INFLUENCE OF METAL ION ON STRUCTURE AND CAPACITANCE PERFORMANCES OF MANGANESE OXIDE/CARBON MATERIALS FOR SUPERCAPACITORS

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Abstract

A composite of manganese oxide /carbon powders for supercapacitors was prepared by a redox of acidic $KMnO_4$ and active carbon(AC) in this paper, and Ni^{2+}、Co^{2+} ions were added during the preparation .The influence of AC specific surface area and metal ions on structure and electrochemical properties of obtained manganese oxide /carbon powders were investigated. The crystal structure and surface morphology of manganese oxide /carbon powders were examined by X-ray diffraction(XRD) , X-ray photoelectron spectroscopy(XPS) and scanning electron microscope. Cyclic voltammetry(CV) and electrochemical impedance were performed to evaluate the electrochemical properties of obtained manganese oxide /carbon powders. The XRD result indicated that the obtained manganese oxide had poor crystallinity, and the crystal structure of manganese oxide was changed after the composite doped with $Ni^{2+}$and Co^{2+}. The results of CV showed that obtained manganese oxide /carbon powders possess the ideal capacitive property, and the specific capacitance reached to 185F/g after doping $Ni^{2+}$and Co^{2+} ions.

Key words: supercapacitor；manganese oxide /carbon；Cyclic voltammetry；XRD

Introduction

The supercapacitors are very attractive for delivering high energy with high specific power , long cycle-lives, wide range of operation temperature, rapid race of charging and discharging. These features make wide applications of supercapacitors in various electric devices, which included electric vehicle(EV) or hybrid electric vehicles (HEV). The performances of supercapacitors were thought to depend principally on electrode materials. Although most of supercapacitors used activated carbons as electrodes, many efforts have been devoted to develop transition metal oxides and doped conducing polymers. Compared with activated carbons transition metal oxides and doped conducing polymers exhibit higher energy density. MnO_2 is a promising material for the application of supercapacitors due to the low coast of raw materials. The synthetic methods of MnO_2 for supercapacitor included electrochemical deposition and chemical deposition. And the MnO_2 materials prepared by electrochemical deposition exhibit ideal capacitance behavior but not yet achieved particularly high specific capacitance [1-4]. The research works of chemical deposition were mainly on the method of reducing $KMnO_4$ by manganese of low chemical valence [5,6]. A sample redox deposition method for coating manganese oxide onto the surface of a graphite disc electrode was reported [7]. The manganese oxide coating exhibited ideal capacitance behavior, achieved a maximum value of average capacitance of 45mF/cm^2. In this paper, a active carbon, which has poor crystallinity and good reduction activation than that of the graphite, was used as reducing agent to the preparation of manganese oxide /carbon powder active materials for supercapacitor, the effect of surface area of the active carbon on the performances of the products was discussed, and the capacitance performance was improved evidently by incorporation of some metal ions, such as Co^{2+}, Ni^{2+}.

Experimental

The manganese oxide/carbon powders were prepared by redox deposition method, which was to add 0.2M $KMnO_4$ solution to the solution of 0.4M H_2SO_4 containing activated carbon powder. The depositions were carried out for durations of 4 hours with homogeneous stirring. The obtained manganese oxide /carbons powders was

filtered, washed with distilled water, and dried at 105℃. Two kind of activated carbon with specific surface area 750m^2/g(AC1), 1770m^2/g(AC2), respectively were used in this study. During the deposition, $NiSO_4$、$CoSO_4$ were added to obtain manganese oxide doping with $Ni^{2+}$and Co^{2+} , and the ratio of atom of Mn and Ni, Mn and Co was 10:1. The content of manganese oxide in manganese oxide/carbon powders is about 80wt. %.

The manganese oxide/carbon composite electrodes were prepared by loading the mixture of 95wt.% of manganese oxide/carbons powders and 5wt.% of PTFE(polytetrafluroethylene) on the macroporous nickel current collector, and heat-treated at 105℃ to obtained sample electrodes. The electrochemical capacitance performances of composite electrodes were determined in a conventional three-electrode system using cyclic voltammetric(CVs) and ac impedance spectroscopy in 0.5M $NaSO_4$ electrolytic solution. A saturated calomel electrode (SCE) was used as the reference electrode. The potential sweep rate was 2mv/s. All Electrochemical measurements were carried out with a Princeton Applied Research 263A potentiostat/ galvanostat and model 5210 lock in amplifier (USA). The surface microstructure of manganese oxide/carbons powders was examined by scanning electron microscope (SEM),and the SEM micrographs are obtained on an S-250 Cambridge instrument(UK). The X-ray diffraction(XRD) patterns of the sample were observed by a Rigaku Model D/Max2500vb X-ray diffractometer using a Cu K_α source. The X-ray photoelectron spectroscopy(XPS) was measured by a MKⅡphotoelectron spectrometer using Mg K_α source.

Results and discution

The obtained manganese oxide/carbon powders were characterized by XPS. Figure 1. present the XPS spectra for $Mn2p_{3/2}$ orbit of the powders prepared by reducing acidic $KMnO_4$ with AC1 and doping with Ni^{2+}(MnO_2-Ni/AC1), doping with Ni^{2+} and Co^{2+}(MnO_2-Ni-Co/AC1). The spectra of both powders are similar and have peaks with binding energy of 642.3Ev for MnO_2-Ni/AC1 and 642.9eV for MnO_2-Ni-Co /AC1. It has been reported in [5] that the binding energies of the $Mn2p_{3/2}$ electron for Mn^{3+} and Mn^{4+} are 641.6 and 642.6eV, respectively. The analytic results shown in Fig.1indicate that these manganese oxides obtained by reducing acidic $KMnO_4$ with active carbon are tetravalent manganese oxides.

The XRD patterns of MnO_2-Ni/AC1 and MnO_2-Ni-Co /AC1 are presented in Figure 2. The crystallinity is not so high as we can see from the intension and half peek breadth of the XRD patterns. In the Fig.2, in addition the peaks around 23° attribute to the active carbon, there are three peaks around 37, 56 and 66° for the MnO_2-Ni/AC1, the pattern correspond to γ-MnO_2. For the MnO_2-Ni-Co /AC1, there two clear peaks around 37 and 66°, the intensity of the peak around 56° decreased, the pattern correspond to α−MnO_2. The analytic results of XRD indicate that the structure of the product changed from γ -MnO_2 to α -MnO_2 when the Co^{2+} and Ni^{2+} was co-doped to the product .

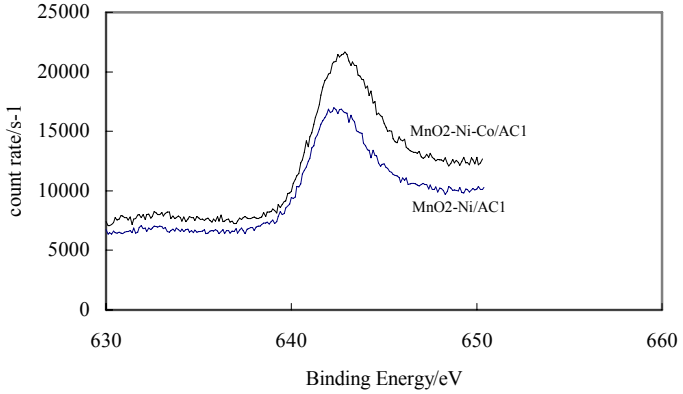

Figure 1. The XPS spectra for $Mn2p_{3/2}$ orbit of MnO_2-Ni/AC1 and MnO_2-Ni-Co/AC1

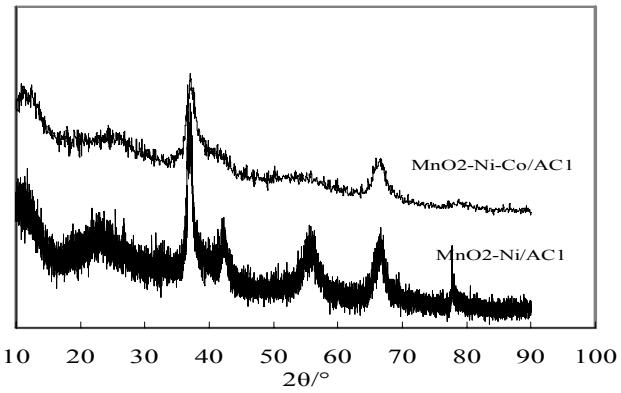

Figure 2. The XRD diffraction patterns of MnO_2-Ni/AC1 and MnO_2-Ni-Co/AC1

The images of the MnO_2-Ni/AC1 are shown in Figure 3. As we can seen from Fig.3a , the large irregular particles are AC. And the round MnO_2 particles, which has dendritic pattern in its surface, aggregate together and distribute in around the surface of AC (Fig. 3b)

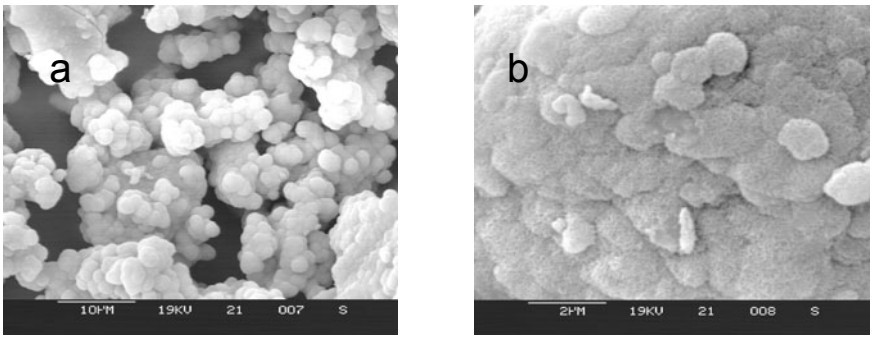

Figure 3. SEM images of MnO_2-Ni/AC1)

Figure 4 presents typical cyclic voltammograms(CVs) of the manganese oxide/carbon doping with Ni^{2+} and Co^{2+} electrodes at 2mv/s of scan rate. There are no clear peaks in these CVs. These CVs show clearly the rectangular and symmetric current-potential characteristics of a capacitor. The result of the CVs shown in Fig.4 indicates that the manganese oxide/carbon doping with Ni^{2+} and Co^{2+} possesses ideal capacitive behavior. In addition, the value of specific current response for electrode doping with Ni^{2+} and Co^{2+} is larger than the doping with only Ni^{2+}, which indicates that Co^{2+} ion can increase the capacitance of electrode. In cyclic voltammetry, for a constant scan rate, the magnitude of the current is a function of the apparent capacitance of the electrode. The capacitance is determined according to the well-known equation: C=di/d(dv/de), where i is the current(in this paper the average current response at the range of potential 0.2~0.7V is elected to calculate C), dv/dt is the potential scan rate. Table 3 presents the specific capacitance(C_{sp}) calculated from Fig.4. It is clearly seen that the values of C_{sp} depend on the kind of active carbon and metal ion. When doping with only Ni^{2+} the sample obtained by reducing with active carbon of large specific area exhibits large C_{sp}, 170 $F.g^{-1}$ for MnO_2-Ni/AC2. The value of C_{sp} increases with adding Co^{2+}. The sample of MnO_2-Ni-Co/AC1 reached the maximum C_{sp} value of 185$F.g^{-1}$. The reason of improvement in capacitance of sample doping with Co^{2+} may be that Co^{2+} ion has changed the crystal structure of manganese oxide.

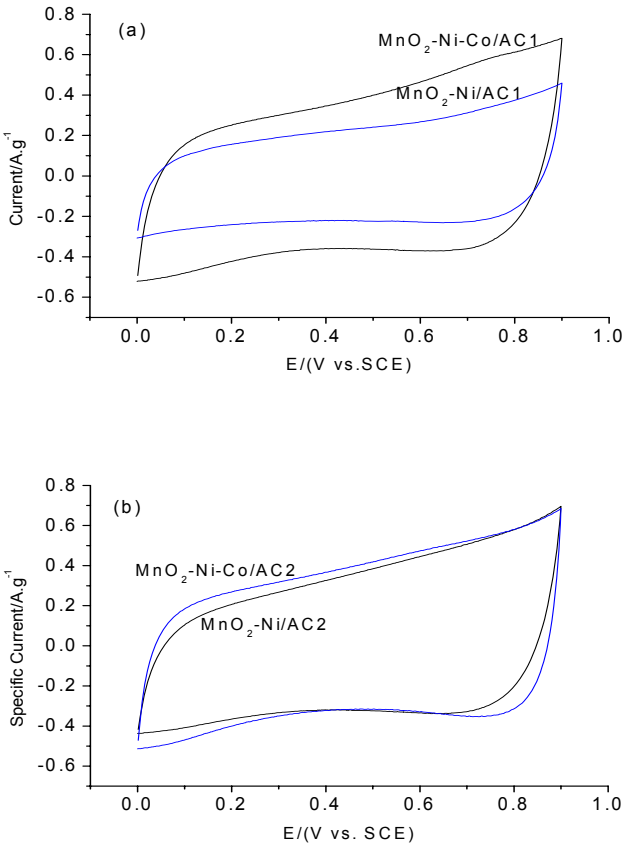

Figure 4. Cyclic voltammograms for the MnO_2-Ni/AC1and MnO_2-Ni/AC1(a); MnO_2-Ni/AC2 and MnO_2-Ni-Co/AC2(b)

Table 1. The specific capacitance for manganese oxide/active carbon electrodes

Sample	**MnO_2-Ni/AC1**	**MnO_2-Ni-Co/AC1**	**MnO_2-Ni/AC2**	**MnO_2-Ni-Co/AC2**
C_{sp}/F•g^{-1}	112	185	170	177

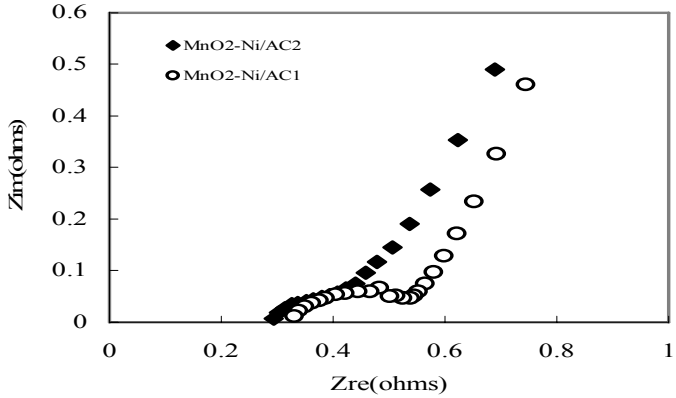

Figure 5. Nyquist plots of MnO_2-Ni/AC1and MnO_2-Ni/AC2

A typical Nyquist plot of MnO_2-Ni/AC1 and MnO_2-Ni/AC2 are shown in Fig.5. The frequency range is 10^5 to 0.1Hz. The plot starts as semicircle arc at high frequency, and as the frequency decreases, it changes to a straight line at low frequency. In the range of high frequency, the intercept of the curve in the abscissa reflects the ohmic impedance of the material, which is composed of several terms: ionic resistance of the electrolyte, the intrinsic resistance of the active material, and the contact resistance at the interface active material/current collector. The radius of the circular arc depends on the electrochemical reaction impedance of the electrode, while the straight-line indications the capacitance characteristic of the electroactive species. As we can see from Fig.5, the ohmic resistance（0.29Ω）of MnO_2-Ni/AC2 electrode is lower than that of the MnO_2-Ni/AC1（0.33Ω）, and the reaction resistance of the MnO_2-Ni/AC2 (0.18 Ω)also lower than that of the MnO_2-Ni/AC1(0.27Ω), this is the main reason why the specific capacity of the MnO_2-Ni/AC2 is higher than that of the MnO_2-Ni/AC1.

CONCLUSION

The manganese oxide/carbon composite materials prepared by reducing $KMnO_4$ with active carbon possess good electrochemical capacitor behavior. The metal ions and specific area of active carbon reductant would affect on the C_{sp} of manganese oxide/carbon composite materials. The Co^{2+} improves Csp.

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