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A symmetric MnO_2/MnO_2 flexible solid state supercapacitor operating at 1.6 V with aqueous gel electrolyte

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ABSTRACT

The demand of microelectronic devices postulated high energetic flexible energy storage devices. Flexible solid state supercapacitor is flawless possible candidate to fulfill the requirement of microelectronic devices. This investigation provides practical evidence of the use of flexible solid state supercapacitors based on MnO_2 electrodes with polyvinylpyrrolidone (PVP)-$LiClO_4$ gel electrolyte. Initially, different acid mediated growths of MnO_2 have been carried. Later, the electrochemical performances of MnO_2 electrodes have been carried out. Impressively, the fabricated symmetric flexible solid state supercapacitor (FSS-SC) device demonstrates the highest operating potential window of 1.6 V with extended cycling stability. Moreover, the cell exhibits high energy density of 23 Wh/kg at power density of 1.9 kW/kg. It is interesting to note that the device shows excellent flexibility upon bending at angle of 180° for number of times. These results clearly evidenced those symmetric FSS-SC devices based on MnO_2 electrodes are promising energy storage devices for microelectronic applications.

1. Introduction

Enhancing global warming and pollution of world demanded the substitution of petroleum with electric propulsion is an imperative across the world. The batteries are anticipated to power the next generation portable electronic devices such as mobile phones, laptops, E-paper, hybrid electrical vehicles, bio-medical devices, military devices. However, the limited life time, safety issue and small-scale power imbedded the usefulness of batteries in various applications. The supercapacitors (SCs) is an emerging class of energy storage device, getting the highest attention from scientists and industrialists due to their best capabilities like excellent power density, much longer cycle lifetimes, maintenance free and safe as compared to the present battery technology [1–4].

For the full exploitation of flexible electronics, flexible and light weight energy storage devices are recognized as one of the key components. However, presently available energy storage devices are too bulky and stubborn to employ in flexible electronics. FSS-SCs are recently developed energy storage device, attracted considerable attention due their high power density, long cycle life, environmental friendliness and safety [5]. With these routine characteristics, FSS-SCs have high mechanical integrity upon twisting, light weight, small in size, making them very reliable for flexible electronics [6]. However, the major chokepoint of existing FSS-SCs is the limited energy density because of its smaller operating potential window. According to equation $E = 0.5CV^2$, where C is capacitance and V is operating potential window. Improving energy density of FSS-SCs without losing their other electrochemical features is a challenge for the scientists. The electrochemical features of cell are strongly relevant on two pillars; the active electrode material and the electrolyte. Meanwhile, the combination of excellent active electrode material with suitable electrolyte effectively increases both the energy and power capability of the cell. Literature reviews suggests that, several active electrode materials with various electrolytes have been tested to get better performance for FSS-SCs [6]. The beneficial, economical and effective way to enhance the energy density of FSS-SCs is the employment of low cost pseudocapacitive material such as MnO_2 [7,8], NiO_2 [9], CuO [10] as an active electrode material. There fast and reversible redox reactions near the surface and on the surface of active electrode material effectively improve the energy storing capacity of SCs [11]. Despite to this, the cycling stability of pseudocapacitive material is limited, due to the dissolution of active electrode material in liquid electrolyte [8]. By interchanging the liquid electrolyte with polymer gel electrolyte (PGE) effectively cease the dissolution of active electrode material in electrolyte, result in enhanced cycling stability. Typically, the PGE is prepared by entrapping the liquid electrolyte within the polymeric network. The ionic conduction occurs

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through the motion of liquid electrolytes, whereas polymer provides the mechanical integrity to PGEs. The advantages of PGEs are higher ionic conductivity (comparable to liquid electrolyte), sufficient potential window, mechanical flexibility, and interfacial stability [12–14].

This investigation provides an integrated approach using cost-effective method for direct deposition of MnO_2 on flexible substrate with high energy density symmetric FSS-SC device. Nanostructured MnO_2 thin films were deposited on flexible stainless steel substrate by chemical bath deposition (CBD) method. The effects of different reducing agents (HCl, HNO_3 and H_2SO_4) on the structural, morphological and electrochemical properties of MnO_2 thin films were investigated. Further, symmetric FSS-SC device based on MnO_2 electrodes with PVP-$LiClO_4$ gel-electrolyte was fabricated. This device achieved a high operating voltage of 1.6 V with high energy density and power density.

2. Experimental

2.1. Synthesis of MnO_2 thin films

Simple CBD method was employed to prepare the MnO_2 thin films. $KMnO_4$ was used as the precursor salt and different acids were used as the reducing agents. Initially, the 0.02 M $KMnO_4$ was dissolved in the 50 mL DDW in three different beakers. Further, 10 mL 0.5 M HCl, HNO_3 and H_2SO_4 were added in the prepared solution and stirred for 20 min at room temperature. The prepared bath with vertically immersed stainless steel substrates was kept at temperature of 338 K for 6 h. After the reaction time, substrates were taken out from the bath and repeatedly rinsed in DDW to remove the loosely bounded active electrode material and dried at room temperature. The films with HCl, HNO_3 and H_2SO_4 are symbolized as H1:MnO_2, H2:MnO_2 and H3:MnO_2, respectively.

2.2. Characterization techniques

The surface morphology was studied by scanning electron microscopy (FEI Quanta 650F Environmental SEM). The X-ray diffraction to study the structural properties of MnO_2 thin films using the Bruker AXS D8 Advance Model with copper radiation ($K\alpha$ of $\lambda = 0.154$ nm). Raman spectra were collected using Jobin Yvon Horibra LABRAM-HR visible spectrometer with an argon-ion continuous-wave laser (488 nm) as the excitation source. Electrochemical properties of all MnO_2 thin films were investigated by assembling three-electrode setup to decide the excellent electrode to fabricate the symmetric FSS-SC device. The three electrode setup comprising a working electrode (MnO_2), counter electrode (platinum wire) and reference electrode (saturated calomel electrode (SCE)) in 1 M Na_2SO_4 electrolyte. The electrochemical features of symmetric FSS-SC device were measured using two electrode setup. The electrochemical measurements such as cyclic voltammetry (CV) and galvanostatic charge–discharge measurement were carried out using an Automatic Battery Cycler (WBCS3000).

The CV were employed to calculate the specific capacitance of electrode and SCs at various scan rate using following equation,

$$C_s = \frac{1}{m\nu(V_c - V_a)} \int_{V_a}^{V_c} I(V)dV \quad (1)$$

where, C_s is the specific capacitance (F/g), V is the potential scan rate (mV/s), ($V_c - V_a$) is an operational potential window, $I(V)$ is the current response (mA) of the MnO_2 electrode for unit area (1 cm^2) and m is deposited mass of MnO_2 on 1 cm^2 surface of SS substrate. The deposited mass of MnO_2 on 1 cm^2 is 0.982, 1.073 and 1.177 mg for H1:MnO_2, H2:MnO_2 and H3:MnO_2 thin films, respectively. Further, the energy density (E) and power density (P) were evaluated from the charge–discharge curve using the following equation,

$$E = \frac{0.5 \times C_s \times (V_{max}^2 - V_{min}^2)}{3.6} \quad (2)$$

$$P = \frac{E \times 3600}{T_d} \quad (3)$$

where, C_s is specific capacitance (F/g), T_d is discharging time, V_{max} and V_{min} are maximum and minimum potentials during charging and discharging cycles.

2.3. Preparation of gel-electrolyte and solid-state cell assembly

For preparation of PVP based gel electrolyte, 6 g of PVP was dissolved in DDW at temperature of 338 K with constant stirring. After total dissolution of PVP, 1 M $LiClO_4$ were added into the prepared solution and stirred at room temperature till formation of viscous solution. The ratio of DDW to 1 M $LiClO_4$ was kept constant to 3:2. This viscous solution was used as the gel electrolyte to fabricate the symmetric FSS-SC device. To assemble the symmetric FSS-SC device, flexible MnO_2 electrode and PVP-$LiClO_4$ gel electrolyte were used. Initially, the two identical MnO_2 electrodes was painted with PGE and then dried at 333 K to remove the water content from the gel electrode. Further, two electrodes with PGE are assembled face-to-face and pressed under pressure (~1 ton) for 10 min to improve the interfacial contact of active electrode and PGE. The assembled symmetric FSS-SC device packed in plastic container.

3. Results and discussion

In comparison to other thin film preparation methods, the CBD is the simplest, economical and ecofriendly method to prepare the large area thin films on different supporting substrates with diverse nanostructures at low reaction temperatures. It gives the binder-less and additive-free thin films by improving the interfacial contact of active electrode material and supporting substrate [15]. The deposition of MnO_2 takes place in acidic medium consists of 0.02 M $KMnO_4$ as a source of Mn ions, while the three different acids HCl, HNO_3 and H_2SO_4 were acts as reducing agents. Generally, in CBD thin film formation takes place by two mechanisms: 1) ion-by-ion (homogeneous reactions), 2) cluster-by-cluster (heterogeneous reactions) mechanism [10].

The surface morphology of prepared MnO_2 thin films at two different magnifications is shown in Fig. 1. For H1:MnO_2 thin films, the formation of thin MnO_2 nanoflakes having thickness in the range of 10–15 nm is clearly observed (Fig. 1a, b). At low magnification (Fig. 1a), it is seen that the substrate surface is well covered with highly porous 2D thin nanoflakes. High magnified images (Fig. 1b) revealed that thin nanoflakes are interconnected to each other leaving ample free space for easy intercalation/deintercalation of electrolyte ions. Such a nanostructured surface morphology is favorable for full utilization of active electrode material. Further, the use of HNO_3 as reducing agent, slightly modulates the surface morphology of MnO_2 thin films. The SEM images of H2:MnO_2 thin film (Fig. 1c,d) demonstrate the formation of nanoflakes having high aspect ratio as compared to the H1:MnO_2 thin film. The approximate thickness of nanoflakes for H2:MnO_2 thin film is ranging from 40–60 nm. In case of H_2SO_4 as reducing agent, considerable change in the surface morphology of MnO_2 has been observed. Relatively large sized nanoflakes have been seen (Fig. 1e,f). In general, all three MnO_2 thin films show the formation of highly porous nanostructured surface morphology, which provides much empty space for electrochemical reaction. As nanostructure surface morphology effectively increases the interface of active electrode material to