. The electrodes have stable electrochemical properties in 6 M KOH electrolytes, the capacitor voltage varies linearly with time during both charging and discharging no voltage drop was observed during the discharge process, giving high values of charge/discharge efficiency, but due to the Faradaic reactions, the electrochemical reversibility of the MnO₂·xH₂O supercapacitor was poor. In general, the $E-t$ relationships on these chronopotentiograms are approximately linear, indicating that the MnO₂·xH₂O/CRF electrodes behave as capacitors and have a good cycling stability. The specific capacitance of the supercapacitor can be calculated by the following equation [12]:

$$C = 2 \times \frac{Q}{mV} = 2 \times 3600 \times 0.001 \times \frac{C^*}{mV} = 7.2 \times \frac{C^*}{mV}, \quad (3)$$

where C is the specific capacitance of the supercapacitor, F g⁻¹; Q is electric quantity, C; C^* is the capacitance measured, mAh; M is the weight of simple electrode, g; V is the range of the charge/discharge, V.

Based on the experimental results of Fig. 5, it can be found through calculation of Eq. (2) that the highest capacitance of the MnO₂·xH₂O/CRF supercapacitor was up to 38.6 F g⁻¹, moreover, this specific capacitance value is much higher than the specific capacitance of a carbon aerogel supercapacitor which was 28 F g⁻¹ [12]. It is most likely that there is a significant increase in the capacitance due to a pseudocapacitance of MnO₂·xH₂O. Hence, this material is a suitable electroactive material for supercapacitors.

The cycle life of the MnO₂·xH₂O/CRF supercapacitor is also illustrated in Fig. 6, the specific capacitances of the electrode materials are given as a function of cycle number. The test of cycle life was performed under constant-current (10 mA)

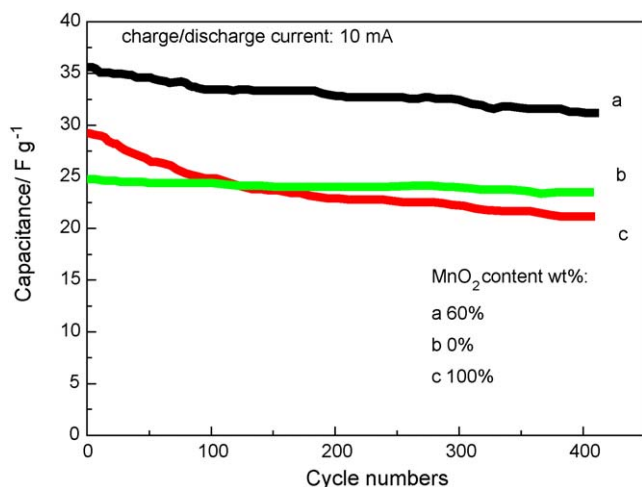


Fig. 6. Cycle life of carbon aerogel, $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ and $\text{MnO}_2 \cdot x\text{H}_2\text{O}/\text{CRF}$ supercapacitors.

conditions. In Fig. 6 (b), the carbon aerogel capacitor has demonstrated a very long cycle life under shallow depths of discharge, but the specific capacitance is lower than the composite material. In Fig. 6(c), it is obvious that the loss of specific capacitance of a $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ supercapacitor is large; in contrast, in Fig. 6 (a), the loss of specific capacitance of $\text{MnO}_2 \cdot x\text{H}_2\text{O}/\text{CRF}$ composite supercapacitor was small and showed a stable cycle life in the potential range of 0–1.0 V, capacitance retention of about 90% was found over 400 cycles. Such a low decrease in specific capacitance after the long charge/discharge cycling test indicates the high stability of the composite and its potential as an electrode material for long-term capacitor applications. Based on the above results, the introduction of $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ can promote the capacitance, and carbon aerogel can improve the stability and the cycle life of the composite materials.

4. Conclusions

In this paper, the preparation of a novel electrode material- $\text{MnO}_2 \cdot x\text{H}_2\text{O}/\text{CRF}$ composite and its electrochemical performance have been studied. Various contents of $\text{MnO}_2 \cdot x\text{H}_2\text{O}/\text{CRF}$ composite electrodes were synthesized successfully by a chemical co-precipitation method. Through XRD examinations and SEM studies, it has been demonstrated that a carbon aerogel is a partly graphitized amorphous material with a pearly net-

work structure, and the $\text{MnO}_2 \cdot x\text{H}_2\text{O}/\text{CRF}$ composite material is a nanoscaled material with a network structure. The optimum amount $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ ratio in the composite material was 60 wt.%, and the specific capacitance of a composite electrode in 6 M KOH electrolyte was approximately 226.3 F g^{-1} , which is two times higher than that of a carbon aerogel electrode. The $\text{MnO}_2 \cdot x\text{H}_2\text{O}/\text{CRF}$ supercapacitor has stable electrochemical properties, excellent reversibility and a long cycle life. Thus it can be concluded that a $\text{MnO}_2 \cdot x\text{H}_2\text{O}/\text{CRF}$ composite can be considered as a promising material for supercapacitors.

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References

- [1] A. Burke, *J. Power Sources* 91 (2000) 37.
- [2] C. Portet, P.L. Taberna, P. Simon, E. Flahaut, C. Laberty-Robert, *Electrochim. Acta* 50 (2005) 4174.
- [3] W.C. Chen, C.C. Hu, C.C. Wang, *J. Power Sources* 125 (2004) 292.
- [4] P.R. Kalakodimi, M. Norio, *Electrochem. Solid-State Lett.* 7–11 (2004) 425.
- [5] W. Gui-Xin, Z. Bo-Lan, Y. Zuo-Long, *Solid State Ionics* 176 (2005) 1169.
- [6] Y.Z. Wei, B. Fang, S. Iwasa, M. Kumagai, *J. Power Sources* 141 (2005) 386.
- [7] T.F. Baumann, J.H. Satcher, *J. Non-Cryst. Solids* 350 (2004) 120.
- [8] S. Gavalda, K.E. Gubbins, Y. Hanzawa, et al., *Langmuir* 18 (2002) 2141.
- [9] N.R. Reddy, G.R. Reddy, *J. Power Sources* 124 (2003) 330.
- [10] Y.U. Jeong, A. Manthiram, *J. Electrochem. Soc.* 149 (2002) 1419.
- [11] X.Y. Chen, X. Li, Y. Jiang, *Solid State Commun.* 136 (2005) 94.
- [12] J. Li, X.Y. Wang, Q.H. Huang et al. *J. Power Sources*, 2005, in press.
- [13] S.J. Kim, S.W. Hwang, S.H. Hyun, *J. Mater. Sci.* 40 (2005) 725.
- [14] R. Saliger, V. Bock, R. Petricevic, et al., *J. Non-Cryst. Solids* 221 (1997) 144.
- [15] R. Saliger, U. Fischer, C. Herta, J. Fricke, *J. Non-Cryst. Solids* 225 (1998) 81.
- [16] R.W. Pekala, J.C. Farmer, C.T. Alviso, et al., *J. Non-Cryst. Solids* 225 (1998) 74.
- [17] E. Raymundo-Pinero, V. Khomenko, E. Frackowiak, *J. Electrochem. Soc.* 152 (2005) 229.
- [18] X.Y. Wang, X.Y. Wang, W.G. Huang, *J. Power Sources* 140 (2005) 211.