Abstract #545, 223rd ECS Meeting, © 2013 The Electrochemical Society

Template-Free Electrodeposition of Freestanding MnO_2 Nanowires and Their Pseudo-Capacitive Properties

Jakub A. Koza, Matthew M. Willmering, and
Jay A. Switzer*
Missouri University of Science and Technology
Department of Chemistry and Graduate Center for
Materials Research
Rolla, Missouri 65409-1170 USA
*E-mail: jswitzer@mst.edu

Electrochemical capacitors store electrical energy using either ion adsorption (i.e., double-layer capacitors) or fast surface redox reactions (i.e., pseudo-capacitors).[1] Electrical capacitors can be fully charged or discharged in seconds. Their energy density (about 5 Wh/kg) is lower than that of batteries, but a much higher power delivery or uptake (10 kW/kg) can be achieved. RuO_2 is currently the best known pseudo-capacitor material.[1] It has multiple oxidation states within a 1.2 V voltage window, but rare Ru is an expensive element.[1] A lot of attention has been given to finding high capacity materials using earth abundant elements. MnO_2 is one of the most promising materials for positive electrodes in pseudo-capacitors with a predicted specific capacity of 1370 Fg^{-1}.[1] MnO_2 owes its high specific capacity to the fast surface redox reaction: $MnO_2 + xC^+ + yH^+ + (x+y)e^- \leftrightarrow MnOOC_xH_y$ (where C is electrolyte cation).[1] The specific capacity is surface limited, hence it is strongly surface area dependent. Nanowires have a large surface area, which should be beneficial for pseudo-capacitor applications.

MnO_2 is electrodeposited from a Mn(II)acetate (OAc) solution (pH=5) at elevated temperatures. Electrodeposition is carried out in a standard three electrode setup. The deposits are obtained galvanostatically onto pyrolytic graphite substrates. The deposition is assumed to proceed according to the following reaction scheme:

$$Mn(II)(OAc)_2 \leftrightarrow Mn^{4+} + 2OAc^- + 2e^- \qquad (1)$$
$$Mn^{4+} + 2H_2O \rightarrow MnO_2 + 4H^+ \qquad (2)$$

Fig. 1 shows the cyclic voltammogram and the corresponding mass changes in the deposition solution, containing 50 mM $Mn(II)(OAc)_2$ and 100 mM Na(OAc) at 90 °C. The MnO_2 deposits above a potential of about 0.4 V vs. Ag/AgCl. X-ray diffraction showed the nanocrystalline nature of the deposits, and the structure matched best the orthorhombic R-MnO_2. Raman spectroscopy of films revealed that the structure is a mixture of R-MnO_2 and β-MnO_2 phases. Electrodeposited MnO_2 can be described by R-MnO_2 structure with β-MnO_2 blocks (De Wolf defects) in it which is assigned as γ-MnO_2.[2] This suggests that our electrodeposited MnO_2 nanowires are γ-MnO_2. Fig. 2 shows SEM images of deposits obtained at 80 °C at 0.25 and 1 $mAcm^{-2}$. The morphology of deposits is affected by the deposition parameters. It was observed that by increasing the current density the morphology of samples changes from nanowires to 'star'-like, and eventually at high currents density dense films are formed. By increasing the electrolyte temperature finer wires are obtained. The specific capacity of electrodeposited MnO_2 was measured in 1 M Na_2SO_4 by cyclic voltammetry (Fig. 3) and galvanostatic charge-discharge experiments. From Fig. 3 a specific capacity of nanowires deposited at 0.25 $mAcm^{-2}$ and 80 °C was 309 Fg^{-1} at 10 mVs^{-1}.The specific capacity of films deposited at different conditions differs due to the changes of the active surface area available for redox reactions.

Electrochemical deposition of MnO_2 nanowires gives an excellent contact to the substrate, i.e., it provides a continuous contact from the conductive electrode surface. Electrodeposition also allows for excellent control of the size, shape, structure, and morphology of the film,[3] which makes it an attractive approach for synthesis of novel materials for super-capacitors.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Grant DE-FG02-08ER46518.

References:
1. P., Simon; Y., Gogotsi; *Nat. Mater.* **7**, 845 (2008).
3. C., Julien; M., Massot; S., Rangan; M., Lemal; D., Guyomard; *J. Raman Spectr.* **33**, 223 (2002).
3. J.A., Switzer; G., Hodes; *MRS Bulletin* **35**, 743 (2010).

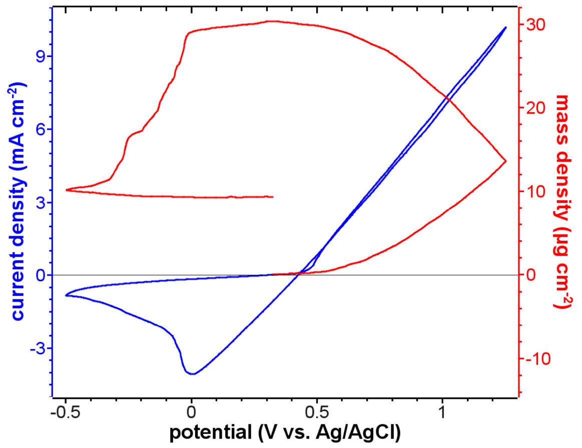

Fig. 1. Cyclic voltammogram and corresponding mass changes of Au electrode at 50 mV/s in 50 mM $Mn(II)(OAc)_2$ and 100 mM Na(OAc) electrolyte at 90 °C.

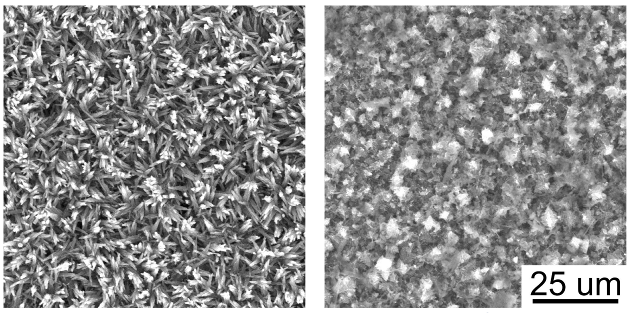

Fig. 2. SEM images of films deposited at 80 °C at 0.25 $mAcm^{-2}$ (left) and 1 $mAcm^{-2}$ (right).

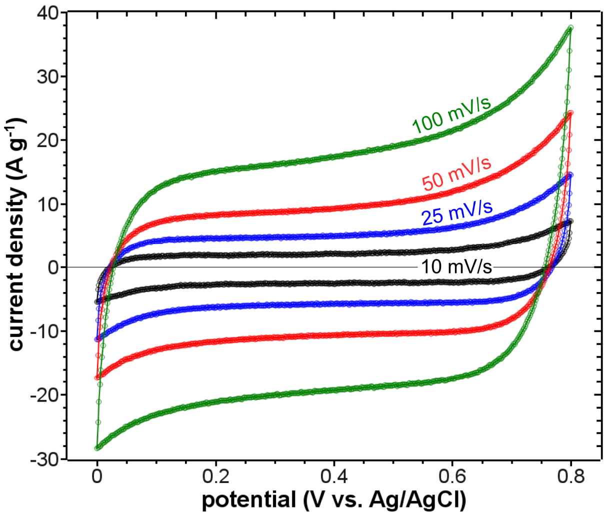

Fig. 3. Cyclic voltammograms measured in 1 M Na_2SO_4 at different scan rates for MnO_2 deposited at 0.25 $mAcm^{-2}$ and 80 °C.