MnO_2-based electrochemical supercapacitors on flexible carbon substrates

Marko J. Tadjer[1,a], Michael A. Mastro[2], José M. Rojo[3], Alberto Boscá Mojena[1], Fernando Calle[1], Francis J. Kub[2], Charles R. Eddy, Jr.[2]

[1] Institute for Systems based on Optoelectronics and Microtechnology, ISOM-UPM, Madrid, Spain
[2] United States Naval Research Laboratory, Washington DC, 20375, USA
[3] Instituto de Ciencias de Materiales de Madrid (ICMM), CSIC, Spain
mtadjer@die.upm.es

Abstract

There is an increasing need for supercapacitors as they are unique in their ability to deliver high power levels over a time span unattainable by a traditional capacitor. We present a low-cost MnO_2-based chemistry on large area sheets of carbon aerogel paper. The specific capacitance of manganese oxide is typically lower than the best in class of ruthenium oxide; however, the much lower cost and available supply of manganese makes this material much more attractive [1].

MnO_2 nanostructures were deposited in aqueous solutions in a covered Teflon container on a commercially available carbon nanofoam paper substrate with specific capacitance of 47 F/g [2]. Prior to growth, the carbon nanofoam (aerogel) paper was washed in methanol and DI water. The MnO_2 structures were formed on large area samples of this flexible substrate by an initial reaction based on 20 mL 0.01 M $KMnO_4$ as the vessel was ramped in temperature to 150 °C. Subsequently, the reaction was augmented by a continuous drip over 1 hr of a mixture of 20 mL of 0.01 M $KMnO_4$ and hexamethylenetetramine (HMTA) (0.005 M) at 150 °C. Examination of the X-ray diffraction pattern shows the film formed as α-MnO_2. The two experiments of α-MnO_2 growth resulted in morphologies resembling nanoflower and nanocube structures. Cyclic voltammetry was performed at 1 mV/s or 5 mV/s rate in the safe 0-0.8 V range, where the applied potential would not dissociate the oxide into Mn^+ cations and O^- anions [3].

Specific capacitance of MnO_2 ($C_{SP,MnO2}$) and series resistance (R_S) at 1 mA and 5 mA of galvanostatic charging current (I_{CH}) were calculated according to the expression $C_{SP,M} = m_{REF}\cdot C_{REF}/(m_{REF} + m_{ELECTRODE}) + m_{MnO2}\cdot C_{SP,MnO2}/(m_{REF} + m_{ELECTRODE})$. The mass of the MnO_2 sample under test is denoted by $m_{ELECTRODE}$, the mass and specific capacitance of the carbon aerogel (C-aerogel) are m_{REF} and C_{REF}, respectively, and C_{REF} is the measured total capacitance of the MnO_2/C-aerogel composite, from which the specific capacitance of MnO_2 ($C_{SP,MnO2}$) can be extracted. Specific capacitance for sample B at 1 mA charging current was increased from 47 F/g to 64 F/g, a 36% improvement over a bare carbon paper surface. However, at 5 mA the CSP of all samples was comparable to within 4 F/g. Compared to the control sample, the series resistance of sample B had increased by a factor of about 2.4 at 1 mA and about 4.7 at 5 mA, whereas R_S of sample C had remained comparable, albeit slightly lower. This was a consequence of the better surface coverage of sample B with the low-conductivity MnO_2 film.

Acknowledgements

M.J.T. acknowledges support from the PICATA program at the Moncloa Campus of International Excellence (CEI), Universidad Politécnica de Madrid, Spain. Research at NRL was supported by the Office of Naval Research (ONR).

References

[1] M. A. Mastro, et al., Surface Rev. and Lett., vol. 16, no. 4 (2009) 513-517.
[2] S. Hu, R. Rajamani, and X. Yu, 100, 104103 (2012).
[3] D. Kalpana, K.S. Omkumar, S.S. Kumar, N.G. Renganathan, Electrochim. Acta 52 (2006) 1309-1315.

Figures

Table I: Charging current (I_{CH}), specific capacitance (C_{SP}), and series resistance (R_S) measurements.

	Sample A C-paper only (Reference)		Sample B MnO_2 nanoflowers		Sample C MnO_2 nanocubes	
I_{CH} (mA)	1	5	1	5	1	5
$C_{SP,MnO2}$ (F/g)	47	43	64	39	42.9	41.2
R_S (Ω)	10.5	6	25	28	9.6	8

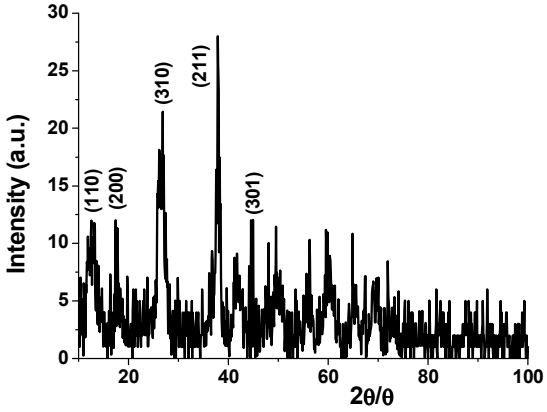

Figure 1: X-ray diffraction indicates that the coating formed as α-MnO_2.

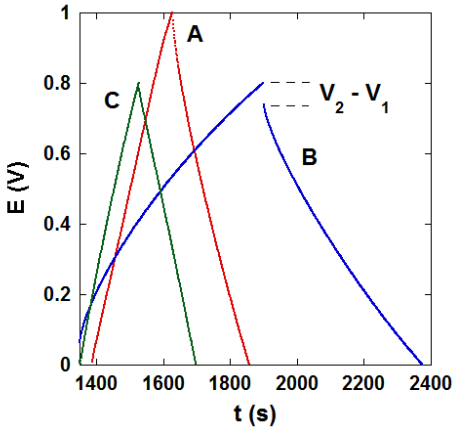

Figure 2: Galvanostatic measurements comparing charge/discharge cycles. Series resistance was determined from $\Delta V = V_2 - V_1$.

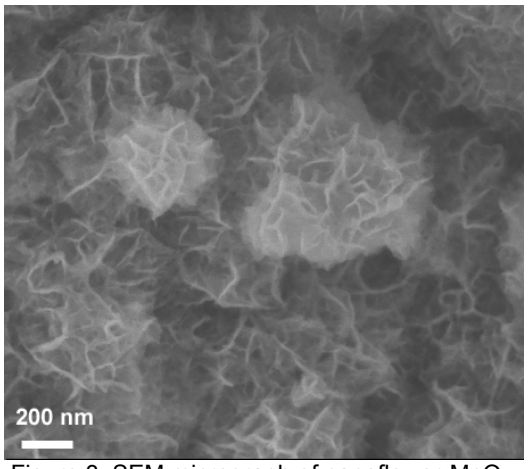

Figure 3: SEM micrograph of nanoflower-MnO_2 (Sample B).

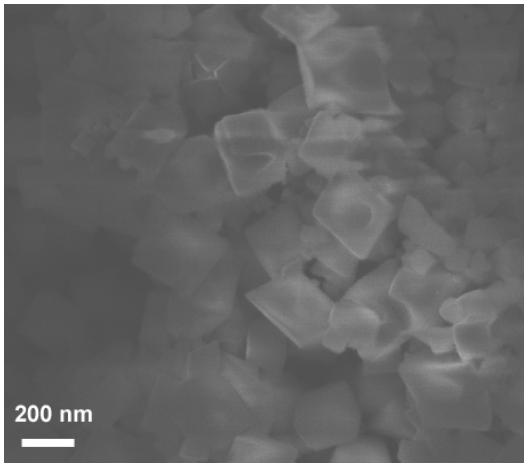

Figure 4: SEM micrograph of nanocube-MnO_2 (Sample C).