

Effect of Ag-Doping on the Capacitive Behavior of Amorphous Manganese Dioxide Electrodes

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Abstract Amorphous MnO₂ and Ag-doped MnO₂ thin films were galvanostatically deposited on a polished stainless steel substrate from 20 mM KMnO₄ aqueous solutions without and with AgNO₃ additions at cathodic current density of 1 mA/cm² for the application in electrodes of electrochemical supercapacitors. The supercapacitive properties of the deposited thin films have been studied in 0.5 M Na₂SO₄ electrolyte by cyclic voltammetry, impedance spectroscopy, and charge-discharge measurement techniques. The Ag-free MnO₂ film showed better capacitive behavior and lower charge transfer resistance compared to the Ag-doped MnO₂ films. The specific capacitance and charge transfer resistance values for Ag-free MnO₂ films were 160 F/g at a scan rate 10 mV/s and 3.87 Ω, respectively. Cyclic stability using charge-discharge measurement technique indicates the excellent stability of Ag-free MnO₂ films and its possible use as a low cost electrode for supercapacitor applications.

Keywords Cyclic Voltammetry, Manganese Dioxide, Power Density, Energy Density, Cyclic Stability

1. Introduction

Several energy storage devices, such as compressed air, hydrogen, flywheels, batteries, capacitors, and fuel cells, have been developed for various practical applications. Among these devices, high performance batteries and capacitors have presented themselves as one of the achievable, economically feasible options for meeting today's severe energy demands. Supercapacitors have received a lot of attention as viable electrical energy storage devices owing to their ability to deliver high powers, excellent reversibility, and longer cycle life than batteries[1-3]. On the basis of the energy storage mechanism, supercapacitors can be classified into two categories[4-6], namely the electrical double-layer capacitor (EDLC) and the pseudo-capacitor. The capacitance of the former comes from the charge accumulation at the electrode/electrolyte interface (double-layer capacitance), therefore it strongly depend on the surface area of the electrode accessible to the electrolyte. The capacitance of the latter is due to the reversible faradic transfer of charge between electrode and electrolyte, such as surface functional groups and transition metal oxides. Supercapacitors fill the gap between batteries (low specific power and high specific

energy) and conventional capacitors (high specific power and low specific energy), i.e. they have a specific power as high as conventional capacitors and a specific energy close to that of batteries. It is obvious that the electrode is the key in the development of supercapacitors.

MnO_x is a promising electrode material for electrochemical capacitors because of its the relatively low cost, excellent electrochemical performance, environmentally friendly character in comparison with the ruthenium oxides or other transition metal oxides[7-9]. Hydrous ruthenium oxide has been extensively studied[10,11] as an active electrode material for supercapacitors with capacitance as high as 720 F/g in aqueous acidic electrolytes. Although RuO₂ gives high specific capacitance, its disadvantages of high cost and toxic nature limit its further commercial application. As an inexpensive alternate to RuO₂, hydrous manganese oxide prepared by both chemical and electrochemical methods was found to possess capacitive characteristics with acceptable values of specific capacitance[12-16]. A specific capacitance of 130 F/g was reported[16] at a scan rate of 5 mV/s, for manganese dioxide synthesized by sol-gel method.

Recent investigations showed that 1–8 wt.% Ag addition to lithium manganese dioxide electrode can significantly improve battery performance due to the increase in conductivity[17]. In another investigation the increase in conductivity of Ag-doped RuO₂ compared to pure RuO₂ was reported[18]. As a result, Ag-doped RuO₂ showed much higher

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Published online at <http://journal.sapub.org/eee>

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SC compared to the SC of undoped RuO_2 [18]. Therefore, it is important to fabricate and investigate the Ag-doped MnO_2 films. MnO_2 films for application in electrochemical supercapacitors (ES) can be prepared by anodic or cathodic electrodeposition from aqueous solutions. However, anodic electrolytic deposition of MnO_2 on metallic current collectors presents difficulties related to the anodic oxidation and dissolution of metals. In contrast, cathodic electrodeposition can be performed on various metallic substrates. It should be noted that cathodic electrodeposition is an important industrial technique for the deposition of metals. Therefore, cathodic electrodeposition is a promising method for the co-deposition of oxides and metals and the fabrication of doped films and composites.

The goal of the present study is to fabricate Ag-free MnO_2 and Ag-doped MnO_2 thin films by galvanostatically cathodic deposition on polished stainless steel substrate from KMnO_4 aqueous solutions without and with AgNO_3 additions for the application in electrodes of ES.

2. Experimental

Stainless-steel (SS) sheet of grade 316 LN, thickness 0.25 mm and surface area of $6 \text{ mm} \times 15 \text{ mm}$ was used as current collector and substrate for the electrodeposition of the active materials. Prior to the electrodeposition experiments, the substrate were mechanically polished with SiC papers down to 2000.

MnO_2 and Ag-doped MnO_2 thin films were galvanostatically deposited from 20 mM KMnO_4 solution without and with AgNO_3 additions (0.5, 2, and 4 mM) at cathodic current density of 1 mA/cm^2 onto SS substrate for 0.5 hour. The weight of the deposited films was measured by means of a Sartorius micro-balance (Model BP211D). The structure was characterized by means of X-ray diffractometer (Shimadzu, XRD-7000) using $\text{Cu K}\alpha$ radiation.

All electrochemical investigations were performed at $30 \pm 1.0^\circ\text{C}$ using two compartment three electrodes electrochemical cell with platinum foil as an auxiliary electrode and a saturated Ag/AgCl reference electrode. The capacitive performance of the deposited films was examined in 0.5 M Na_2SO_4 electrolyte using the electrochemical impedance spectroscopy (EIS), cyclic voltammery (CV) measurement techniques, and galvanostatic charge-discharge. The CV measurements were carried out at potential ranges of 0–0.9 V vs. Ag/AgCl (sat.) at scan rates of 10–90 mV/s. The excitation amplitude for impedance measurements was 10 mV root mean square (RMS) in a frequency domain of 10^{-1} to 10^5 Hz.

3. Results and Discussion

3.1. Structure

Figure 1 shows XRD patterns of Ag-free MnO_2 and Ag-doped MnO_2 thin films prepared by galvanostatic cathodic deposition method on polished SS substrate from 20 mM KMnO_4 aqueous solutions without and with 2 mM

AgNO_3 addition at 1 mA/cm^2 . As seen, the XRD patterns show no reflection peaks typical characteristics of any crystalline or nanocrystalline MnO_2 -based oxide films. This indicates the formation of amorphous Ag-free MnO_2 and Ag-doped MnO_2 thin films with very high degree of structure disorder.

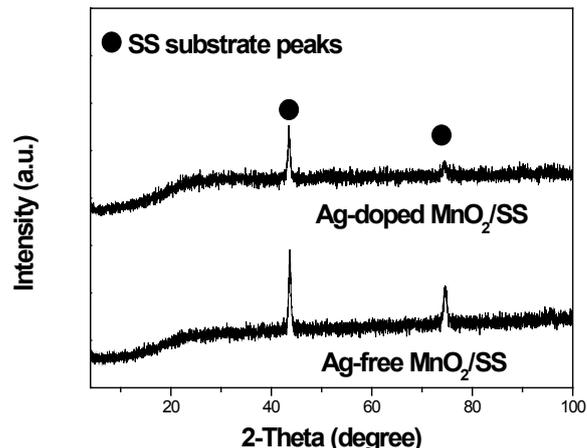


Figure 1. XRD patterns for Ag-free MnO_2 and Ag-doped MnO_2 (2 mM AgNO_3) films deposited on polished SS substrate

Sharp reflection peaks from SS substrate are also detected in the diffraction patterns of both oxides referring to the formation of thin deposit films on the SS substrate. It's also worth noting that Ag-free MnO_2 and Ag-doped MnO_2 thin films show almost identical diffraction patterns.

3.2. Supercapacitive Properties of the Deposit Film

3.2.1. Cyclic Voltammetry

Figure 2 shows the CV curves of the Ag-free MnO_2 and Ag-doped MnO_2 films in the potential range of 0–0.9 V vs. Ag/AgCl (sat.). All the curves are near-rectangular in shape and show symmetrical anodic and cathodic halves which indicate ideal capacitive behavior of the deposited films. As it can be seen in Fig. 2, the capacitive current density of Ag-free MnO_2 is higher than those of Ag-doped MnO_2 .

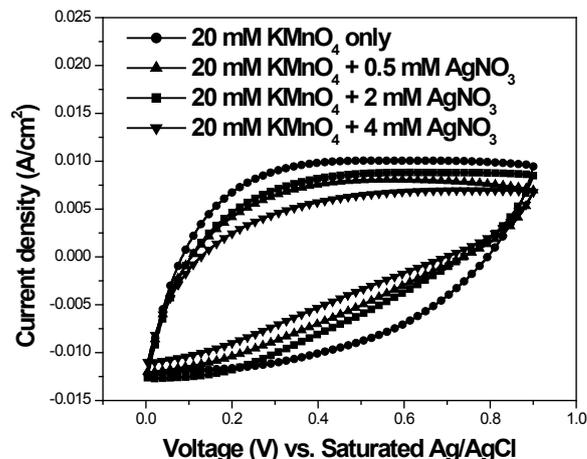


Figure 2. Cyclic voltammetric curves of Ag-free MnO_2 and Ag-doped MnO_2 films measured in 0.5 M Na_2SO_4 solution at a scan rate of 90 mV/s

For estimating the specific capacitance (SC) of the deposited oxide films, the amount of capacitive charge (Q) was obtained using half the integrated area of the CV curve presented in Fig. 2, and then the SC was calculated from dividing the capacitive charge by the film mass (m) and the width of the potential window (ΔV) using equation (1).

$$SC = \frac{Q}{m \cdot \Delta V} \quad (1)$$

Figure 3 summarizes the dependence of the SC on the CV scan rate for Ag-free MnO_2 and Ag-doped MnO_2 films. In general, the specific capacitance decreases as the scan rate increases. This behavior can be attributed to the high probability of exposing both inner and outer surface of the deposited oxide to the ions with the decrease in the scan rate [19].

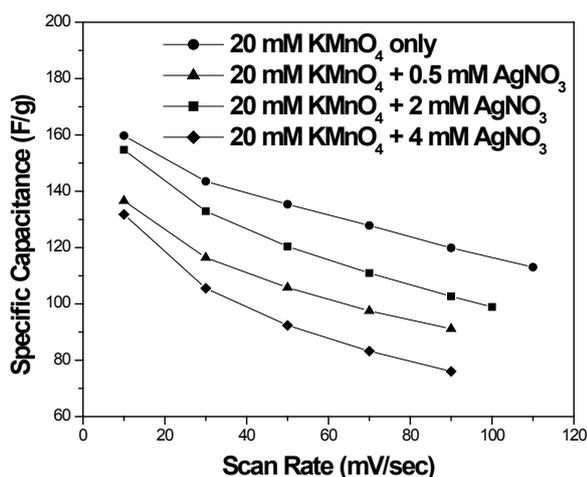


Figure 3. Variation of the specific capacitance with the scan rate of CV measurement for MnO_2 and Ag-doped MnO_2 films

Meanwhile, the maximum values of the specific capacitance for the films deposited from 20 mM $KMnO_4$ aqueous solutions with 0.0, 0.5, 2, and 4 mM $AgNO_3$ additions at a scan rate of 10 mV/s are 160, 137, 155, and 132 F/g, respectively. This fact indicates that the introduction of Ag in the matrix of the deposited MnO_2 has no beneficial effect on its capacitive properties.

3.2.2. Electrochemical Impedance Spectroscopy

In principle, the power output capability of electrochemical supercapacitor depends strongly on not only the rates of ionic mass transport [20] but also the equivalent series resistance (ESR) [21]. The ESR is the sum of two major parts, an electronic resistance and an ionic one. EIS has been widely used to study the redox (charging/discharging) processes of electrode materials and to evaluate their electronic and ionic conductivities.

Figure 4 shows the measured Nyquist plots of MnO_2 and Ag-doped MnO_2 electrodes in 0.5 M Na_2SO_4 electrolyte. The inset of Fig. 4 represents the high frequency region of the recorded full impedance plots. In Fig. 4, two well-separated patterns are observed: an arc is obtained at frequencies high enough, which is related to interfacial processes; the

low-frequency region of such plots indicated a capacitive behavior related to the film charging mechanism.

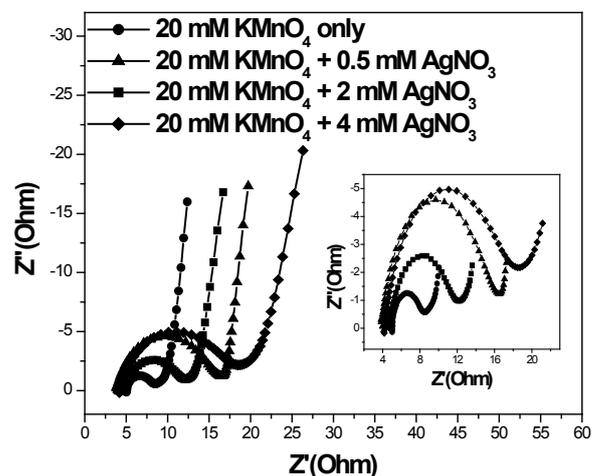


Figure 4. The Nyquist plots of MnO_2 and Ag-doped MnO_2 electrodes investigated in 0.5 M Na_2SO_4 electrolyte in the frequency range of 0.1 Hz–100 kHz at 10 mV amplitude

The initial non-zero intersect with the real impedance axis at the beginning of the semicircle indicates the typical ESR value of all system [19,22]. The estimated ESR values for the films deposited from 20 mM $KMnO_4$ aqueous solutions with 0.0, 0.5, 2, and 4 mM $AgNO_3$ additions are 5, 4.1, 4.85, and 4.17 Ω , respectively. These results indicate that the ESR value of MnO_2 deposited film has not been significantly affected by Ag doping.

On the other hand, all spectra showed a clear semi-circle at the high frequency region, which corresponds to the charge transfer resistance (R_{ct}). The magnitude of the R_{ct} can be derived from the difference in the real part of the impedance between low and high frequencies [1,23] using fitting program provided with the electrochemical workstation. The estimated R_{ct} values for the films deposited from 20 mM $KMnO_4$ aqueous solutions with 0.0, 0.5, 2, and 4 mM $AgNO_3$ additions are 3.87, 12.79, 7.81, and 15.3 Ω , respectively. The increase in the R_{ct} value of MnO_2 with Ag addition may refer to the detrimental effect of Ag addition on the electronic transport properties of the deposited oxide.

Meanwhile, a comparison of the imaginary impedance (Z'') data at the same frequencies for all the deposited films indicates that the capacitance for Ag-free MnO_2 film is higher than those of Ag-doped MnO_2 films. This fact is in a good agreement with the SC data presented in Fig. 3.

3.2.3. Galvanostatic Charge–Discharge

Figure 5 presents the charge–discharge curves for the films deposited from 20 mM $KMnO_4$ aqueous solutions with 0.0, 0.5, 2, and 4 mM $AgNO_3$ additions. The curves were measured in the potential range between 0 and +1 V at a discharge current density of 1.1 mA/cm².

In Fig. 5, there is a linear variation of potential during charging process, indicating the capacitive behavior of MnO_2 and Ag-doped MnO_2 films. The discharge part of the curves consists of three segments: a resistive component

from the sudden decrease of voltage (iR drop) related to the internal resistance of the deposit, the capacitance component which is related to the voltage change due to ions separation at electrode interface in the double layer region and the faradaic component which is attributed to charge transfer reaction of deposit. Detailed analysis of the results in Fig. 5 clearly shows that the Ag-free MnO_2 film has longer time for charging-discharging processes and lower iR drop value than those recorded for Ag-doped MnO_2 deposited films. These facts indicate the higher energy and power densities of Ag-free MnO_2 than those of Ag-doped MnO_2 .

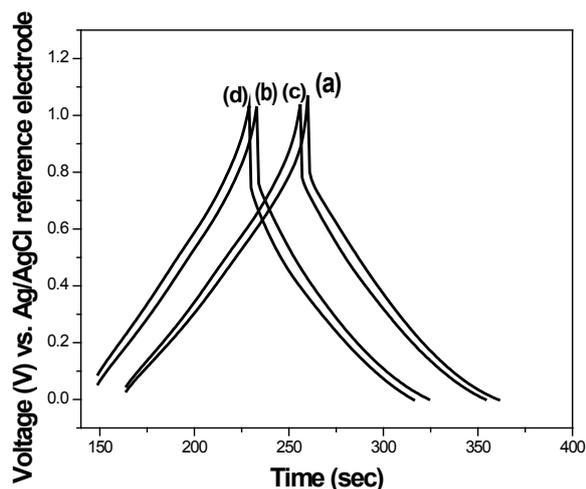


Figure 5. Charge-discharge curves in 0.5 M Na_2SO_4 electrolyte for thin films deposited from 20 mM KMnO_4 aqueous solutions with (a) 0.0 M AgNO_3 , (b) 0.5 mM AgNO_3 , (c) 2 mM AgNO_3 , and (d) 4 mM AgNO_3 .

3.2.4. Cyclic Stability using Galvanostatic Charge-Discharge

The cyclic stability test of Ag-free MnO_2 film was performed at discharge current density 5.5 mA/cm^2 and the results are presented in Fig. 6.

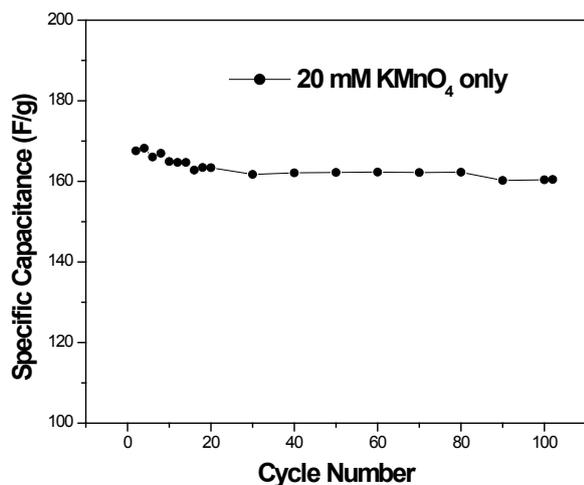


Figure 6. Life-cycle data of the Ag-free MnO_2/SS electrode at discharge current density 5.5 mA/cm^2

As it can be clearly seen in Fig. 6, there is a little decrease in the value of specific capacitance during the first 30 cycles and then the specific capacitance value remained almost

constant. A decrease of about 4 % in the initial specific capacitance was observed after 100 cycles. This decrease in the value of specific capacitance is very less compared to the reported value in the literature[24] and indicates the high stability of the deposited film.

4. Conclusions

The results presented in this investigation indicated that amorphous Ag-free and Ag-doped manganese dioxide thin films were successfully prepared by galvanostatic cathodic deposition onto polished SS electrodes from KMnO_4 solution without and with AgNO_3 addition. The Ag-doped manganese MnO_2 films showed lower capacitive behavior and higher charge transfer resistance compared with Ag-free MnO_2 deposited film. The specific capacitance and charge transfer resistance values for Ag-free MnO_2 films were 160 F/g at a scan rate 10 mV/s and 3.87 Ω , respectively. The Ag-free MnO_2 film prepared by the cathodic electrolytic deposition on low cost stainless steel substrate can be considered as possible electrode materials for supercapacitor application.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the Missions Sector-Higher Education Ministry, Egypt for financial support through this work.

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