Surface Review and Letters, Vol. 16, No. 4 (2009) 513–517

SYNTHESIS OF MANGANESE OXIDE NANOSTRUCTURES ON CARBON PAPER FOR SUPERCAPACITOR APPLICATIONS

M. A. MASTRO*,†, C. R. EDDY Jr. and F. KUB
US Naval Research Laboratory,
Electronics Science and Technology Division,
4555 Overlook Ave., SW, Washington DC 20375, USA
**mastro@ccs.nrl.navy.mil*

J. PARK and J. CHO
School of Advanced Materials Engineering, Kookmin University,
Seoul, South Korea

J. KIM†
Department of Chemical and Biological Engineering,
Korea University, Seoul, South Korea
jhkim@prosys.korea.ac.kr

Received 16 February 2009

A simple hydrothermal growth process was developed to deposit conformal manganese oxide nanospheres with a diameter of 10 to 20 nm on mesoporous carbon paper. The coating of nanospheres increased the cyclic-voltammogramic response of carbon paper by a factor of 5 with a slight dependence on the scan rate. For comparison, a related chemistry was also developed to fabricate a dense packing of manganese oxide nanorods with a diameter of 20 to 50 nm and a length of approximately 500 nm. The nanorods also increased the cyclic-voltammogramic response of carbon paper but only by a factor of approximately 3.

Keywords: Supercapacitor; manganese oxide; nanostructures.

1. Introduction

The billion dollar supercapacitor market is expected to increase rapidly as the device expands into new automotive and digital device applications. The traditional supercapacitor design is an electrochemical double-layer capacitor (EDLC) that stores charge at the electrolyte interfaces of two highly porous carbon electrodes.[1,2] A pseudocapacitor extends this idea by leveraging the Faradic response of a metal oxide to increase the energy storage capacity beyond that available with a simple double-layer capacitance mechanism.[3] The highest power density pseudocapacitor was constructed with hydrated RuO_2 in a highly acidic sulfuric acid electrolyte.[4,5] The high cost of ruthenium and a desire to operate in a neutral electrolyte has positioned MnO_2 as the cost-effective solution.[6,7] To avoid the negative voltage limitations of MnO_2, the most useful design is as an asymmetric device with an activated-carbon negative electrode and a pseudocapacitive MnO_2 positive electrode.[8]

This paper describes a process to deposit a conformal coating of MnO_2 nanospheres within the

---

[†] Corresponding authors.

high surface area, connected pore structure of a carbon paper electrode. The carbon nanostructure also provides a low-resistance three-dimensional current collector.[8] Therefore, the requirement to maintain a minimal distance for electrons to transfer across the electroactive MnO_2 coating overrides the electrolyte/electrode interfacial-area metric.[9,10] To illustrate this mechanism, a coating was also applied with high-aspect ratio MnO_2 nanowires, which showed improved cyclic-voltammogramic characteristics relative to the bare carbon electrode yet inferior cyclic-voltammogramic characteristics when compared with the MnO_2 nanosphere coating.

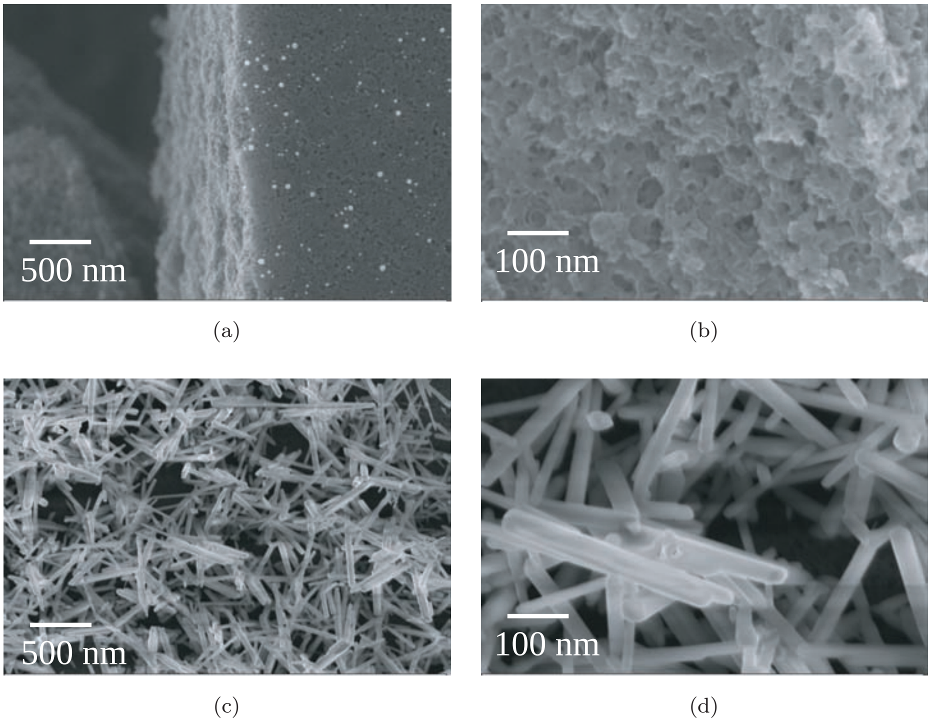
2. Experimental

In this study, MnO_2 nanostructures were deposited in aqueous solutions in a Parr pressure restricted chamber.[11,12] Prior to growth, the carbon nanofoam (aerogel) paper (Marketech International Inc.) was washed in methanol and DI water. The MnO_2 nanorods were formed on the carbon paper by a hydrothermal reaction of 10 mL 0.01 M $KMnO_4$ and 1 mL 0.001 M NaOH solution in the Parr chamber for 2 h at 170°C. The nanospheres were formed by a two-step process: the carbon paper was immersed in solution as described above for 1 min at 90°C in an open beaker; the seeded carbon paper was then immediately transferred into a mixture of 10 mL 0.01 M $KMnO_4$ and 2 mL HF in the hydrothermal chamber, which was held at 150°C for 2 h.

Electrochemical studies were performed using cyclic voltammograms (model: compactstat, IVIUM) in a three-electrode configuration with MnO_2 as the working electrode, Ag as the counter, and saturated calomel electrode as the reference. The cyclic-voltammetry was performed between -0.2 and 0.8 V in 0.5 M Na_2SO_4. The upper voltage is limited by the onset of a nonreversible redox oxygen evolution process and the lower voltage is limited by the nonreversible reduction and dissolution of the Mn ion. Structural characterization was performed with a Panalytical X'pert X-ray diffraction system and a LEO field emission scanning electron microscope.

3. Results

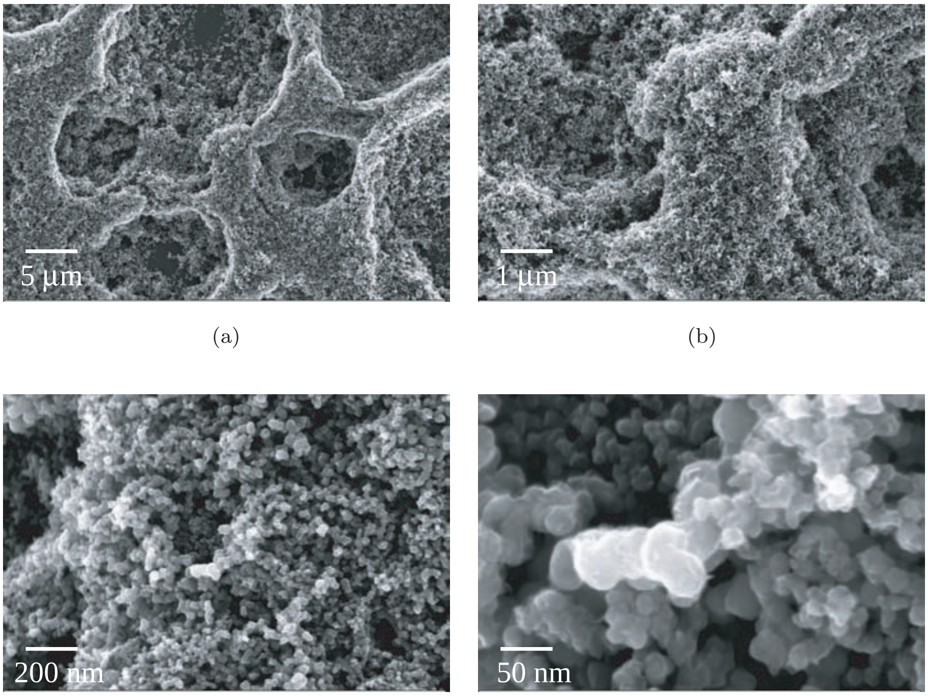
The electron micrograph of as-received carbon nanofoam in Figs. 1(a) and 1(b) shows that the carbon paper-like electrode material achieves both



(a) (b)

(c) (d)

Fig. 1. Electron micrographs of (a), (b) as-received carbon paper with (c), (d) hydrothermal MnO_2 nanorods.



(a) (b)

(c) (d)

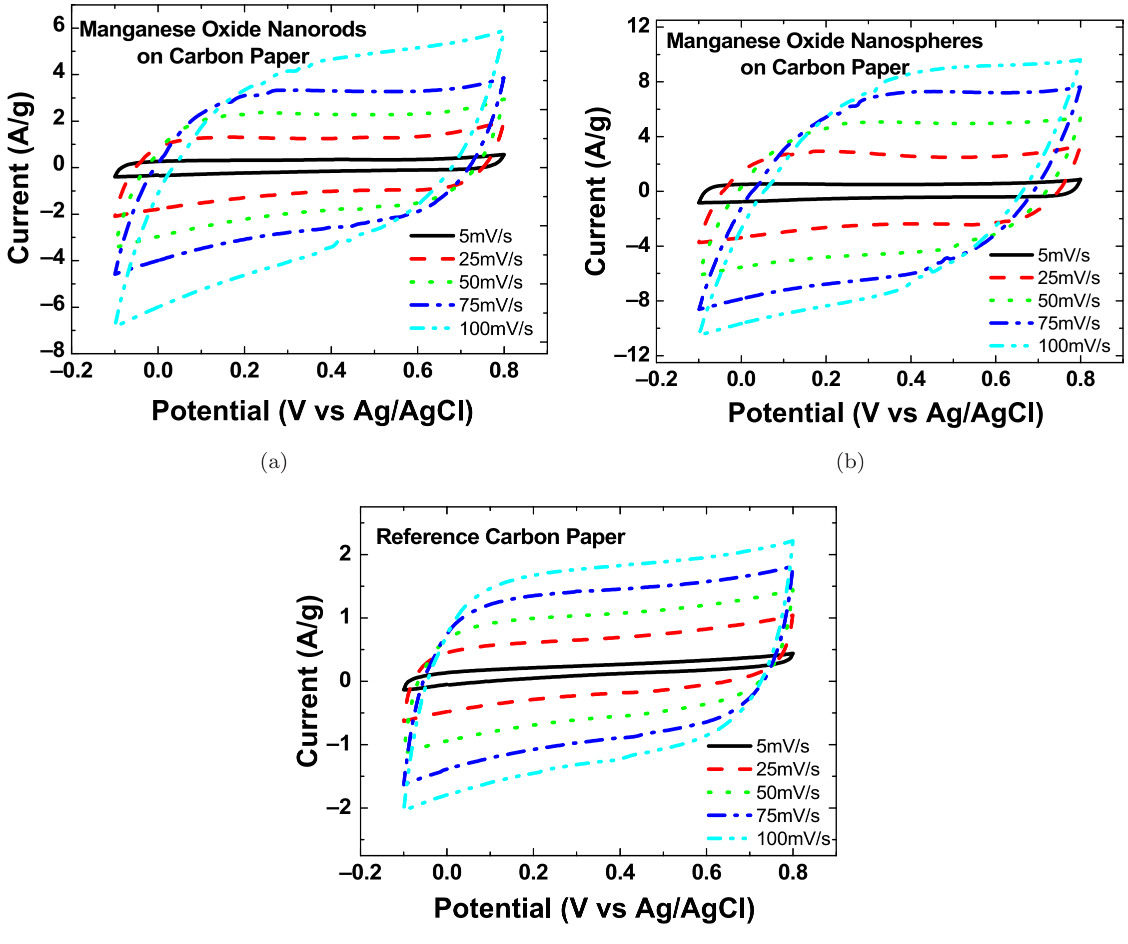
Fig. 2. Electron micrographs of MnO_2 nanospheres deposited into mesoporous carbon paper. The MnO_2 nanospheres conformally deposited along the sidewalls and base regions of the carbon pore structure.

nano- and mesoporosity. Subsequent MnO_2 deposition produced a dense packing of vertical nanowires as observable in Figs. 1(c) and 1(d). The solution growth of the MnO_2 nanowires proceeded rapidly with large areas of the carbon paper covered after 10 min of growth. A deposition time beyond approximately 1 h yielded a packed array of ZnO nanowires approximately 500 nm in length. Beyond 2 h of deposition, the reactants were rapidly depleted although the growth could be extended by simply restarting the growth with fresh solution.

The two-step nanosphere growth process is depicted in the electron micrographs of Fig. 2. The initial pre-seed step encouraged deposition deeper into the mesoporous carbon structure. Conceivably, the alkaline solution discouraged deposition at unstable nucleation sites along the pore sidewalls. The acidic solution of step two creates a simultaneous etch-deposition mechanism. The pre-seed acts as a second source of reactant with some small percentage present at or near the bottom of the pores. Thus, this second-source reactant would not necessarily have to diffuse through the entire pore structure. A self-limiting process was observed with morphology unchanged beyond 2 h of reaction.

Cyclic-voltammetry measurements of the MnO_2 nanospheres and nanorods on carbon paper as well as the bare carbon electrode are displayed in Fig. 3. The profile deviated from ideal with increasing scan rate particularly for the nanorods on carbon paper sample. Limitation of the redox reaction at high scan rates is caused by the inability of the alkali ion from the electrolyte to rapidly insert–deinsert in the mesoporous structure.[4] The decrease in the interaction between the ions and the electrode effectively reduces the capacitance of the structure. Nevertheless, at a scan rate of 25 mV/s, the MnO_2 nanospheres on carbon paper displayed a specific capacitance of 140 F/g and the MnO_2 nanorods on carbon paper displayed a specific capacitance of 83 F/g compared with a specific capacitance of 47 F/g for bare carbon electrode.

A comparison of the MnO_2 nanospheres and nanorods on carbon paper with a bare carbon electrode in Fig. 4 clearly shows the capacitance enhancement provided by the MnO_2, particularly for the MnO_2 nanosphere coating.



(a)

(b)

(c)

Fig. 3. Cyclic-voltammetry of (a) MnO_2 nanorods and (b) MnO_2 nanospheres on carbon paper, and (c) reference carbon paper electrode in 0.5 M Na_2SO_4.

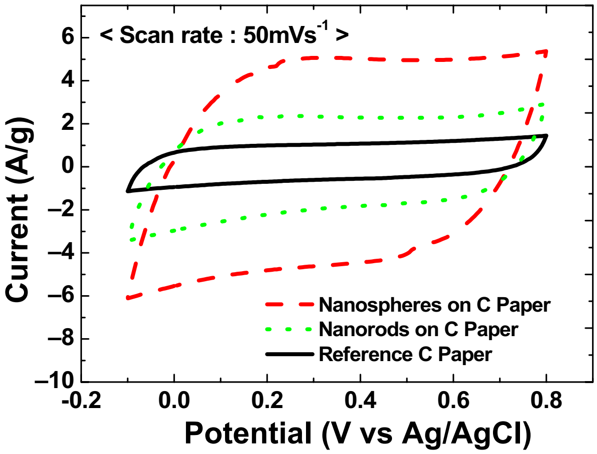


Fig. 4. Comparison of cyclic-voltammetry of MnO_2 nanorods and MnO_2 nanospheres on carbon paper as well as a reference carbon paper electrode in 0.5 M Na_2SO_4 at a scan rate of 50 mV/s.

4. Discussion

A pseudocapacitor operates by an electrochemical reversible Faradaic redox reaction at a solid electrode of a conducting polymer or a metal oxide. The fast redox reaction gives the pseudocapacitor superior energy density but at a lower power density compared with an EDLC.[1,2] A nanoscopically thin MnO_2 coating in close proximity to the highly conductive carbon minimizes the impact of the low conductivity of MnO_2 in addition to minimizing the distance for solid-state transport of the insertion cations.[8] This mechanism explains why the nanorod sample (Figs. 1 and 4) with a higher surface area displayed a smaller cyclic-voltammetry response compared with the nanosphere samples. In effect, the internal resistance of the MnO_2 limited the functionality only to the base region of the nanorod, which is in close electrical contact with the underlying conductive carbon conductor.

5. Summary

Creating a conformal coating of MnO_2 within carbon paper mesopores is nontrivial; this paper outlines a simple, scalable solution approach to fabricate a MnO_2 on carbon paper structure with high cyclic-voltammetry metrics. The mesoporous carbon material provides a convenient conductive template to create a hybrid MnO_2 mesoporous structure suited to the infiltration and rapid transport to the electrolyte.[8]

Acknowledgments

The research at NRL was supported by ONR. The research at Korea University was supported by BK21 program. This work was also supported by ERC Program of KOSEF grant funded by the Korea government (MEST) (R11-2005-048-00000-0).

References

1. A. E. Fischer, K. A. Pettigrew, D. R. Rolison *et al.*, *Nano. Lett.* **7** (2007) 281.
2. A. E. Fischer, M. P. Saunders, K. A. Pettigrew *et al.*, *J. Electrochem. Soc.* **155** (2008) A246.
3. V. Subramanian, H. Zhu, R. Vajtai *et al.*, *J. Phys. Chem. B* **109** (2005) 20207.
4. J. P. Zheng, P. J. Cygan and T. R. Jow, *J. Electrochem. Soc.* **142** (1995) 2699.
5. C.-C. Hu and Y.-H. Huang, *Electrochim. Acta* **46** (2001) 3431.
6. M. Toupin, T. Brousse and D. Belanger, *Chem. Mater.* **14** (2002) 3946.
7. Y. U. Jeong and A. Manthiram, *J. Electrochem. Soc.* **149** (2002) 1419.
8. J. W. Long, *Interface* **17**(1) (2008) 33.
9. J. W. Long, B. Dunn, D. R. Rolison *et al.*, *Chem. Rev.* **104** (2004) 4463.
10. J. W. Long, C. P. Rhodes, J. C. Lytle *et al.*, *Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem.* **51**(1) (2006) 41.
11. M. A. Mastro, J. A. Freitas Jr, C. R. Eddy Jr *et al.*, *Physica E Low-Dimensional Syst. Nanostruct.* **41** (2008) 487.
12. M. A. Mastro, M. J. Tadjer, F. J. Kub *et al.*, in preparation.