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ARTICLE

Electrochemical Property of Ru-Mn-AC Multi-Element Composite Electrode Materials

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Abstract: In order to improve the performances of electrode materials for super-capacitors, multi-element composite electrodes were prepared using RuO_2 and MnO_2 as active materials，and active carbon as basic materials. Good electrochemical performances of the composite electrodes were confirmed by cyclic voltammetry, galvano static charge/discharge and ac impedance measurements. When the content of MnO_2 is 20wt% in composite electrode materials, the specific capacitance of MnO_2/AC composite electrodes can reach 128 F/g with a resistance of 2.62 Ω. When the contents of RuO_2 and MnO_2 are separately 20wt% in composite electrode materials, the specific capacitance of RuO_2/MnO_2/AC composite electrodes can reach 266 F/g with a resistance of 0.86 Ω almost without any change of capacitance during 1500 cycles of charge/discharge. It is indicated that the multi-factor composite electrodes with RuO_2/ MnO_2 / AC are ideal electrode materials for super-capacitors.

Key Words: super-capacitor; composite electrodes; RuO_2; MnO_2; specific capacitance

Supercapacitor has been recognized as a promising device exhibiting high power and energy density characteristics with long cycle life for energy storage and management in future power sources, such as pulse source and UPS. Recently, the studies of electrode materials that generally would determine the performance of supercapacitor have been focused on the synthesis of composite materials and nano materials and the improvement of impedance and frequency properties of supercapacitor.[1~3] Active carbon (AC) is a favored choice for electrode materials from their accessibility and low cost. However, due to the high resistance, their usage is rather limited.[4] One approach to enhance the performance of electrodes is to add active materials (such as $RuO_2{\cdot}xH_2O$ and MnO_2) into AC.[5,6] In this work the composite electrodes composed of the AC, $RuO_2{\cdot}xH_2O$ and MnO_2 are investigated.

1 Experimental

1.1 Electrode material preparation

0.3 mol/L NaOH solution was slowly dropped into the stirred 0.1 mol/L $RuCl_3{\cdot}\boldsymbol{x}H_2O$ solution until PH ≈ 7. Then, the precipitates were found after sedimentation, and then washed with distillated water for several times. Finally, amorphous hydrous ruthenium oxide powders were formed by drying at 150 °C for 10 h in air.[7]

For MnO_2 synthesis, 0.17 mol /L $KMNO_4$ solution was added slowly into the 0.15 mol/L Mn $(CH_3COO)_2$ solution and kept stirring vigorously for 6 h using PEG400 as the dispersant in this reaction. The products after sedimentation were washed with distillated water for three times and then with absolute alcohol for the last time. These clean precipitates were dried at 110 °C to yield the amorphous manganese oxide powder of dark brown colour.[8]

1.2 Electrode preparation

The AC well-mixed with the active material (MnO_2 and $RuO_2{\cdot}xH_2O$) in special mass ratios, as seen in Table.1, was ground with 5% PTFE in agate mortar and rolled into a film with a thickness of 0.2 mm, then pressed on Ta current collector. The size of the electrodes was 1 cm×1 cm. The obtained electrodes were marked as 1#~6# with different parameters as Table 1, respectively.

1.3 Electrochemical experiment

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Table 1 Performance parameters of composite electrodes

Sample	C:Mn:Ru, ω/%	C_p/ $F \cdot g^{-1}$	ESR/ Ω	f/Hz
1#	100:0:0	90	3.5	37110
2#	40:60:0	95	2.4	37110
3#	60:40:0	117	2.57	29390
4#	80:20:0	128	2.62	28900
5#	70:20:10	130	1.91	37110
6#	60:20:20	266	0.86	37110

The electrochemical measurements were performed by means of an electrochemical analyzer system, CHI660A, in 30% H_2SO_4 solution at room temperature.

Cyclic Voltammetry (CV) was tested in a three-electrode cell assembly using a given electrode as the working electrode, a saturation calomel as the reference electrode and a Pt wire as the counter electrode in the potential range of –0.6 to +0.4 V at 2 mV/s.

Impedance spectroscopy and constant current (charge/discharge) measurements were carried out with the system of two same composite electrodes separated by a separator. Impedance analyzer was made over the frequency range from10 kHz to 0.1 Hz with an ac signal of 5 mV. The charge-discharge curves were obtained at 2 and 20 mA in the potential range of 0 to 1 V.

1.4 X-ray diffraction (XRD)

XRD analysis was performed with Cu Kα radiation (0.154060 nm) at 2θ=20º~100º

2 Results and discussion

2.1 Cyclic voltammetry measurements

Curves shown in Fig.1 represent the cyclic voltammograms of the composite electrodes prepared in this work. The symmetric curves have good reversibility from –0.4 to +0.6 V, indicating typical capacitive behavior. From the comparison of curve 1# (pure AC) with 4# (AC with 20wt% MnO_2), better capacitive response is found on curve 4#. But increasing the amount of MnO_2 from 40wt% to 60wt%, the capacities instead decrease as shown in curve 3# and 2#. The result reveals that the proper content of MnO_2 in AC materials can improve the specific surface and capacitance of composite electrode materials. Moreover, the use of $RuO_2 \cdot xH_2O$ in composite electrodes of AC with MnO_2 powders has obviously increased the capacity. The curve 5# and 6# exhibit that the capacities are both larger than that of curve 1#~3# with increasing the amount of $RuO_2 \cdot xH_2O$, especially the curve 6#. Due to the high specific surface of AC, the active material particles ($RuO_2 \cdot xH_2O$ and MnO_2) were compounded into the surface and inner pores of AC, making easier contact between the active material and the electrolyte.[9] It reveals that the capacitance of composite electrodes is consisted of the double layer capacitance of active carbon and pseudo capacitance of active material. Thus, the double layer capacitive characteristic of AC and the cost performance can be significantly improved by the combination of pseudo capacitive of $RuO_2 \cdot xH_2O$ and MnO_2.

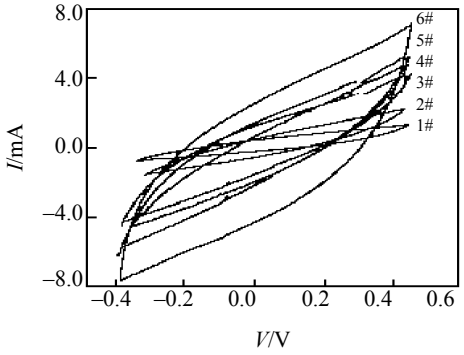

Fig.1 CV curves of composite electrodes

2.2 Impedance measurements

Fig.2 shows the Nyquist plots of the composite electrodes. The results reveal that the ESR and frequency responses f are influenced by the amount of the active materials. It can be observed that the ESR decreases but f increase with increasing the amount of MnO_2 from the comparison of curve 2# with 4#, indicating that the impendence and frequency characteristic were enhanced, as listed in Table 1. The phenomenon is attributable to the distance decrease of electron transfer and the enhancement of electrode conductivity and electron transfer rate when the particles of active carbon are in good contact with the active oxide. The resistance of electrodes composed of AC, $RuO_2 \cdot xH_2O$ and MnO_2 after increasing the amount of $RuO_2 \cdot xH_2O$ was improved from 1.91 to 0.86 Ω as seen in curve 5# and 6#. It indicates that the hydrous ions of $RuO_2 \cdot xH_2O$ has resulted in the ions of electrolyte into the bulk electrodes, not only shortening the diffusion pathway of electrolyte, but accelerating the reversible redox reaction.[10,11]

2.3 Constant current measurements

Based on the results and discussion of 3.1 and 3.2, sample electrode 6# that has larger capacity and lower resistance is a suitable material for supercapacitors. The charge-discharge curves measured at 2 and 20 mA for 6# electrodes are shown in Fig.3, indicating that it has a linear characteristic of charge-discharge rate with current. In addition, its stability has been confirmed from the cycling performance of specific capacitance as shown in Fig.4. Note that the specific capacitance C_P increases initially, reaches a maximum after dozens of cycles that due to the activation reaction of the active material[12], and then is much more stable in the following 1500 cycles.

The result implies that the electrode can be operated with acceptable stability. The specific capacitance can be estimated from the following equation:

$$C_P = \frac{4i}{m\mathrm{d}V/\mathrm{d}t} \quad (1)$$

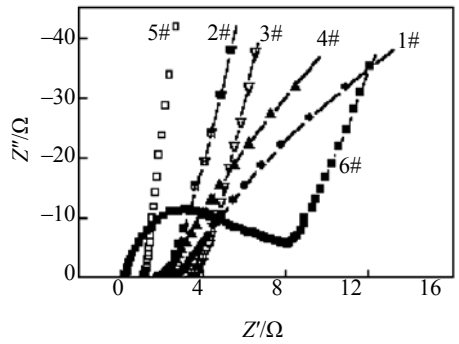

Fig.2 Nyquist plots of composite electrodes

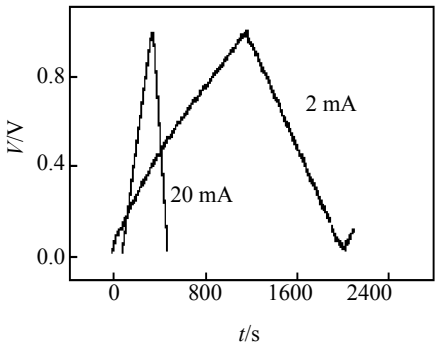

Fig.3 Charge/discharge curves of supercapacitor

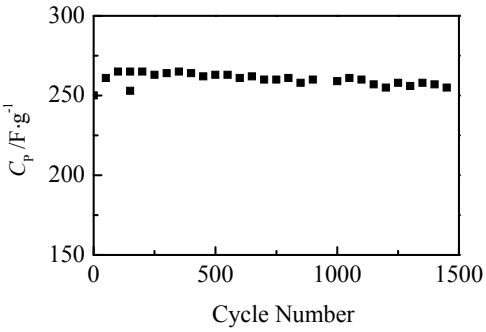

Fig.4 Cycling performance of supercapacitor

where C_P is the specific capacitance for a single electrode in F/g , i is the discharge current in A, dV/dt is the rate of charge potential in V/s, and m is average mass of the electrode in g. The values of specific capacitance were deduced to be 90, 95, 117, 128, 130 and 266 F/g, respectively, as listed in Table1.

2.4 X-ray diffraction

The typical XRD patterns of composite electrodes 1#~3# are shown in Fig.5, respectively. Comparing the curves, it is shown that there is no influence of active oxide adding into the AC on the crystal structure and peak intensity. The results show that the structures of $RuO_2{\cdot}xH_2O$ and MnO_2 both are amorphous.

2.5 Effect of mass ratios on the material characteristics

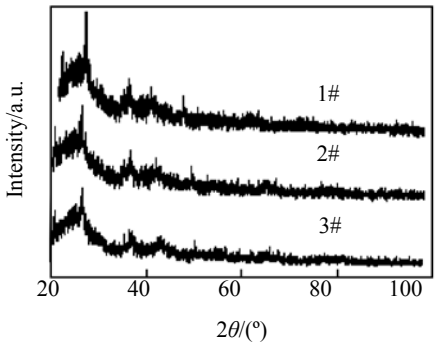

Fig.5 XRD patterns of composite electrodes

The specific capacitance and resistance of the composite electrode of AC with 20wt% MnO_2 are both large, and decreased with increasing the amount of MnO_2. This might be the reason that the redundant particles of MnO_2 cover the surface of active carbon to block the pores on the surface, decreasing the efficient specific surface and the utilization of the double layer capacitance formed in the porous structure. Moreover, although MnO_2 as transition metal oxide has lower conductivity, the amorphous MnO_2 particles adsorbed on the surface of AC have the positive effect to electric charge so as to improve the conductivity of the composite. The capability and impedance characteristics are further enhanced by mixing $RuO_2{\cdot}xH_2O$ into the composite material of AC with MnO_2. Note that the specific capacitance and resistance can be significantly improved by adding $RuO_2{\cdot}xH_2O$ into the composite electrode materials with a content of 10wt%. But the specific capacitance and resistance would increase and decrease, respectively, when the content of $RuO_2{\cdot}xH_2O$ is up to 20wt%. Of course, the increase of $RuO_2{\cdot}xH_2O$ amount would increase the cost of electrode materials, and decrease the ratio of capacity to cost.

3 Conclusions

The multi-element composite electrodes composed of $RuO_2{\cdot}xH_2O$, MnO_2 and active carbon have a promising capability and stable capacitance of 128 and 266 F/g for AC/MnO_2 and AC/MnO_2/$RuO_2{\cdot}xH_2O$, respectively, up to 1500 cycles. But the performances of electrodes are affected by the element mass ratios of the composite electrode materials. The best performance is obtained at mass ratio 3:1:1 of AC, MnO_2 and $RuO_2{\cdot}xH_2O$. The double layer and pseudocapacitance of the composite electrodes have the complementary advantages to improve the performance of the electrodes.

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Ru-Mn-AC多元复合电极材料的电化学性能

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摘　要：以提高超级电容器电极材料的电化学性能为目的，在活性碳粉末中掺入二氧化钌和二氧化锰，作为电极材料的活性物质，从而制备氧化物/活性炭多元复合电极，组装成超级电容器单元。经循环伏安、恒流充放电和交流阻抗测试的结果表明：在活性碳粉末中掺入 20%的二氧化锰时，复合电极的比容量为 128 F/g，阻抗为 2.62 Ω；在活性碳粉末中掺入二氧化钌和二氧化锰各 20%时，多元复合电极的比容量为 266 F/g，阻抗为 0.86 Ω，经 1500 次循环充放电后，电容量几乎无衰减，得出由活性炭、二氧化钌和二氧化锰构成的多元复合电极是一种理想的超级电容器电极材料。

关键词：超级电容器；多元复合电极；二氧化钌；二氧化锰；比电容

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