

Short communication

Nanostructured MnO_2 : Hydrothermal synthesis and electrochemical properties as a supercapacitor electrode material

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Abstract

The structural, morphological and electrochemical properties of the hydrothermally prepared manganese oxide (MnO_2) nanostructures are discussed in this paper. Interesting nanostructures of MnO_2 , mixture of nanostructured surface with a distinct plate-like morphology and nanorods, have been prepared by employing hydrothermal synthesis under mild conditions. The specific surface area of the prepared material was $132 \text{ m}^2 \text{ g}^{-1}$. Electrochemical properties of the synthesized nanostructured material were studied using galvanostatic cycling and cyclic voltammetry in a mild aqueous electrolyte that showed a high specific capacitance of 168 Fg^{-1} . In addition, the synthesized nanomaterial showed a good reversibility and cycling stability.

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1. Introduction

Supercapacitors or electrochemical capacitors are energy storage devices that have gained importance in recent years owing to their technological significance ranging from satellites to consumer electronic devices [1]. Supercapacitors are categorized into two based on the fundamental mechanisms that govern the capacitances. First is the electrical double layer capacitor (EDLC) where the capacitance arises as a result of the accumulation of charges at the electrode–electrolyte interface and second is the redox capacitors where an actual battery-type oxidation–reduction reaction occurs leading the pseudocapacitance. Various carbon materials exhibit EDLC while a series of transition and noble metal oxides show the pseudocapacitance behavior. Among the various metal oxides studied, $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ is considered to be the most promising pseudocapacitor material when a highly acidic electrolyte is used ($5 \text{ M H}_2\text{SO}_4$) [2]. However, using such a strong acid has not only raised the environmental concerns but also led to dissociation of the metal ions in the course of cycling the capacitor. Also, another impeding part of using RuO_2 is its cost when the capacitor is envisioned for the large scale applications such as in electric vehicles. The aforementioned factors have been leading to the search for an

alternative material which should have fairly comparable electrochemical properties to RuO_2 and also be more economically and environmentally friendly in nature. Various metal oxides such as MnO_2 , NiO , MoO , CoO , vanadium based oxides etc., are being studied for their electrochemical capacitor properties in different aqueous electrolytes [2–6]. Manganese oxide is being tried as a pseudocapacitor material mainly because of its abundance in nature, cost and environmental friendliness [7–10].

There has been always a strong correlation between the synthesis route adopted to prepare a material and its electrochemical properties. Hydrothermal technique is a cheap, environmentally friendly method to prepare materials in different nanoarchitectures such as nanorods, nanowires and nanoparticles etc., [11,12]. Here in this paper, the advantages of MnO_2 as pseudocapacitor material is combined with the supremacy of the hydrothermal technique to make interesting nanostructures of MnO_2 so as to get the best electrochemical properties in a neutral electrolyte system.

2. Experimental

Nanostructured MnO_2 was synthesized by hydrothermal technique under mild conditions as described elsewhere [12,13]. Briefly, aqueous solutions of MnSO_4 and KMnO_4 were mixed and loaded to Teflon[®] lined Stainless Steel pressure vessel (PARR Vessel, USA). The pressure vessel was heated at 140°C

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for 6 h in an oven and then allowed to cool to room temperature naturally. The formed brownish black precipitate was filtered and washed copiously to remove any unreacted starting material and the soluble byproducts formed during reaction. The precipitate was dried at 100 °C for 1 h and systematically characterized using various analytical techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), BET surface measurement, and electrochemical studies.

XRD (siemens X-ray diffractometer, Germany) was employed to study the phases purity of synthesized material. The nanostructural morphology was studied by SEM (Hitachi, Japan) and HR-TEM (JEOL, Japan). The surface area of the synthesized materials was studied using BET measurements (Quantachrome, USA). The electrode for evaluating the electrochemical properties of the synthesized MnO₂ were fabricated by mixing prepared MnO₂ with 20 wt.% carbon black (Black Pearl 2000 (BP 2000), Cabot Corp., USA) and 5 wt.% PVdF-HFP binder. A slurry of the above mixture was made using NMP as a solvent which was subsequently brush-coated on to a Ni mesh. The mesh was dried at 110 °C in air for 1 h for the removal of the solvent. After drying the coated mesh was uni-axially pressed to better adhere the electrode material with the current collector.

A three electrode cell configuration was used to study the cyclic voltammetry (CV) and galvanostatic cycling using a potentiostat/galvanostat (PGSTAT20, Autolab, EchoChemie, The Netherlands) in which a Ni mesh coated with MnO₂ as the working electrode, Pt-wire as the counter and saturated calomel electrode (SCE) as the reference. CV was done between -0.2 and 0.8 V in a 1 M Na₂SO₄ electrolyte at different scan rates. The main objective behind using the neutral 1 M Na₂SO₄ electrolyte is to prevent any dissolution metal ions into the electrolyte upon cycling as it happens mostly when a strong acidic electrolyte is used [2]. The specific capacitance was evaluated from the area of the charge and discharge curves of the CV plot. The galvanostatic charge–discharge experiments were performed with a specific current of 200 mA g⁻¹ between 0 and 1 V.

3. Results and discussions

Fig. 1 shows the XRD recorded for the hydrothermally synthesized MnO₂ nanostructures at 140 °C for 6 h. It can be seen from the figure that the peak profile is broad and most of the peaks are indexable to α -MnO₂ phase. This clearly indicates that the synthesized material is a purely individual phase without any additional second phase. The broadness of the peaks indicates that the formed compound has predominantly nanophase. However, there is always a possibility of coexisting potassium ion in the MnO₂ matrix arising from one of the starting materials used to prepare the manganese oxide. The amount of potassium ion may be very negligible to be detected using XRD.

N₂ adsorption–desorption isotherms for the prepared MnO₂ is shown in Fig. 2. The BET surface area of the nanomaterial was found to be 132 m² g⁻¹. The porosity of the nanomaterial was calculated by the BJH method, which revealed a pore diameter of 9 nm, indicating the mesoporous nature of the sample. The porosity and the surface area of the nanomaterial have always

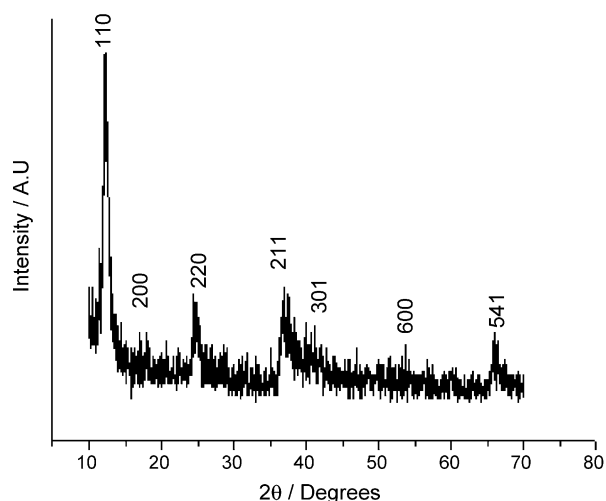


Fig. 1. X-ray diffraction pattern of nanostructured MnO₂ synthesized hydrothermally at 140 °C for 6 h.

shown a corresponding impact on the electrochemical properties as discussed later.

SEM picture for the synthesized material is shown in Fig. 3(a). The morphology of the particles shows a mixture of nanorods and nanostructured surface with a distinct plate-like morphology. The well defined regions of the nanoplate exhibit definite pores which will play an important role in the redox process when used as an electrode material in a supercapacitor. In order to further verify the morphology of the material, TEM studies were performed and are shown in Fig. 3(b). Here, we can observe the highly agglomerated nanorods of MnO₂ as shown in the inset of Fig. 3(b). EDX was also performed to ascertain the elemental composition in the formed MnO₂ nanorods.

Electrochemical properties of the synthesized MnO₂ nanostructures were studied using CV and galvanostatic cycling. The cell assembled in a three electrode configuration with a Pt counter and a SCE as reference showed an OCV of 0.40 V. The CV recorded at scan rate of 5 mV s⁻¹ for MnO₂ in a 1 M

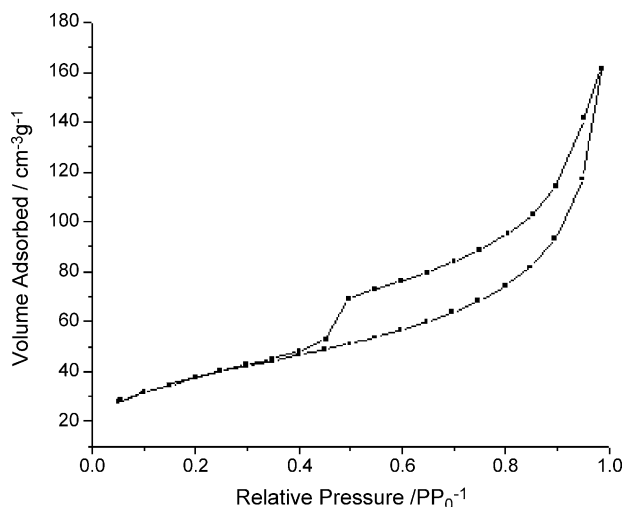


Fig. 2. N₂ adsorption–desorption isotherms for nanostructured MnO₂ synthesized hydrothermally at 140 °C for 6 h.

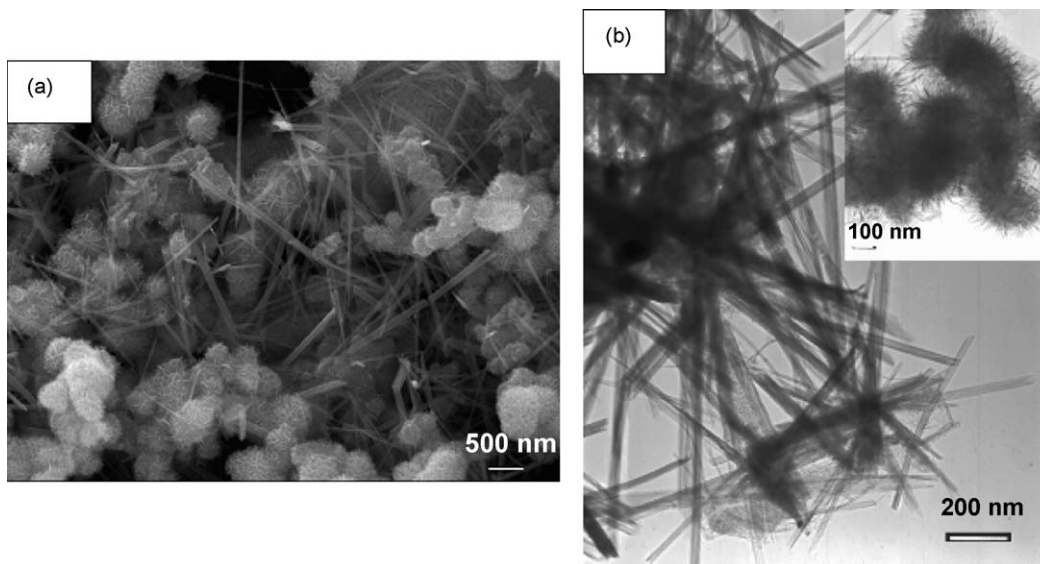


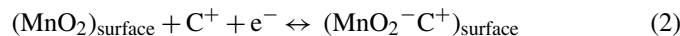
Fig. 3. SEM (a) and TEM (b) pictures of MnO_2 synthesized hydrothermally at 140°C for 6 h.

Na_2SO_4 aqueous electrolyte is shown in Fig. 4(a). The CV profile clearly indicates the capacitive behavior with almost an ideal rectangular shape, indicating a reversible system. The capacitance calculated from the area of the CV curve was found to be 160 Fg^{-1} . In order to get more information on the electrochemical behavior of the synthesized nanostructured MnO_2 , CV characterizations were done at different scan rates starting from 1 to 50 mVs^{-1} and the results are shown in Fig. 4(b). This will lead to a better understanding of the actual participation of the MnO_2 electrode in the redox process.

There have been two mechanisms proposed for the charge storage in MnO_2 -based electrodes. The first one is based on the concept of intercalation of H^+ or alkali metal cations (C^+) such as Na^+ in the electrode during reduction and deintercalation upon oxidation [7].



The second one is the adsorption of cations in the electrolyte on the MnO_2 electrode [8];



In the present study, the redox process is mainly governed by the insertion and deinsertion of Na^+ and or H^+ from the electrolyte into the porous nanostructured MnO_2 matrix. Increasing the scan rate has a direct impact on the diffusion of Na^+ ions into the MnO_2 matrix. In other words, the faster scan rate will lead to the Na^+ ions reaching only the outer surface of the electrode and not the interior pores of the MnO_2 matrix. This greatly reduces the available capacity from 168 to 72 Fg^{-1} when the scan rate is increased from 1 to 50 mVs^{-1} . The actual contribution from the outer surface, which is the outer voltammetric charge, can be calculated from the CV at different scan rates by plotting the inverse of scan rate versus the voltammetric charge and extrapolating the voltammetric charge at scan rate to infinity [7–10]. The value in the present case was found to be 83 Fg^{-1} which is approximately half of the total available charge (168 Fg^{-1}).

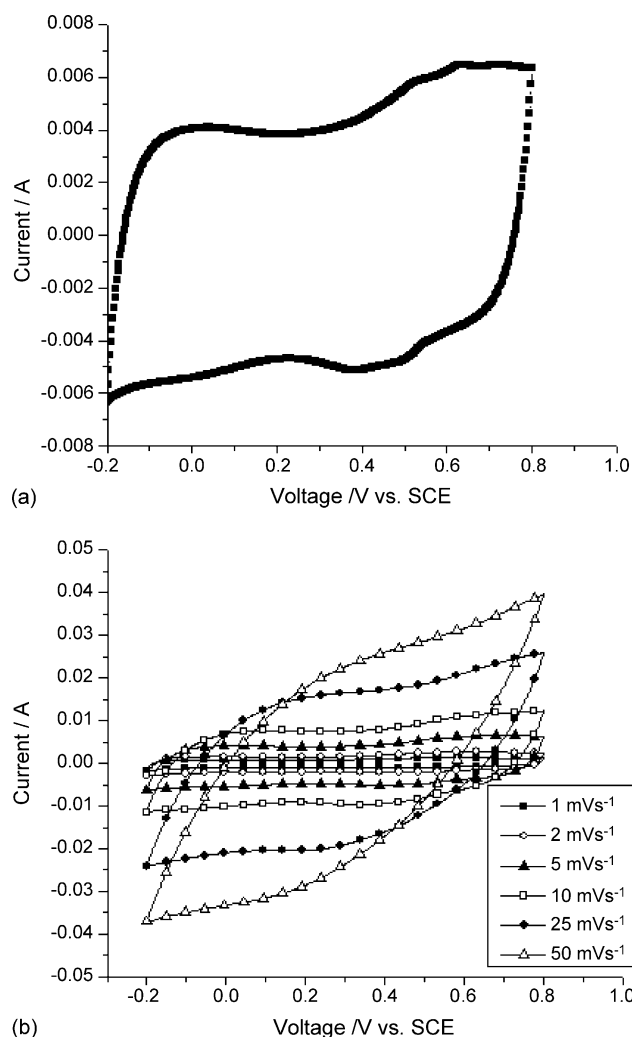


Fig. 4. (a) CV at a scan rate of 5 mVs^{-1} (b) CV at different scan rates from 1– 50 mVs^{-1} .

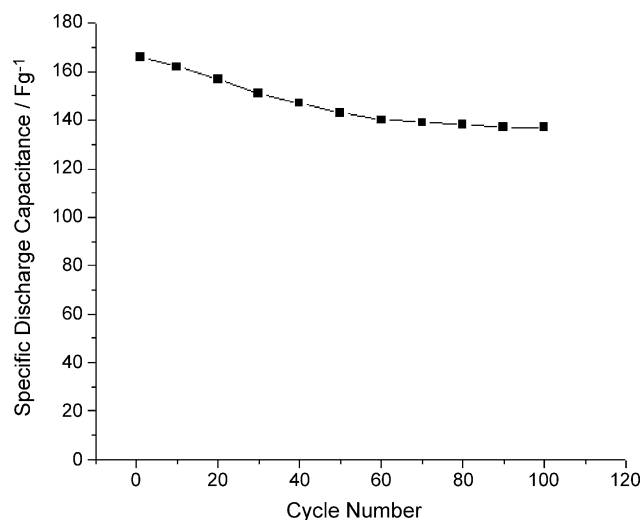


Fig. 5. Variation of specific discharge capacitance with respect to cycle number.

Hence, it is clear that when the scan rate is higher the participation of the MnO_2 electrode is limited only to the outer surface and not the interior pores leading to a lower specific capacitance.

In order to understand the effect of varying the concentration of the electrolyte on the capacitance of MnO_2 , CV studies were performed at three different concentrations namely 0.1, 1 and 2 M Na_2SO_4 aqueous electrolytes at a scan rate of 5 mV s^{-1} between -0.2 and 0.8 V . There has been no appreciable change in the capacitance with values corresponding to 0.1, 1 and 2 M being 151, 160 and 165 Fg^{-1} . The small differences in the capacitance among the different electrolyte concentrations possibly arises from the conducting carbon black (BP 2000) which has a finite contribution from the double layer capacitance, which has a direct dependence on the concentration of the electrolyte. Since the present electrode is a composite one with a significant amount of carbon black, BP 2000, its contribution has to be subtracted from the total specific capacitance. The capacitance of BP 2000 has been reported to be 70 Fg^{-1} in a 1 M Na_2SO_4 electrolyte [14]. The specific capacitance values reported in this paper are after the elimination of the contribution from BP 2000 in a 1 M Na_2SO_4 electrolyte. From this study it is clear that the capacitance observed in the hydrothermally synthesized MnO_2 nanostructures is predominantly pseudocapacitive in nature.

Charge–discharge studies were performed at a constant current (200 mA g^{-1}) between 0 and 1 V and the variation of specific capacitance for 100 cycles is shown in Fig. 5. The starting

voltage for the experiments was $\sim 0.3 \text{ V}$. There has been a good reversibility with a coulombic efficiency of 83% after 100 cycles.

4. Conclusions

Hydrothermal technique was employed to prepare MnO_2 with interesting nanostructures under mild conditions. The SEM and TEM studies revealed a mixture of nanostructured surface with a distinct plate-like morpholog and nanorods of MnO_2 . The specific surface area was found to be $132 \text{ m}^2 \text{ g}^{-1}$. The synthesized nanostructured MnO_2 showed a good pseudocapacitive behavior with a specific capacitance of 168 Fg^{-1} with a cycling efficiency of 83% for 100 cycles at fairly high current, 200 mA g^{-1} . Fine tunings of pore structures and structural morphologies using hydrothermal technique can further improve the capacitance and cycling efficiency of the electrochemical system.

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References

- [1] B.E. Conway, *Electrochemical Capacitors: Scientific Fundamentals and Technological Applications*, Kluwer Academic/Plenum, New York, 1999.
- [2] J.P. Zheng, P.J. Cygan, T.R. Jow, *J. Electrochem. Soc.* 142 (1995) 2699.
- [3] K.C. Liu, M.A. Anderson, *J. Electrochem. Soc.* 143 (1996) 124.
- [4] Y.S. Yoon, W.I. Cho, J.H. Lim, D.J. Choi, *J. Power Sources* 101 (2001) 126.
- [5] B.E. Conway, V. Briss, J. Wojtowicz, *J. Power Sources* 66 (1997) 1.
- [6] C. Lin, J.A. Ritter, B.N. Popov, *J. Electrochem. Soc.* 145 (1998) 4097.
- [7] S.C. Pang, M.A. Anderson, T.W. Chapman, *J. Electrochem. Soc.* 147 (2000) 444.
- [8] H.Y. Lee, J.B. Goodenough, *J. Solid State Chem.* 144 (1999) 220.
- [9] M. Toupin, T. Brousse, D. Belanger, *Chem. Mater.* 14 (2002) 3946.
- [10] M. Toupin, T. Brousse, D. Belanger, *Chem. Mater.* 16 (2004) 3184.
- [11] G.H. Du, Z.Y. Yuan, G. Van Tendeloo, *Appl. Phys. Lett.* 86 (2005) 063113.
- [12] X. Wang, Y. Li, *Chem. Commun.* (2002) 764.
- [13] V. Subramanian, H.W. Zhu, R. Vajtai, P.M. Ajayan, B.Q. Wei, *J. Phys. Chem. B* 109 (2005) 20207.
- [14] H. Kim, B.N. Popov, *J. Electrochem. Soc.* 150 (2003) D56.