STUDY OF SUPERCAPACITIVE BEHAVIORS OF Co AND Fe DOPED MANGANESE OXIDES PREPARED BY ANODIC ELECTRODEPOSITION

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Abstract

Supercapacitive behavior of Co and Fe doped manganese oxide films prepared by anodic deposition were characterized using cyclic voltammetry (CV) and impedance spectroscopy (EIS). Results showed that the highest specific capacitance of 186.2 F/g and stability of 84% obtained with Co doped manganese oxide after scaning 500 cycles. For Fe doped manganese oxide, those parameters were 298.4 F/g and 83%, respectively. The Co, Fe doped manganese oxide film-coated electrodes showed ideal pseudocapacitive behaviors. The appearance of Co and Fe decreased diffuse resistance and charge transfer resistance of the film. They also increased electric double layer capacitance and capacitor response frequency.

Keywords: Binary oxide, supercapacitor, manganese dioxide.

1. INTRODUCTION

Supercapacitors are charge storage devices that are characterized by a greater power density and longer cycle life than that of batteries and a higher energy density than that of conventional capacitors [1]. Accordingly, they have been developed for a wide range of applications, such as in hybrid electric vehicles, electronic devices, medical electronics, and military missile systems.

Manganese oxide is considered one of the most promising electrode materials for supercapacitor applications due to its satisfactory electrochemical performance and its natural abundance and environmental compatibility. Its preparation methods include electrodeposition, thermal decomposition, co-precipitation and sol–gel processes and physical vapor deposition and hydrothermal synthesis [2, 3]. However, the electrochemical stability of plain manganese oxides is not quite satisfactory and specific capacitance decays during charge-discharge cycling [4, 5]. In order to further improve the pseudocapacitive performance of plain Mn oxide, addition of other transition metal oxides has been attempted such as: Ni, Co, Fe… [6 - 8]. However, Co and Fe are considered to be among the most promising candidates since they can improve significantly supercapacitive behavior of the materials [8-11]. In the previous studies, we have investigated the electrodeposition process and characterized the morphology and the structure of Co and Fe doped manganese oxides for supercapacitive applications.

In this paper, we continue to present results on effect of Co and Fe doping on supercapacitive behavior of manganese oxides.

2. EXPERIMENTAL

Co and Fe doped manganese oxides were electrodeposited on graphite 1 cm^2 work surface area plates by anodic deposition. Prior to electrodeposition, the graphite plates were treated ultrasonically in 0.2 M H_2SO_4 for 5 minutes and rinsed with distilled water. The electrodeposition was carried out in electrolyte containing 0.15 - 0.25 M $MnSO_4$, 0.05 - 0.15 M sulfate salt of Co or Fe, 0.2 M EDTA, pH = 6.5 - 7.0, $T^0 = 80^oC$, i = 50 mA/cm^2. The concentration of M^{n+} (M= Co,Fe) and Mn^{2+} were varied so that the ratio $[M^{n+}]/[Mn^{2+}]$ = 0/30; 5/25; 10/20; 15/15 and the total amount of cation was kept constant of 0.3 M ($[M^{n+}]+[Mn^{2+}]$ = 0.3 M). Thickness (d) of the obtained manganese oxides was controlled by deposition time so that d = 5 - 6 μm. A three- electrode cell configuration which consists of a platinum counter electrode placed parallel

graphite working electrode and a saturated calomel electrode (SCE) reference, was used for electrodeposition. The oxide electrodes obtained were dried at $100^{\circ}C$ in air for 2 hours. Chemical compositions of the deposited oxides were examined with X-ray energy dispersive spectroscope (EDS). Electrochemical behavior and specific capacitance of the deposited oxides were characterized by cyclic voltammetry (CV) in 2 M KCl solution at $25^{\circ}C$. The adopted potential scan rate (v) was in a range of 10 - 150 mV/s. In order to quantitatively evaluate the pseudocapacitance of the oxides, the specific capacitance (C) of oxide electrode can be quantitatively calculated according to the following equation [4]:

$$C = \frac{\text{Specific voltammetric charge}}{\text{Potential range}} \quad (1)$$

Here the specific voltammetric charge (voltammetric charge per gram of the oxide) was

integrated from positive sweep to negative sweep of the CV curve. Moreover, electrochemical stability of the oxide electrodes was evaluated by repeating the CV test for 500 cycles. The decay in the specific capacitance versus the cycle number was recorded. For further investigate effect of doping M (M = Co, Fe) on electrochemical behavior impedance spectroscopy was used with frequency in a variety of 0.01 Hz - 100 kHz and alterative amplitude of 5 mV at the open potential. All measurements were carried out by using IMex6 potentiostat equipment.

3. RESULTS AND DISCUSSION

The electrochemical performance of the oxide electrodes was evaluated by cyclic voltammetry in 2 M KCl electrolyte. Fig. 1 displays the obtained voltammograms measured at various potential scan rates of doped manganese oxides obtained from different electrolytes.
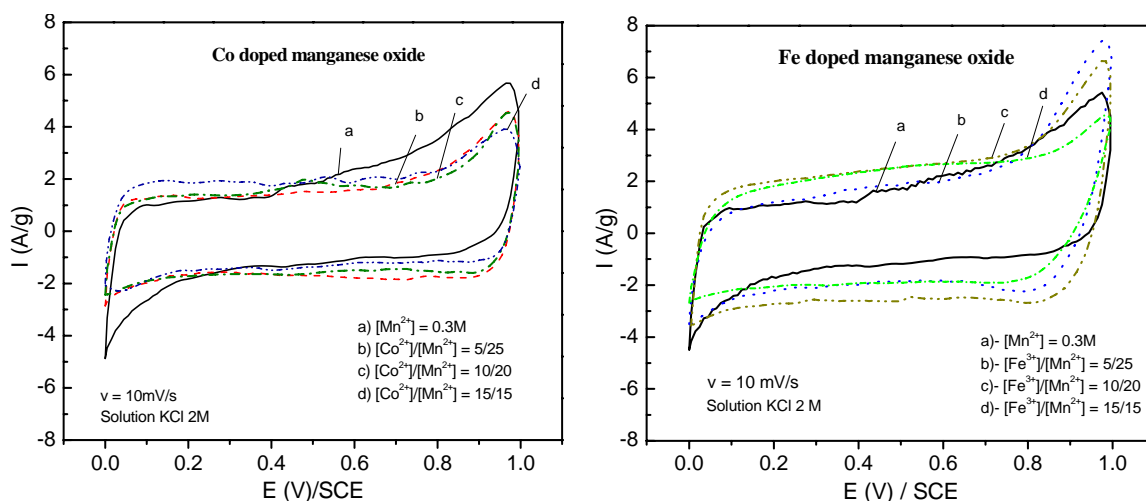

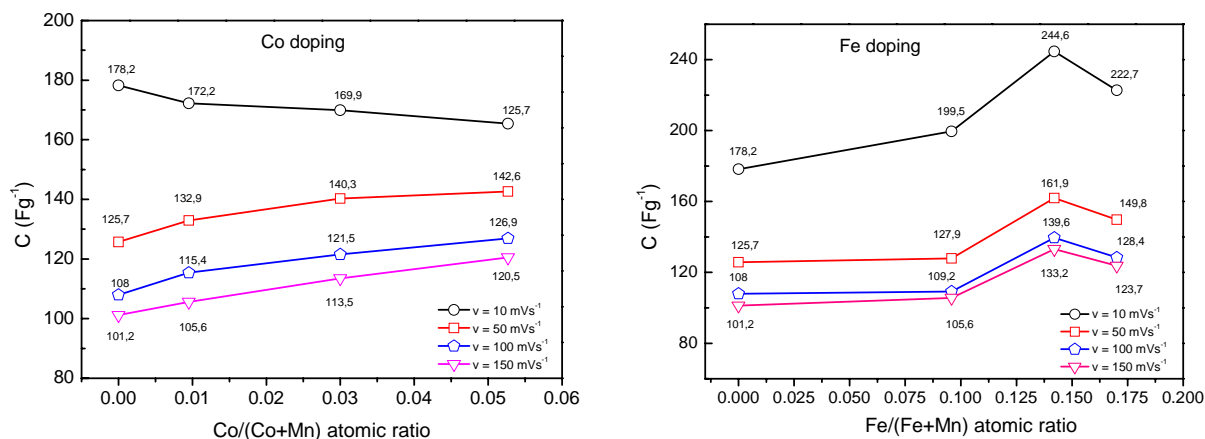*Fig. 1:* Cyclic voltammetry curves of doped manganese oxides

Fig. 2: Dependences of the specific capacitance of materials on different potential scan rates and dopant contents (a) Co doped materials (b) Fe doped materials
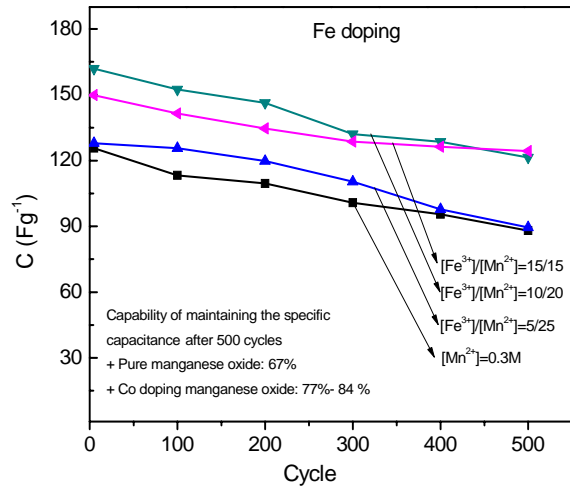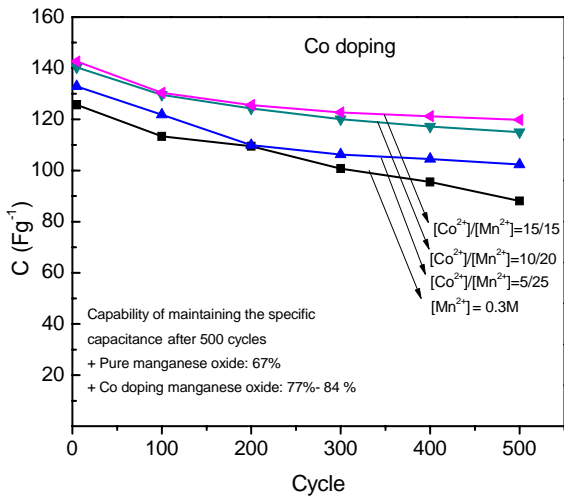
Fig. 3: Fading of the specific capacitance of various manganese oxide samples following cycles
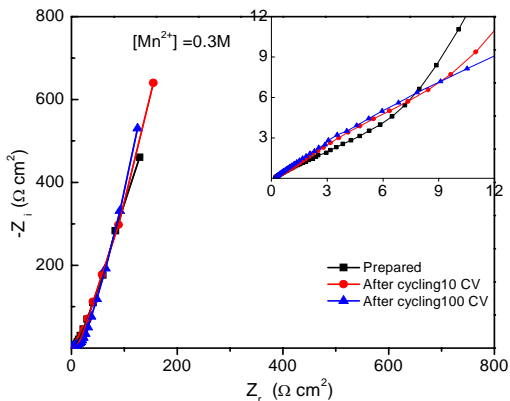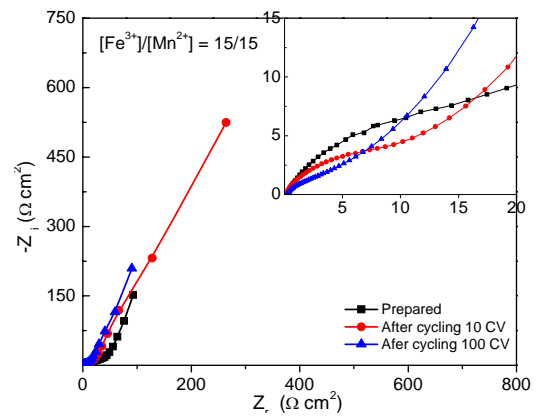

Figure 4: Nysquist of manganese oxides obtained from different electrolytes
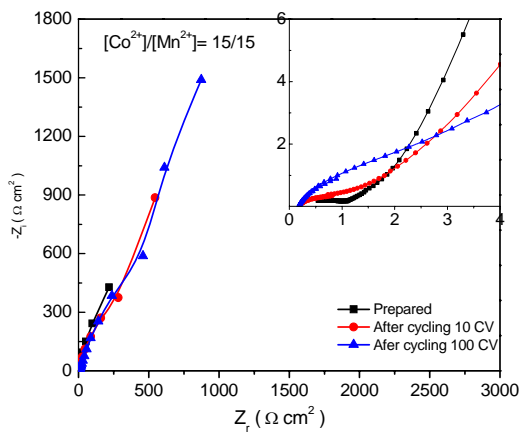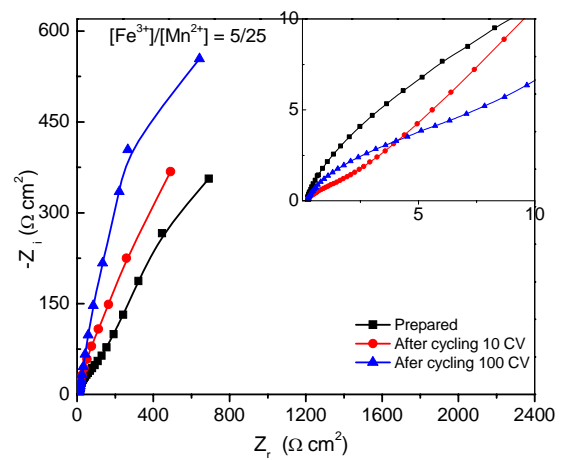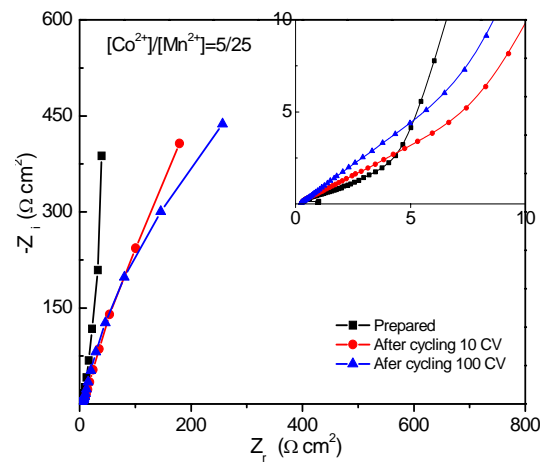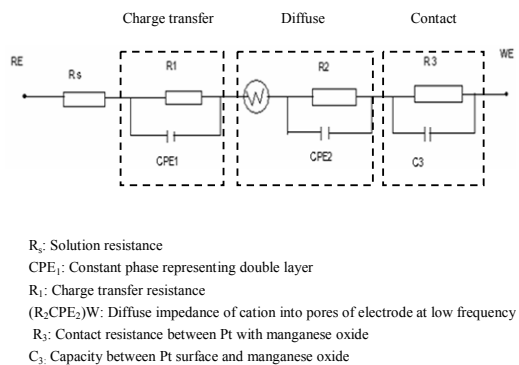

R_s: Solution resistance

CPE_1: Constant phase representing double layer

R_1: Charge transfer resistance

$(R_2 CPE_2)W$: Diffuse impedance of cation into pores of electrode at low frequency

R_3: Contact resistance between Pt with manganese oxide

C_3: Capacity between Pt surface and manganese oxide

Figure 5: An equivalent circuit model of the manganese oxide lectrodes

It can be observed that all the CV curves of electrodes on which both Co and Fe doped manganese oxides coated were symmetric in anodic and cathodic areas. The CV responsive current remained nearly constant during forward and backward scans. It is important to note that the rectangular shapes and mirror image characteristics of these CV curves represent the ideal pseudocapacitive behavior. These results suggested that M doped manganese oxides are promising electrode materials for supercapacitive applications. In this figure, although the CV curves of these materials show similar curves, Co doped manganese oxides had the smaller enclosed area than pure manganese oxides. This reflects their degraded charge storage performance mean while that of the addition of Fe into materials had more enlarged area, which corresponds to their increased charge storage.

However, in order to quantify influence of doping Co and Fe on this manganese oxide material variations of the specific capacitance of samples with different potential scan rates and dopant contents were calculated from CV. The obtained results are shown in Fig. 2. Dopant contents were analyzed by EDS and the Co/(Co+Mn) corresponsive contents were respectively 0.00%, 0.95%, 3.00% and 5.27%. Meanwhile, with Fe dopant, these ratios were 0.00%, 9.58%, 14.20% and 17.02%, respectively. It can also be observed that atomic ratio M/(M+Mn) (M = Co, Fe) increases with increasing $[M^{n+}]/[Mn^{2+}]$ ratio.

At the first glance, it is important to see that doping Co increased the specific capacitances for manganese oxide at high sweep rates. After doping Fe the specific capacitances of materials increased at all sweep rates. The obtained maximum specific capacitances corresponds to ratio Fe/(Mn+Fe) = 14.6% was obtained from solution with $[Fe^{3+}]/[Mn^{2+}] = 20/10$. This can be explained that with appearances of Co and Fe in materials made the average valence of Mn element increase (from +3.808 to +3.867 after doping Co and from +3.808 to +3.846 after doping Fe). Moreover, both Co and Fe doped manganese oxides had specific capacitances decayed with increasing of potential sweep rate. Since at high scan rates cations do not keep up with diffusing deeply into layer structure of materials, the Faradic reactions were prevented.

Electrochemical stability of the doped oxide electrodes was also evaluated by repeating the CV test for 500 cycles. Fig. 3 shows the variations in the specific capacitance after scanning 500 cycles.

As observed M doped manganese oxides had the higher charge-discharge stability than pure material.

The decay of specific capacitances can be explained by two following reasons:

(i) The first reason is the corrosion of materials during active process. If as this, doping Co and Fe diminished defects of lattice structure making materials stable and inert.

(ii) The second reason is the intercalation or deintercalation of H^+ and K^+ ion in the bulk of manganese oxides:

$$MnO_2 + H^+ + e- \rightarrow MnOOH \qquad (2)$$
$$MnO_2 + K^+ + e- \rightarrow MnOOK \qquad (3)$$
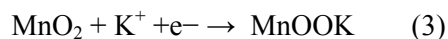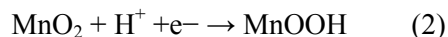
If the intercalation or deintercalation happens easily and the change of volume of oxides is negligible, the specific capacitances of these oxides decay fewer after 500 cycles.

To clarify those explanations electrochemical impedance spectroscopy were carried out. Figs. 4 and 5 display Nysquist and model an equivalent circuit model of manganese oxides.

The equivalent circuit model shown in Fig. 5 consists of three parts representing three processes: charge transfer, diffuse and contact. Data obtained from fitting with the circuit model summarizing in Tab.1 showed that the appearance of Co and Fe decreased diffuse resistance, charge transfer resistance and contact resistance of the films. They also increased electric double layer capacitance and capacitor response frequency. These caused the specific capacitance and stability of manganese oxides after doping Co and Fe increase.

4. CONCLUSION

Supercapacitive behavior characterized by CV and EIS methods showed that the highest specific capacitance of 186.2 Fg^{-1} and stability of 84% after scanning 500 cycles were obtained with Co doped manganese oxide. For Fe doped manganese oxide, those parameters were 298.4 Fg^{-1} and 83%, respectively. The Co, Fe doped manganese oxide film-coated electrodes showed ideal pseudocapacitive behaviors. The appearance of Co and Fe decreased diffuse resistance, charge transfer resistance of the films. They also increased electric double layer capacitance and capacitor response frequency.

Table 1: Selected data obtained from fitting the experimental impedance data to
the equivalent circuit in Fig. 5

Oxides obtained from electrolytes		CPE1, μF	R_1, $\Omega.cm^2$	R_2, $\Omega.cm^2$	R_3, $\Omega.cm^2$	$f_{\varphi=45^0}$, Hz
$[Mn^{2+}] = 0.3$ M	as prepared	2.201	3.76	1.62	6.27	1.22
	after 100CV	*3.72*	*4.47*	*4.95*	*9.32*	*0.52*
$[Co^{2+}]/[Mn^{2+}]=$ 5/25	as prepared	2.38	5.23	3.61	5.80	0.967
	after 100CV	*3.81*	*3.43*	*3.23*	*8.65*	*2.11*
$[Co^{2+}]/[Mn^{2+}]=$ 15/15	as prepared	12.42	5.37	2.15	4.68	4.27
	after 100CV	*10.45*	*2.25*	*3.84*	*7.65*	*8.21, 526, 5715*
$[Fe^{3+}]/[Mn^{2+}]=$ 5/25	as prepared	10.32	3.36	4.61	5.32	53.5, 1600
	after 100CV	*7.54*	*4.01*	*2.56*	*7.93*	*0.967*
$[Fe^{3+}]/[Mn^{2+}]=$ 15/15	as prepared	9.48	4.53	2.64	6.12	0.032, 6760
	after 100CV	*8.84*	*3.45*	*3.48*	*8.98*	*10200*

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