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Electrochemical study of Al doped MnO_2 Nanorods Over Stainless Steel Substrate

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Abstract: In this work, Al- MnO_2 nanorods have been successfully synthesized using a simple chemical route. The as-synthesized nanostructure was coated over a stainless steel substrate, which acts as an electrode material. The crystal structure and morphology were investigated by X-Ray diffraction (XRD) and scanning electron microscopy (SEM). The electrochemical performance was investigated using cyclic voltammetry with different scan rates. The Al doped MnO_2 nanorods exhibit a specific capacitance of 26 Fg^{-1} at the scan rate 5 mVs^{-1}. The power density and energy density values were obtained as 0.5 $mWcm^{-3}$ and 1.3 $mWhcm^{-3}$ for 5 mVs^{-1} scan rate. The good cyclic behavior with almost a rectangular type pattern, constant specific capacitance for longer scan rates and compatible energy density/power density value, suggesting that it is a promising electrode material for high power applications.
Keywords: Supercapacitors; MnO_2 nanorods; hydrothermal method; Specific capacitance.

Introduction and Experimental

Smaller, slimmer and lighter is today's trend of electronics. But energy storage is a big issue since the size of the energy storage device must be smaller than the entire device. Supercapacitor emerges as a solution for this problem. It has many advantages such as fast recharge, large energy density, low manufacture cost, low per charge cost, longer life time, and environmental friendly[1,2]. Incorporating new pseudo-capacitance materials and designing materials with nanoscale hierarchical structures are necessary to enable high energy density supercapacitors while maintaining high power operation. Due to this, supercapacitors are marketed for high density applications as batteries for future energy storage[3]. In our earlier report, we have developed MnO_2 honey-bee like structure over nanoporous gold with high specific capacitance[4]. Herein we develop a simple, cost-effective Al doped MnO_2 nanorods over stainless steel as electrode material for supercapacitor and studied its electrochemical performance. Aluminium was doped with very low concentration in order to increase the stability of the nanorods[5].

In a typical synthesis, 0.05g of polyvinylpyrrolidone (PVP) and 40 ml of 0.015 M $KMnO_4$ aqueous solution were mixed. 0.0011g of$Al_2(SO_4)_3.H_2O$ was added to the mixture with vigorous magnetic stirring for 3 hrs to form the homogeneous solution for the hydrothermal reaction and then transferred into a 100 ml Teflon lined autoclave apparatus. The apparatus was sealed and maintained at 160 ºC for 10 hrs in a preheated oven and then naturally cooled down to room temperature. The precipitates were collected by filtration and the obtained powder was subsequently dried at 60 ºC for 8 hrs and then calcined at 300 ºC for 10 hrs in a muffle furnace. Commercially available stainless steel substrate was treated with ultrasonic bath in ethanol for 15 min. The electrodes for electrochemical measurement were prepared by mixing the sample powders with acetylene black and polytetrafluoroethylene (PTFE) in a weight ratio of 7:2:1, respectively. A few drops of ethanol were added to the sample mixture to form a homogeneous paste. The resulting sample mixture was coated over the stainless steel substrate and subsequently dried at 110ºC for 12 hrs in hot air oven.

Results and Discussion

Figure 1 shows the XRD pattern for as-synthesized Al doped MnO_2 using hydrothermal method. The diffraction peak was in good agreement with the standard value of α–MnO_2 (JCPDS #72-1982). A broad peak at 12.36° confirms the presence of α–MnO_2 in (110) plane. Peak at 25.06· corresponds to Aluminium oxide formation (JCPDS #89-3073). Al^{3+} sits in the void place of MnO_2 structure forming AlO matrix in the host MnO_2. The morphology of the α–MnO_2 sample as synthesized was shown in Figure 2. It is clearly seen that the nanorods of diameter 50–70 nm are present with equal length.

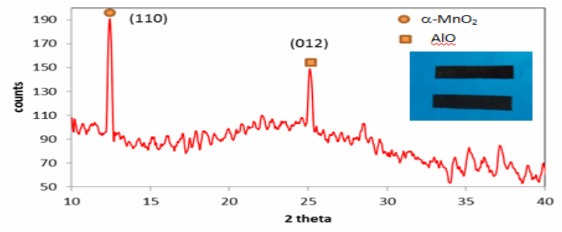

Figure 1 XRD pattern of Al doped MnO_2 nanorods and Inset picture is the photo image of the prepared electrode.

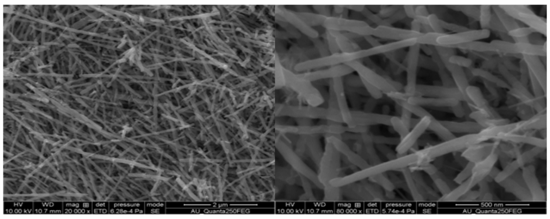

Figure 2 SEM images of Al doped MnO_2 nanorods.

To evaluate the power capability of the prepared electrode, cyclic voltammetry (CV) experiments were performed at scan rates ranging from 5mVs^{-1} to 20 mVs^{-1}. Figure 3 shows the CV performance for the prepared electrode at different scan rates.

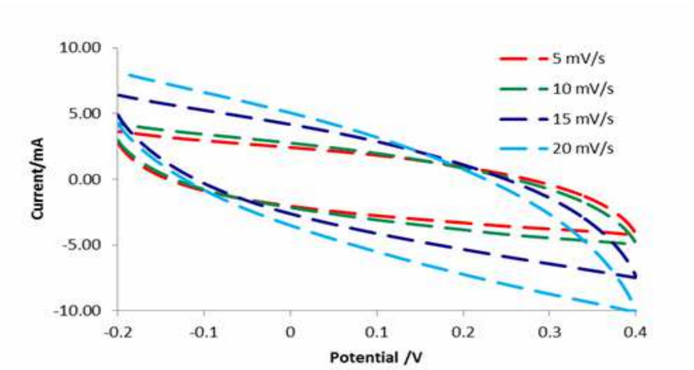

Figure 3 CV curves at different scan rates for the prepared electrode showing good rectangular behavior.

The capacitance values were calculated from CV data according to the following equations,

$$C_{device} = \frac{1}{v(V_f - V_i)} \int_{V_i}^{V_f} I(V) dV \quad \text{and} \quad C = \frac{C_{device}}{m}$$

where v is the scan rate, V_f and V_i are integrated potential limits of voltammetric curve, I(V) is the voltammetric discharge current and m is the mass of the electrode material. We obtained a specific capacitance value of 26 Fg^{-1} for the scan rate 5 mVs^{-1}. This value is more or less compatible for MnO_2 over substrate [6], as known the substrate is important to pseudo-capacitor electrode materials. This value is nearly 40 times lower than the theoretical value for MnO_2 [7] and 10 times lower than the results reported for MnO_2 structure without substrate. To demonstrate the potential of our electrode material, we use the Ragone plot, which is presented in the Figure 4. The energy and power density of the device were obtained from the following equations,

$$E = \frac{1}{2}\frac{C(\Delta V)^2}{3600} \quad \text{and} \quad P = \frac{E}{\Delta t} \times 3600$$

where E is the energy density (in Whcm^{-3}), C is the specific capacitance (F/g), ΔV is the discharge voltage range (in volts), P is the power density (in Wcm^{-3}) and Δt is discharge time (in seconds).

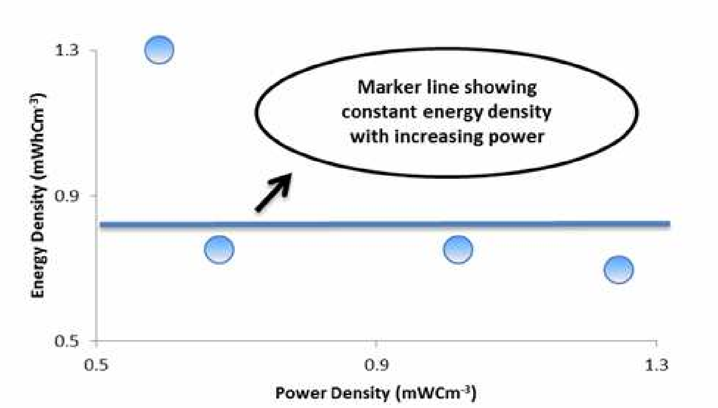

Figure 4.Comparision for energy density and power density (Ragone plot)

From the Figure 4, it is observed that constant value of the energy density of increasing power density, which is the potential need for building supercapacitor devices for high power applications.

Conclusion

Al doped MnO_2 nanorods were synthesized using Hydrothermal method. The crystal and morphological studies were investigated using XRD and SEM analysis. The electrochemical property of the as-prepared electrode revealed that it has good cyclic behavior with almost a rectangular type pattern, constant specific capacitance for longer scan rates and compatible energy density/power density value, suggesting that it is a promising electrode material for high power applications.

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