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"Efficient Potentiostatically Electrodeposited MnO₂ Electrode for Electrochemical Pseudocapacitor Applications"

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ABSTRACT

A manganese oxide (MnO₂) electrode has been developed by using potentiostatic electrodeposition method and characterized for its compositional, morphological and afterward envisaged in pseudocapacitor applications. The elemental analysis of MnO₂ electrode was studied using X-ray photoelectron spectroscopy (XPS). The supercapacitive properties of MnO₂ electrode studied using cyclic voltammetry and galvanostatic charge-discharge measurements in 1M Na₂SO₄ electrolyte. A high specific capacitance of 626 Fg⁻¹ was obtained within the potential range of –0.3 to 0.8 V in 1M Na₂SO₄ electrolyte. Additionally, MnO₂ electrode exhibited high charge/discharge efficiency of 98.32%. The present study signifies successful application of potentiostatic electrodeposited MnO₂ thin films as a supercapacitor electrode.

Keywords: Manganese Oxide; X-ray Photoelectron Spectroscopy; SEM, Cyclic Voltammetry; Galvanostatic Charge-Discharge.

I. INTRODUCTION

Supercapacitors as one of the most significant energy devices want to be designed with high energy density and high levels of important mechanical properties, especially flexibility to meet the power needs of modern gadgets and various designs [1]. From the materials points of view, three families of materials have been used in supercapacitors until now, that is, conducting polymer, metal oxide, and carbon [2]. Each type of material they have its own advantages and disadvantages. Carbon materials have good mechanical and long cycle life, but low specific capacitance [3]. Conducting polymers are eminent for their high flexibility, but low specific capacitance with poor cyclability [4]. In metal oxides, MnO₂ is considered as the most capable material for the next generation of supercapacitors because of its environmentally friendly nature, high specific capacitance, high energy and power densities, excellent rate capability, excellent long-term cycle stability [5].

A number of techniques including coprecipitation [6], simple reduction [7], thermal decomposition [8], sol-gels [9] and electrochemical methods (potentiostatic [10], galvanostatic [11] and potentiodynamic [12]) are available to prepare this metal oxide. In the present study, electrochemical potentiostatic electrodeposition was chosen because it allows for the material to be homogeneous, rapidly

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and reproducibly deposited on a stainless steel substrate as electrode in ECs.

In the present work, MnO₂ thin film electrode was synthesized by potntiostatic electrodeposition method and characterized using various techniques such as XPS (X-ray Photoelectron Spectroscopy), and SEM (Scanning Electron Microscope) respectively. The electrochemical performance was carried out using cyclic voltammetry (CV), and Galvanostatic charge– discharge for its application as pseudocapacitors. The electrochemical performance is studied in 1M Na₂SO₄ aqueous electrolytes. The obtained MnO₂ electrode shows outstanding capacitive performance in terms of specific capacitance and high coloumbic efficiency which is promising for supercapacitor application.

II. EXPERIMENTAL DETAIL

The potentiostatic electrodeposition method were used for the deposition of the MnO₂ thin film electrode on stainless steel substrate. For the depostion, 0.1 M manganese sulphate (MnSO₄) of high purity 99.9% was used as precursor in 100ml distilled water. Stainless steel (SS) substrate of 304 grades is used as conducting substrate for deposition of active material. The optimized potential and time for deposition of manganese on stainless steel is 1.2V and 10 minutes respectively. By potentiostatic method the formation of manganese on stainless steel is uniform, homogeneous and well adherent. The electrodeposited material film was annealed at 400°C for 1 hrs. After annealing well deposited black colored manganese oxide films were obtained which were used for compositional, morphological and supercapacitive characterization.

Chemical state of the prepared electrode was investigated by X-ray photoelectron spectroscopy (XPS) using a Kratos AXIS Ultra X-ray photoelectron spectrometer.Scanning Electron Microscopy (SEM) was used to explore the surface morphology of prepared MnO₂ electrode. The mass of deposited

material was measured using high precision analytic balance (CONTECH, with 0.01 mg sensitivity).

Electrochemical study on MnO₂ electrodes were carried out on a CH Instruments Electrochemical Workstation (CH608E). All electrochemical study were investigated in a conventional three-electrode system equipped with, platinum electrode as a counter electrode, prepared MnO₂ as a working electrode and a saturated calomel electrode (SCE) as a reference electrodes. Cyclic voltammetry (CV) and galvanostatic charge–discharge (CP) methods were used to examine capacitive properties of MnO₂ electrode.

III. RESULT AND DISCUSSION

X-ray photo-electron spectroscopy (XPS) is a most extensively used technique for analyzing the chemical states of the surface elements.

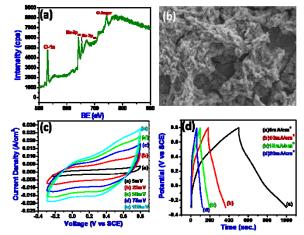


Figure 1. (a) XPS, (b)SEM, (c)CV &(d)GCD of MnO2

Figure 1(a) shows the XPS survey spectra of MnO₂ electrodede. The two peaks at binding energies of 641.44 and 653.17 eV corresponding to the spin-orbit doublet attributed to the Mn 2p3/2 and Mn 2p1/2 and the peak at 529.7 eV gives the Mn-O-Mn bond, the peak at 531.8 eV is due to the adsorbed oxygen species. Hence from XPS spectra we confirm the formation of MnO₂. Figure 1(b) shows SEM image of the asprepared MnO_2 electrode. The potentiostatic deposited MnO2 is uniformly coated on stainless substrate and builds up an interconnected network with highly porous structure. Importantly, the porous

structure is beneficial for improved electrochemical performance of the active materials, since it would lead to fast ion/electron transfer and sufficient contact between electrolytes and active materials[13].

The MnO₂ thin films deposited by potentiostatic electrodeposition were used in the development of electrochemical supercapacitors and their performance was examined by studying cyclic voltametry test. Figure 1(c) shows the CV curves of MnO₂ electrode with different scan rates in 1M Na₂SO₄ electrolyte within voltage range of -0.3 to 0.8 V. The MnO₂ electrode exhibited the maximum specific capacitance of 626 Fg⁻¹ at 5mV scan rate. Fig. 1(d) shows galvanostatic charge/discharge plot of MnO₂ electrode in 1M Na₂SO₄. The charge/discharge cycles of MnO₂ electrode was studied by galvanostatic charge/discharge technique under a constant current of 5 to 20 mA cm⁻² between -0.3 to 0.8V. The MnO₂ electrode shows high coloumbic efficiency of 98.32% in 1M Na₂SO₄ electrolytes, indicating the material has potential application for energy-storage device.

IV. CONCLUSION

In summary, MnO_2 thin film electrode has been developed by simple and inexpensive potentiostatic elecrodeposition method. The MnO_2 electrode exhibited the high specific capacitance of 626 Fg⁻¹ with high coloumbic efficiency. These results demonstrate that MnO_2 thin film deposited by potentiostatic electrodeposition method is a good candidate as electrode material for electrochemical capacitor.

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