High Capacitive behaviour of nanostructured manganese oxide films prepared by galvanostatic electrodeposition

***N. Boukmouche*[1*], *N. Azzouz*[1], *L. Bouchama*[1], *J.P. Chopart*[2]**
1 : Laboratory of the Interactions Materials-Environment (LIME), University of Jijel P.O.Box 98 Ouled Aissa 18000 Algeria. E-mail: nawboukmouche@yahoo.com
2: Laboratory for Analysis of Mechanical Constraints – Transfers to Interface Dynamics (LACM-DTI), University of Reims Champagne-Ardenne (French).

Abstract

The manganese dioxide thin films nanostructured MnO_2 was successfully electrodeposited onto graphite electrode in a bath containing [$Mn(CH_3COO)_2$ $4H_2O$] aqueous solutions. The MnO_2 thin films were studied by X-ray diffraction analysis (XRD), followed the observations by the scanning electron microscope (SEM) and atomic force microscope (AFM), with a crystalline structures and many small nanowires. The electrochemical characterization was performed using cyclic voltammetry (CV), showing capacitive behavior in the voltage 1.4 V/SCE in 0.5 M Na_2SO_4 electrolyte solution. The supercapacitance obtained is 136 $F.g^{-1}$. In addition, the electrochemical process, such as ion transfer and surface capacitance, was also investigated with electrochemical impedance spectroscopy. The long cycle-life and stability of the MnO_2 coatings on graphite via the presented electrodeposition were also demonstrated.

Keywords: galvanostatic deposition, MnO_2 thin film, supercapacitors.

1 Introduction

Supercapacitors, also termed ultracapacitors, large-capacity capacitors or electrochemical capacitors, which are novel energy storage devices between conventional capacitors and batteries, with higher specific capacitance and energy densities than conventional capacitors, and greater power densities than batteries [1-3].
In recent years, supercapacitors have attracted lot of interests due to their potential applications as energy storage and power supply devices, which can be regarded as an intermediate device between batteries and conventional capacitors, allowing applications for various power and energy requirements, such as cardiac pacemakers, mobile phones, electric and hybrid vehicles, airbags, engine start, digital cameras, and solar cell power storage, etc [4-8].

Many chemically deposited metal oxide thin films including ruthenium oxide, iridium oxide, manganese oxide, cobalt oxide, nickel oxide, tin oxide, iron oxide, pervoskites, ferrites, etc. have been applied in supercapacitors. The thin film deposition methods involving the growth from solution are called as chemical methods. Here, a fluid surface precursor undergoes a chemical change at a solid surface, leaving a solid layer. In chemical deposition the solutions contain precursor molecules for a variety of elements in the thin film of interest. These methods are inexpensive and enable the synthesis of film materials with complex chemical compositions [9]. Depending on applications, one would prefer thin films which have a special texture, low grain boundary density, or smooth surfaces. The methods usually have low operating temperature. Apart from the obvious advantages in terms of energy saving, the low deposition temperature avoids high temperature effects such as interdiffusion,

contamination and dopant redistribution. They offer mysterious morphologies of the thin films which can be easily controlled by preparative parameters. Unlike physical deposition methods, they do not require high quality target and/or substrates nor do they require vacuum at any stage, which is a great advantage if the methods are used for industrial applications. Chemical methods include electrodeposition, chemical bath deposition (CBD), successive ionic layer adsorption and reaction (SILAR), electroless deposition, anodization, spray pyrolysis, liquid phase epitaxy, spin coating, dip drying, etc [10]. The different methods significantly affect the surface morphology, crystal structure and hence the supercapacitive properties of deposited material. It is well-known that the performance is highly dependent on MnO_2 morphologies as well as crystallographic forms [11].

The goal of this study is the preparation of MnO_2 thin films using by electrodeposition. The supercapacitive properties, the cyclic voltammetry and impedance of MnO_2 thin films have been studied in 0.5 M Na_2SO_4 electrolyte.

2 Experimental

The manganese oxide (MnO_2) films were electrodeposited at temperature 15 °C from 0.2 M [$Mn(CH_3COO)_2$ $4H_2O$] aqueous solutions. Electrodeposition was obtained on graphite substrate, using a three-electrode cell, the working electrode (0.5 mm×10 mm×1 mm). The counter electrode was platinum, and the reference electrode was a standard calomel reference electrode (SCE). The substrates were degreased thoroughly with sulfuric acid (H_2SO_4), acetone and deionised water. The deposition was performed at 2.5 $mA.cm^{-2}$.

The obtained thin films were characterised by X-ray diffraction (XRD) analysis, followed the observations by the scanning electron microscope (SEM) and atomic force microscope (AFM). The thin electrodeposited films was studied using a potentiostat/ galvanostat Radiometer Analytical type Voltalab 40 PGZ301 controlled by a computer using a software Voltamaster 4 for treatment and data acquisition. Electrochemical characterization of the film was performed using a standard three-electrode cell configuration with 0.5M Na_2SO_4 aqueous solution as an electrolyte. The surface area of the working electrode was 0.5 cm^2. The counter electrode was platinum, and the reference electrode was a standard calomel reference electrode (SCE). Cyclic voltammetry (CV) studies were performed for different scan rate for 10, 50, 100 and 200 $mV.s^{-1}$ for a potential of 1.4V versus SCE, and the electrochemical impedance spectroscopy (EIS), the analyzed frequency range f_{max} to f_{min}: 100 kHz to 10^{-6} kHz.

3 Results and discussion

3.1 XRD analysis

Samples previously treated were then subjected to analyse by the X-Ray diffractometer, D 8-ADVANCE model of BRUKER-AXS (University of Jijel). Fig.1 shows an XRD diagram of the manganese oxide (galvanostatic method) films, where we indicate the formation of the crystalline structure of a film of manganese oxide. With the presence of an amorphous part is feasible for supercapacitor application due to easy penetration of ions through the bulk of the active material [12]. The structure is tetragonal with the space group P4/mnm and lattice parameters a = b = 4.38 Å, c = 2.85 Å.

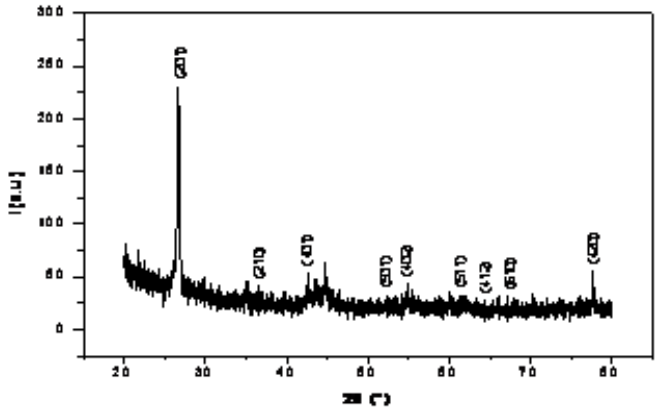


Figure 1: XRD patterns of MnO_2 thin films on to graphite substrate

3.2 Characterization by AFM

Fig. 2 shows the AFM images of MnO_2 thin films. The deposit shows a rough, highly porous and nanostructured morphology with many small nanowires. This type of nanostructured and microporous structures are expected to produce high specific capacitance values when used for capacitor applications.

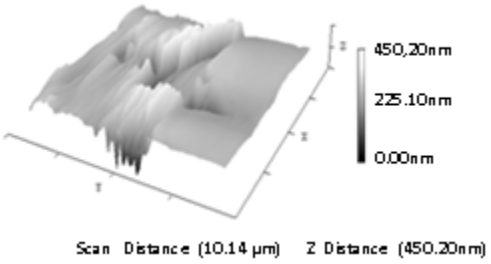


Figure 2: AFM images of MnO_2 thin films

3.3 CV studies

CV is an important tool to investigate the capacitive behavior of materials. The CV curve provides the measure of a supercapacitor's charge response with a charging voltage and hence can be used to evaluate the capacitance. The cyclic voltammogram of a supercapacitor is just an electrochemical hysteresis that stores the energy in redox process (charging and discharging). Due to a complete electrochemical reversible process, an ideal capacitor has a rectangular shape which is widely known.

The fig.3 shows Cyclic voltammetry for MnO_2 thin films obtained by anodic deposition at different scan rate for 10, 50, 100 and 200 $mV.s^{-1}$.

The stored charges at the interface in the EDLC are strongly dependent on the electrode potential and the electrode is charged and discharged at a constant for potential: 1.4 V/ECS. It is also clear that there are no redox peaks.

All the curves were rectangular in shape and exhibit mirror-image characteristics which indicate capacitive behavior.

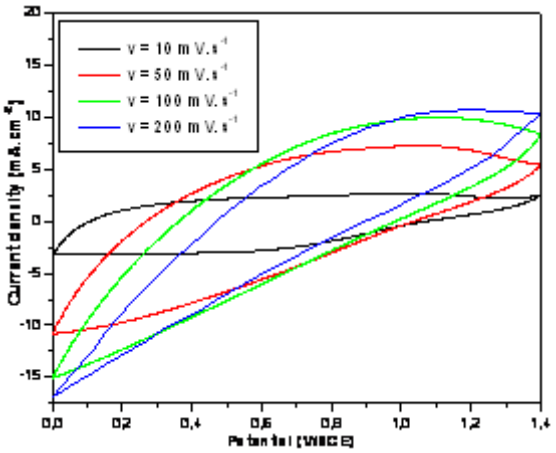


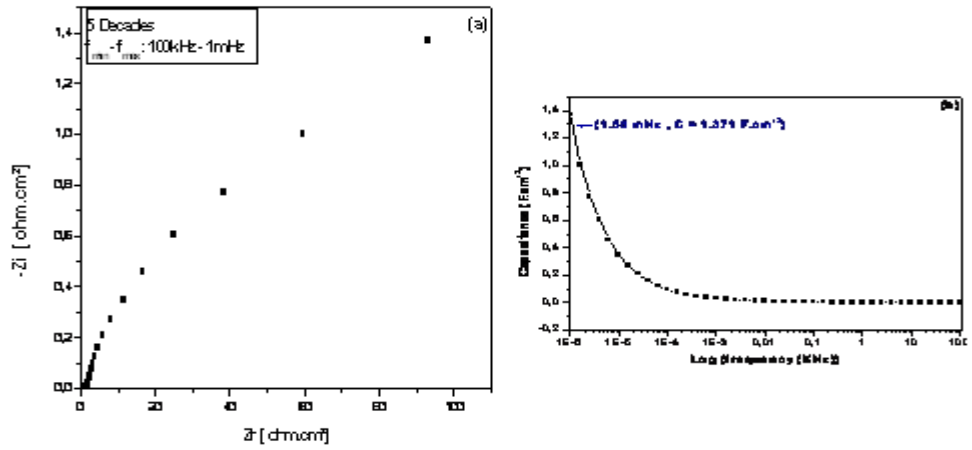
Figure 3: Cyclic voltammetry for MnO_2 thin films

The table 1 shows the specific capacitance and energy for different scan rate, where the specific capacitance decreases with increased scan rate for MnO_2 thin films.

Table 1- Specific capacitance for different scan rate.

Scan rate / mV s^{-1}	10	50	100	200
Specific capacitance / F g^{-1} (ED: MnO_2)	136.20	81.91	58.80	34.56

3.4 Electrochemical impedance spectroscopy (EIS)



The fig. 4 shows the impedance spectra of MnO_2 thin films, Where Z' and Z'' are the real part and the imaginary part of the impedance, respectively. The system is pseudocapacitive with a surface capacitance of a value C_S = 1.37 F.cm^{-2}, at very low frequency (fig. 4b) and Fig. 4c represents the real

part in function of frequency. The practical results show that the minimal value of the real part is obtained for values of high frequencies.

4 CONCLUSION

We have successfully prepared MnO_2 thin films by electrodeposition method. XRD patterns of MnO_2 thin films revealed the formation of crystalline phase with structure tetragonal. From AFM, highly porous and nanostructured morphology with many small nanowires. The values specific capacitance decreases with increased scan rate MnO_2 thin films for CV test.
It has been found that the electrode has excellent electrochemical reversibility; high stability of the material was demonstrated.

References

[1] Y. Zhang, H. Feng, X. Wu, L. Wang, A. Zhang, T. Xia "Progress of electrochemical capacitor electrode materials: a review", Int J Hydrogen Energy.Vol. 34, 4pp889-4899, 2009.

[2] P.J. Sebastian, A.L. Ocampo, J. Moreira "Sintered $Mo_xS_y(CO)_n$ and $Mo_x(CO)_n$: application in oxygen reduction reaction, hydrogen evolution and supercapacitors", Int J Hydrogen Energy, Vol. 26, pp 139-143, 2001.

[3] 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.

[4] L. Wang, T. Morishita, M. Toyoda, M. Inagaki "Asymmetric electric double layer capacitors using carbon electrodes with different pore size distributions", Electrochim Acta, Vol. 53, pp 882-886, 2007.

[5] L. Zhang, H. Liu, M. Wang, L. Chen "Structure and electrochemical properties of resorcinol-formaldehyde polymer-based carbon for electric double-layer capacitors", Carbon, Vol. 45, pp 1439-45, 2007.

[6] C. Chen, D. Zhao, X. Wang "Influence of addition of tantalum oxide on electrochemical capacitor performance of molybdenum nitride", Mater Chem Phys, Vol. 97, pp 156-61, 2006.

[7] W. Xing, , S.Z. Qiao, R.G. Ding, F. Li, GQ. Lu, Z.F. Yan "Superior electric double layer capacitors using ordered mesoporous carbons", Carbon, Vol. 44, pp 216-224, 2006.

[8] J.P. Zheng "Theoretical energy density for electrochemical capacitors with intercalation electrodes", J Electrochem Soc, Vol. 152, pp A1864- A1869, 2005.

[9] G. Hodes "Chemical Solution Deposition of Semiconductor Films", Marcel Dekker Inc, 2001, NewYork.

[10] C.D. Lokhande, D.P.Dubal , O.S. Joo "Metal oxide thin film based supercapacitors", Current Applied Physics, Vol. 11, pp 255-270, 2011.

[11] S. Jana, S. Basu, S. Pande, S.K. Ghosh, T. Pal "Shape-selective synthesis, magnetic properties, and catalytic activity of single crystalline MnO_2 nanoparticles", J. Phys. Chem, Vol. C 111, pp 16272-16277, 2007.

[12] T.P. Gujar, V.R. Shinde, C.D. Lokhande, W.Y.Kim, K.D. Jung, O.S. Joo, "Spray deposited amorphous RuO2 for an effective use in electrochemical supercapacitor", Electrochem.Commun, Vol. 9, pp 504 510, 2007.