Preparation of MnO_X Nano-supercapacitor with Silver Addition by Electrochemical Deposition

Yi Hu, Jiun-Shing Liu, Chien-Lung Huang, Tung-Cheng Liu

***Abstract*— The electrode for nano-supercapacitors with silver/manganese oxides thin film were obtained by electrochemical deposition method. These thin films were potentiostaticly deposited (-0.7V v.s. open circuit) on ITO substrate with potassium permanganate and silver acetate solution for 200s. The thickness of the thin films was in the range of 100~300nm and composed of MnO_x nanoparticles. The morphology and the microstructure of the samples were examined by scanning electron microscopy (SEM), and the states of the ions were investigated by X-ray photoelectron spectroscopy (XPS). The silver acted as a reduction agent and resulted in the valence change for Mn from +4 to 3+. Such a nanostructure of the thin film with MnO_x nanoparticles and Ag_2O results in much higher capacitance. It was suggested that the addition of silver oxide would promote the pseudo-capacitance by increasing the impedance of the thin films.**

***Index Terms*—nano-supercapacitor, manganese oxides, silver, thin film, electrochemical deposition**

I. INTRODUCTION

RECENTLY, attention has been focused on the development of the electrochemical capacitor with ultra high power, which is called supercapacitor and has application in products as diverse as cardiac pacemakers, cellular phones, electric vehicles, and airbags. Electrochemical capacitors fill the gap between batteries and conventional capacitors in terms of their specific energy and specific power [1]. Typically they exhibit 50–100 times greater capacitance per unit volume or mass than conventional capacitors [2]. These characteristics of supercapacitors are explained with two energy storage mechanisms. (a) electrical double-layer capacitors (EDLCs) which employ carbon or other similar materials as blocking electrodes [3-4], and (b) redox supercapacitors in which electroactive materialssuch as insertion type compounds (e.g. RuO2, MnO2, NiO, etc.) or conducting polymers are employed as electrodes[5–7].

The capability of electrode materials is significantly influenced by their surface area and morphology both for the two energy storage mechanisms. In general the electrode materials with high surface area, ordered pore network of nanometer dimension would be expected to exhibit superior performance. For this purpose, the nanostructured transition metal oxides become important in the field of electrochemical capacitors for their fast redox reactions, high specific surface area, and shortened diffusion path in solid phase. So far, several transition metal oxides such as ruthenium oxides [8–10], manganese oxides [11–19], nickel oxides [20–23], and cobalt oxides [20], have been investigated. Among there oxides the hydrated or amorphous manganese oxides has been paid much attention by many researchers recently [11-18] because of their low cost, great quantity and very high capability. There are many techniques to fabricate manganese oxides thin films such as electrochemical deposition [12], chemical conversion deposition [13]. But more frequently $MnO_2{\cdot}nH_2O$ is synthesized by the reduction of permanganate solution with Mn(II) reducing agents [14], species [11], or thermally [15]. Based on the relatively complicated steps of the other techniques, it is more desirable to employ the electrochemical deposition for preparing the manganese oxides with excellent capacitive characteristics.

In this study, the manganese oxides thin films with different Ag content were electrochemically deposited on ITO substrate as the nano-supercapacitor electrode. And the electrochemical behavior of the nano-supercapacitor was studied by the cyclic voltammetry and impedance.

II. EXPERIMENTAL

The thin films of the supercapacitor electrodes were electrochemical deposited on ITO glass substrate with potentiostatic method (-0.7V vs. open circuit) for 200s. The solutions for the deposition are prepared with the potassium permanganate and silver acetate dissolved in deionized water. The concentration of potassium permanganate was 0.01M and the molar ratio of the Ag/Mn in the solution varied from 0~1.6%.

The morphology of the thin film was investigated using a field emission scanning electronic microscope (JEOL JSM-6700). Transmission Electron Microscopy (TEM) analyses were performed using a JEOL JEM-1200EX electron microscope operated at 200 kV. The states of the ions were measured by an X-ray photoelectron spectroscopy (XPS, VG ESCA Scientific Theta Probe) under Al Kα (1486.6eV) and the X-ray spot size is 15μm.

The electrochemistry behavior of the cell was examined by the cyclic voltammetry with conventional three-electrode testing system (Electrochemical station 5000 Jiehan). The measurements were carried out in a desecrated 0.1 M KNO_3 electrolyte at room temperature after standing the electrode. The counter electrode was platinum, and the reference electrode was a standard calomel reference electrode (SCE). The measurement of cyclic voltammetry (CV) was conducted from 0 to 1V with scan rates of $20mVs^{-1}$.

For impedance measurement we prepared the cell with a sandwich structure. The outset is the glass, the second layer is the thin film electrode, and the mesosphere is a polymer electrolyte membrane used as the separator. KNO_3 (0.1 M) dissolved in distilled water was used as the electrolyte. This measurement was conducted with an impedance spectroscopy (Hioki 3522-50 LCR tester). It was polarized with a 0.01A current ripple under dc

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charging. The ripple frequency was swept between 1Hz and 0.1M Hz.

III. RESULTS AND DISCUSSION

Figure 1 shows the SEM micrographs of the thin films with various ratio of Ag/Mn. The thickness of the thin films with manganese dioxide is in the range of 100~230nm. These thin films as observed basically are composed of MnO_x nanoparticles of about 10nm as in Fig. 1. The film without Ag addition shows two distinct layers with flat bottom layer and porous surface layer as observed in Fig. 1(a). The thickness of the film is about 300nm included the porous layer. As the small amount of Ag (0.2%) was added into the electrodepositing solution, the film became very smooth without porous surface and the thickness of the film did not vary (Fig.1(b)). In addition, it was found that lots of near-spherical particles precipitated on surface of the film were observed and the thickness decreased to 250nm and 150nm when Ag content was further increased as in Fig. 1(c) and (d), respectively. The number of the near-spherical particles increased as the Ag content in the solution increased. The size of the near-spherical particles increased as the ratio of Ag/Mn increased and from 10nm with Ag/Mn of 0.2% to 30nm with Ag/Mn of 0.4%. Finally, the particles on the surface of the thin films became cubic as the Ag/Mn ratio was up to 1.6% as in Fig 1(e). The main composition of the particles was identified as the Ag from the EDX spectra (Fig. 1(f)). It was shown that Mn, Ag and O are the major elements of the thin films from the EDX spectrum investigation. Peaks corresponding to Si and In form ITO glass substrates are also detected.

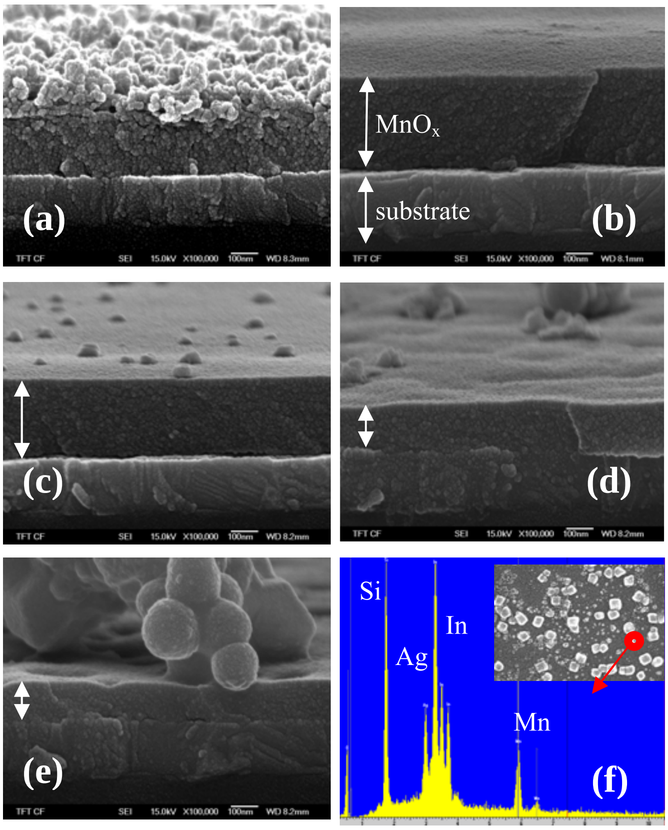


Figure1 The SEM micrographs of the cross-section morphology of the thin films with the Ag/ Mn ratio of (a) 0%, (b) 0.2%, (c) 0.4%; (d) 0.8%; (e) 1.6%; and (f) shows the EDX spectrum of the particles (as arrowed) for the sample with Ag/Mn ratio of 1.6% .

Figure 2 shows the TEM micrographs of the thin film with 0.4% of Ag/Mn. It was found that the film also has the spherical nanoparticles embedded into the films. The size of the nanoparticles (dark image) varied from several nanometers to 15nm, which is much smaller that on the surface of the films (about 50nm). The spotty diffraction pattern suggests the nanoparticles of Ag_2O obtained from the electrochemical deposition possess single-crystal character as in Fig. 2(b). The ringing diffraction pattern of the matrix suggests the crystalline structure of α-Mn_2O_3 with a = b=c = 9.785 Å (Cubic phase; space group: Ia3) as in Fig. 2(c).

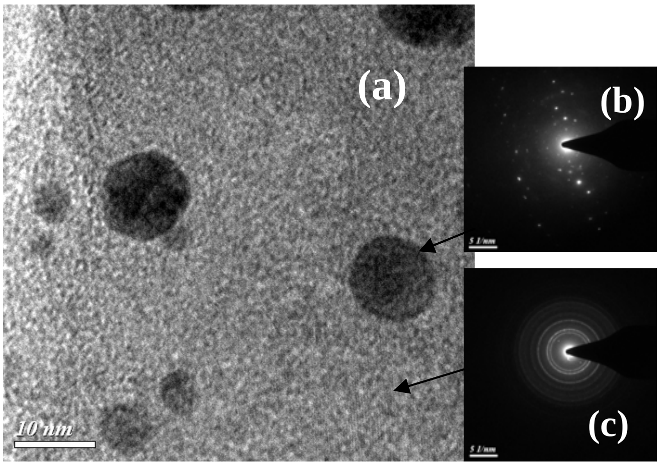


Fig. 2 TEM image and electro diffraction pattern of the thin film with 0.4% of Ag/Mn.

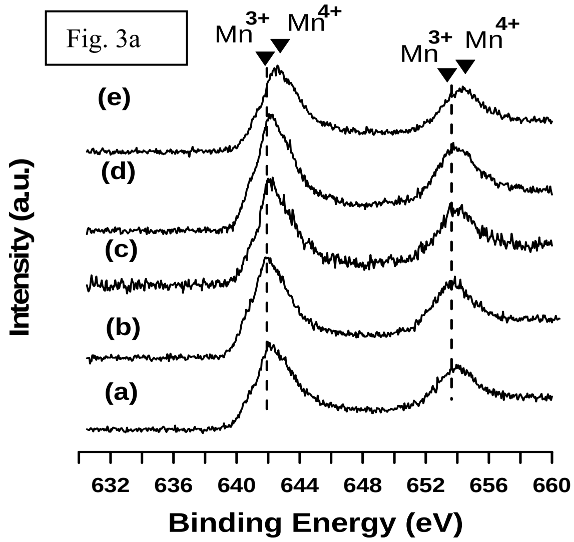
Figure 3 shows the XPS spectra of the thin films with different of Ag content. It is known that there are several oxidation states, including Mn(0), Mn(II), Mn(III), Mn(IV), Mn(V), Mn(VI), and Mn(VII), for manganese oxides and they are difficult to distinguish due to their high similarity in properties. In this study, the interpretation of XPS spectra of manganese oxides is complex due to the small difference between the manganese oxidation states in the binding energy. This would cause small shift of the 2p main peaks and results in broadness of peaks. The binding energy of the Mn2p3/2 for the manganese oxidation state is 640.9eV for the MnO, 641.9eV for the α-Mn_2O_3, 642.5eV for the β-MnO_2.as reported in literature [24]. The binding energy of Mn2p3/2 of the film with/without small Ag content is measured to be 642.01eV, which is much close to 641.9eV. Therefore, α-Mn_2O_3, is the predominant phase in the thin films with/without small Ag content (Fig. 2-1(a)). As the Ag content increased, the values of the Mn2p3/2 increased from 642.05eV for 0.4% Ag to 642.08eV for 0.8% Ag and 642.4eV for 1.6% as in Fig. 3a(c)~(d). This indicates that the valence of Mn shifts from +4 to +3 by increasing Ag content and the predominant phase of the thin film would change from α-Mn_2O_3, to β-MnO_2.

On the other hand, Fig.3b shows the XPS spectra of Ag3d5/2 of the samples with different Ag content. The binding energy of the Ag3d5/2 is 368.2eV for Ag, 367.8eV for Ag_2O and 367.4eV for Ag_2O_2 as reported the literature [25]. The measured binding energy of Ag3d5/2 peak of the thin film is 367.79eV for small Ag content as in Fig.3b(b)~(c) and the near-spherical nanoparticles are identified to be Ag_2O. As the Ag content increased, the binding energy of Ag3d5/2 decreased to 367.63eV for 0.8% Ag content and 367.3eV for 1.6% Ag content. This indicates that the binding state of Ag changes from Ag(I) to Ag(II) as the Ag content increased.

From the results of XPS analysis, we found a charge balance between Mn and Ag. Both Mn and Ag are strong reduction elements. The original oxidation state of Mn is +3 when the Ag content is small. However, the Ag acted as a reduction agent to change the valence of Mn from 4+ to 3+ when the Ag content becomes large. The reaction between Mn and Ag ions can be illustrated for large Ag content as:

$$Ag_2O + \alpha\text{-}Mn_2O_3 + O_2 \rightarrow Ag_2O_2 + 2\beta\text{-}MnO_2 \qquad (1)$$

This reaction also reveals that the reducing ability of Ag_2O is higher than that of Ag_2O_2.



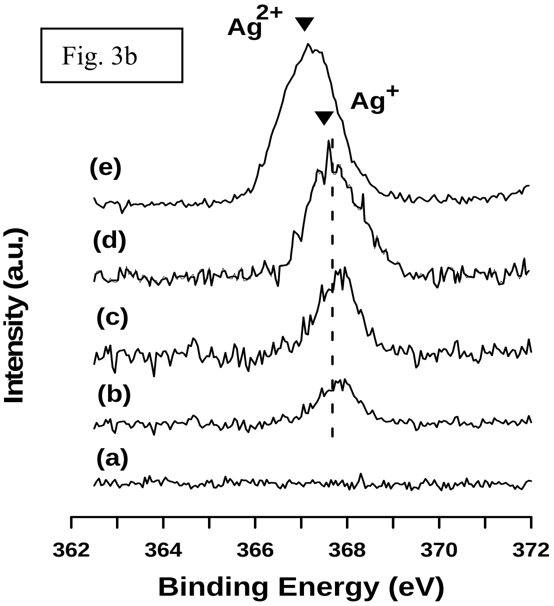


Figure 2 The XPS spectra of the samples with different Ag content. Fig. 3a shows the Mn2p3/2 and Mn2p1/2; Fig.3b shows the Ag3d5/2 with Ag/Mn ratio of (a) 0% (b) 0.2% (c) 0.4% (d) 0.8% (e) 1.6%

Figure 4 shows that the composite electrode material (Ag/MnO_2) tested by cyclic voltammetry in a 0.1M KNO_3 solution. Figure 4(a) shows the cyclic voltammogram (CV) for thin film without Ag addition with capacitance of about 300F/cm^3. The supercapacitors give CV curves of nearly rectangular shape and exhibit mirror-image characteristics as shown in Fig. 4(b)-3(e). The results demonstrate the excellent reversibility and ideal pseudo-capacitive behavior of the electrodes. These results indicated that the specific capacitance and kinetic reversibility of the composite electrodes were significantly enhanced by Ag addition. Because nanoparticles possess special pseudo-one-dimension, high surface area and high aspect ratio dimensions, the interface between the active material and electrolyte increases and conductivity increases. However, the shape of the CV curve became asymmetric triangle with Ag/Mn ratio of 16% (Fig.4(e)).

Figure 5 summarizes capacitances of the samples with different Ag content, which were calculated from the voltammetry curves as in Fig. 4. The capacitance values as found increased with the increase of the ratio of the Ag/Mn up to 8%. This indicates that the capacitance of the supercapacitor increased as the amount of Ag_2O increased. This is ascribed to the strong catalytic property of Ag_2O, which is a strong reduction agent. In addition, the size of the Ag_2O nanoparticles is an important factor which affects the capacitance of the thin films. The surface area becomes very large for the size of Ag_2O in the nano size and promotes the redox reaction. This can be revealed from the shape of the voltammetry curves as in Fig. 4. The capacitance and electrochemical properties decreased when the Ag content was excessive. This is ascribed to the formation of Ag_2O_2 and β-MnO_2, which Ag_2O_2 has less catalytic property.

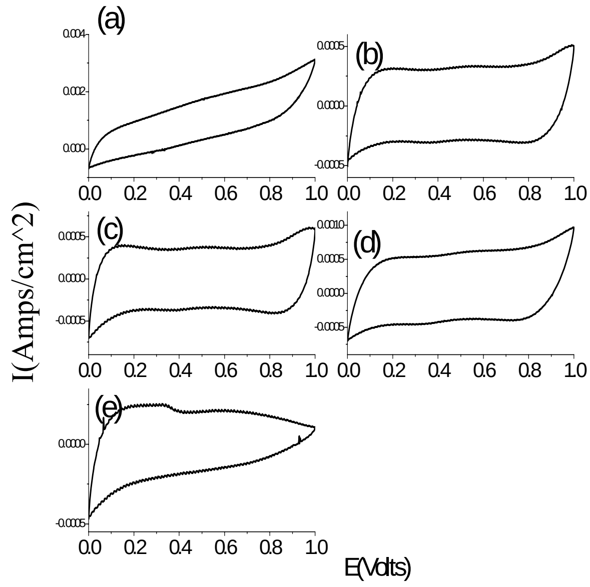


Fig. 4 The cyclic voltammetry of the samples with Ag/ Mn ratio of (a) 0%, (b) 0.2%, (c) 0.4%; (d)0.8%; (e)1.6%

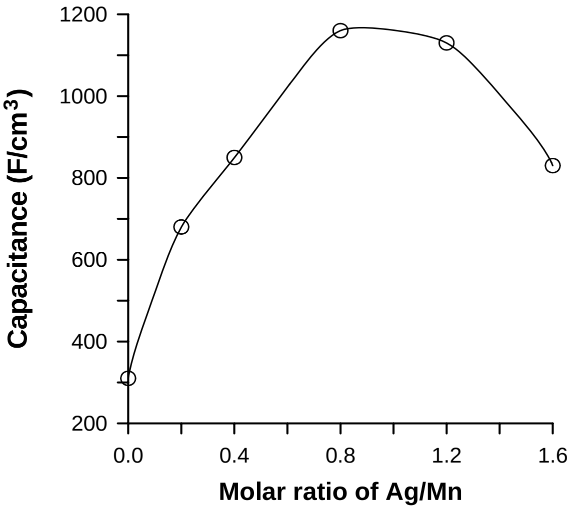


Fig. 5 Calculated capacitances of the samples versus Ag content.

Figure 6 shows the Nyquist plot of the electrochemical impedances of the samples versus Ag content. It was found that both the Z' and Z" resistance of the cell increased with the Ag/Mn ratio up to 0.8%. The curve consists of a high-frequency intercept on the real axis corresponding to the electrolyte resistance, which is very small and almost the same for all samples. The semicircle of the curve is corresponding to a parallel combination of charge-transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}), and finally a linear region at low-frequency range. In general, for a simple electrode-electrolyte system, the low frequency linear plot of impedance should make 45° to the real axis if the process is under diffusion control in the corresponding frequency regime, or it should make 90° if the behavior of the system is purely capacitive in nature. The linear plot of the data of Fig. 4 exhibits an angle of 45° for low Ag content and 70° for high Ag content. The difference is ascribed to the formation of Ag_2O and Ag_2O_2 in different Ag content that the catalytic property of Ag_2O is much higher than Ag_2O_2. On the other hand, R_{ct} , which is found to be equal to the diameter of the semicircle, increased as the Ag content increased.

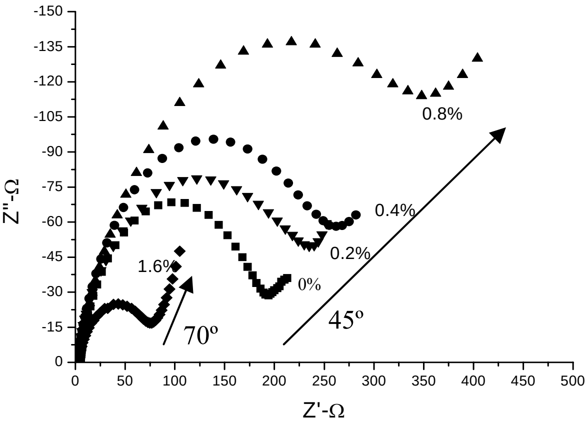


Figure 6 The impedance data of the samples with Ag/Mn ratio of (a)0%;(b)0.2%;(c) 0.4%;(d)0.8%;(e)1.6%

Therefore, we propose that the improvement of activity of the thin films can be attributed not only to a high exposure of nanoparticles to reactants but also to the formation of Ag_2O. Note that compared with the pure MnOx such high improvement of the catalytic reactivity by the formation of nanocrystals of metal oxides inside has rarely been addressed yet.

IV. CONCLUSION

Silver/manganese oxide nano thin films were obtained by electrodeposition from the KMnO4 and Ag (CH_3COO) solutions. The thickness of the thin films manganese dioxide is about in the range of 100~300nm. The thin films are composed of Ag_2O and α -Mn_2O_3 nanoparticles for lower Ag content, whereas Ag_2O_2 and β -MnO_2 is for higher Ag content examined from the XPS analysis. And then Ag nanoparticles acted as a reduction agent to change the valence of Mn from 4+ to 3+. The supercapacitors give CV curves became nearly rectangular shape and exhibit mirror-image characteristics with Ag addition. The capacitance values as found increased with the increase of the ratio of the Ag/Mn up to 8%. In addition, the impedance of the cell increased with the Ag/Mn ratio up to 0.8%. The sample with Ag/Mn is 0.8% has highest capacitance in this work. We conjecture that the formation of Ag_2O will increase the pseudo-capacitance between the active material and electrolyte.

REFERENCES

[1] R. Kötz, M. Carlen: “Principles and applications of electrochemical capacitors”, Electrochimica Acta, vol. 45, pp. 2483-2498, 2000.

[2] P. Gouerec, H. Talbi, D. Miousse, F. Tran-Van, L.H. Dao, K.H. Lee,” Preparation and modification of polyacrylonitrile microcellular foam films for use as electrodes in supercapacitors” J. Electrochem. Soc. Vol. 148, pp. A94-A101, 2001.

[3] S.T. Mayer, R.W. Pekala, J.L. Kaschmitter,“ The aerocapacitor: An electrochemical energy-storage device,” J. Electrochem. Soc., Vol.140, pp. 446-451, 1993

[4] M. Ishikawa, M. Morita, M. Ihara, Y. Matsuda,” Electric double-layer capacitor composed of activated carbon-fiber cloth electrodes and solid polymer electrolytes containing alkylammonium salts,” J. Electrochem. Soc., Vol.141, pp. 1730-1734, 1994.

[5] A. Rudge, J. Davey, I. Raistrick, S. Gottesfeld,” Conducting polymers as active materials in electrochemical capacitors,” J. Power Sources, Vol. 47, pp. 89-107, 1994.

[6] A. Rudge, J. Davey, I. Raistrick, S. Gottesfeld,“ A study of the electrochemical properties of conducting polymers for application in electrochemical capacitors,” Electrochim. Acta, Vol. 37, pp. 273-278, 1994.

[7] S. Sarangapani, B.V. Tilak, C.P. Chen, “Material for electrochemical capacitors”, J. Electrochem. Soc., Vol.143, pp. 3791-3799, 1996.

[8] J. P. Zheng, P. J. Cygan, T. R. Jow,” Hydrous ruthenium oxide as an electrode material for electrochemical capacitor,” J. Electrochem. Soc. , Vol. 142, pp. 2699-2703, 1995.

[9] C. C. Hu, Y. H. Huang,” Cyclic voltammetric deposition of hydrous ruthenium oxide for electrochemical capacitors,” J. Electrochem. Soc., Vol. 146, pp. 2465-2471, 1999.

[10] J. J. Jow, H. J. Lee, H. R. Chen, M. S. Wu, T. Y. Wei,” Anodic, cathodic and cyclic voltammetric deposition of ruthenium oxides from aqueous $RuCl_3$ solutions,” Electrochim Acta, Vol. 52, pp. 2625-2633, 2007.

[11] H. Y. Lee, J.B. Goodenough,“ Supercapacitor Behavior with KCl Electrolyte”, J. Solid State Chem., Vol. 144, pp. 220-223, 1999.

[12] J. Wei, N. Nagarajan, I. Zhitomirsky,’ Manganese oxide films for electrochemical supercapacitor,” J. Mater. Process. Technol., Vol. 186, pp. 356–361, 2007.

[13] M. Wu, G. A. Snook, G. Z. Chen, D. J. Fray,” Redox deposition of manganese oxide on graphite for supercapacitors,” Electrochem. Commun., Vol. 6, pp. 499-504, 2004.

[14] R. N. Reddy, R.G. Reddy, "Sol-gel MnO_2 as an electrode materials for electrochemical capacitors", J. Power Source, Vol.124, pp. 330-337, 2003.

[15] D. J. Jones, E. Wortham, J. Rozi´ere, F. Favier, J. L. Pascal, L. Monconduit,” Manganese oxide nanocomposites: preparation and some electrochemical properties,” J. Phys. Chem. Solids, Vol. 65, pp. 235-239, 2004.

[16] S. C. Pang, M. A. Anderson, T. W. Chapman,” Novel electrode materials for thin film suparcapacitors: comparison of electrochemical properties of sol-gel-derived and electrodeposited manganese dioxide,” J. Electrochem. Soc., Vol. 147, pp. 444-450, 2000.

[17] J. H. Jiang, A. Kucernak,” Electrochemical supercapacitor material based on manganese oxide: Preparation and characterization,” Electrochim. Acta, vol.47, pp. 2381-2386, 2002.

[18] R. K. Sharma, H.-S. Oh, Y.-G. Shul, H. Kim,” Carbon-supported, nano-structured, manganese oxide composite electrode for electrochemical supercapacitor,” J. Power Sources, Vol. 173, pp. 1024–1028, 2007.

[19] Y. T. Wu, C. C. Hu,” Effects of electrochemical activation and multiwall carbon nanotubes on the capacitive characteristics of thick MnO_2 deposits,” J. Electrochem. Soc., Vol.151, pp. A2060-2066, 2005.

[20] K. C. Liu, M. A. Anderson,” Porous nickel oxide/nickel films for electrochemical capacitors,” J. Electrochem. Soc., Vol. 143, pp. 124-131, 1996.

[21] V. Srinivasan, J. W. Weidner,” Electrochemical Route for Making porous nickel oxide electrochemical capacitors,” J. Electrochem. Soc., Vol. 144, pp.L210-213, 1997.

[22] E. E. Kalu, T. T. Nwoga, V. Srinivasan, J. W. Weidner,”Cyclic voltammetric studies of the effects of time and temperature on the capacitance of electrochemically deposited nickel hydroxide,” J. Power Sources, Vol. 92, pp. 163-167, 2001.

[23] M. S. Wu, Y. A. Huang, C. H. Yang, J. J. Jow, ”Electrodeposition of nanoporous nickel oxide film for electrochemical capacitors,” Int. J. Hydrogen Energy, Vol. 32, pp. 4153-4159, 2007.

[24] J. S. Foord, R.B. Jackman, G. C. Allen,” An X-ray photoelectron spectroscopic investigation of the oxidation of manganese,” Philos. Mag., Vol. A49, pp. 657-663, 1984.

[25] G. I.N. Waterhouse, J. B. Metson, G. A. Bowmaker,” Vibrational spectra and thermal stability of Ag_3O_4 and related Ag_7O_8X salts (X= NO^{3-} ,ClO^{4-},HSO^{4-}),” Polyhedron, Vol. 26, pp. 3310-3322, 2007.