

## Performance of obliquely deposited porous thin films in electrochemical capacitors

J.N. Broughton and M.J. Brett

Department of Electrical and Computer Engineering  
University of Alberta, Edmonton, Alberta, T6G 2V4

A novel vapour deposition technique has been used to prepare highly porous thin films for potential application in the field of electrochemical capacitors. The method of glancing angle deposition (GLAD) allows for the development of unique porous structures using a wide variety of metal and dielectric materials<sup>1</sup>. The GLAD technique permits deliberate and controllable formation of columnar, zigzag, chiral and other microstructures with high levels of porosity<sup>2</sup>, which may be beneficial in developing this new class of capacitors. This method of thin film deposition exploits the self-shadowing effect, which promotes competition between columns and results in structures which are significantly less dense than films produced at normal incidence. The particular structures produced using this method are strongly dependent on the melting temperature of the material and the geometry used during the deposition process.

Electrochemical capacitors based on electric double layer (EDL) formation in highly porous carbon materials ( $\sim 10^3$  m<sup>2</sup>/g) have been on the market for several years now. Although porous carbon is a relatively inexpensive material, much of the pore structure is too small for effective transport of ions to utilize effectively<sup>3</sup>. It has been shown that other materials such as Ruthenium can provide substantially higher specific capacitance values through fast reversible redox reactions in addition to the EDL formation<sup>4</sup>. However, Ruthenium is relatively expensive and attention is being drawn to lower cost materials which exhibit similar charge storage behaviour and could be cost effective candidates for commercial development.

Materials such as Ni and Mn have been proposed<sup>5,6</sup> as lower cost alternatives to Ru. These materials possess oxidation states which could provide an interesting combination of EDL and faradaic capacitance if suitable levels of porosity were to be achieved. This study presents an assessment of the performance of these materials when produced through the GLAD technique. Figure 1 shows an image of a Mn film with a porous columnar structure. Figure 2 shows an image of a Ni film with a zigzag structure. Both films are deposited on silicon wafers pre-coated with a Ti/Pt metallization. Figure 3 shows a voltammogram taken using the film in figure 1 with a 1 M KOH electrolyte, an Ag/AgCl reference electrode and a platinum wire counter-electrode. The area of the film used was 0.3 cm<sup>2</sup>. Cyclic voltammetry, scanning electron microscopy and BET porosimetry have been used to characterize these films. We have also constructed prototype capacitors utilizing various electrolytes for cyclic lifetime testing to assess the longer term usefulness of these materials.

1. K.Robbie and M.J. Brett, *J.Vac. Sci. Technol. A*, 15(3) (1997)
2. United States Patent 5866204
3. M. Endo, T. Maeda, T. Takeda, Y.J. Kim, K. Koshiba, H. Hara and M.S. Dresselhaus, *J. Electrochem. Soc.* 148(8) (2001)
4. J.P. Zheng and T.R. Jow, *J. Electrochem. Soc.*, 142, L6 (1995)
5. K.C. Liu and M.A. Anderson, *Mater. Res. Soc. Symp. Proc.*, 432, 221, (1997)
6. S. Pang, M.A. Anderson and T. Chapman, *J. Electrochem Soc.*, 147(2), (2000)

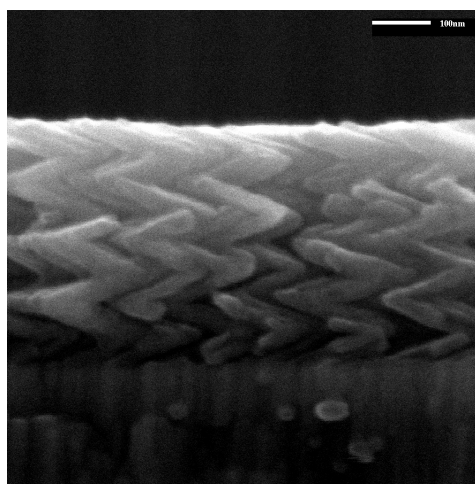


Fig. 1 Manganese film deposited at 82° with a zigzag structure

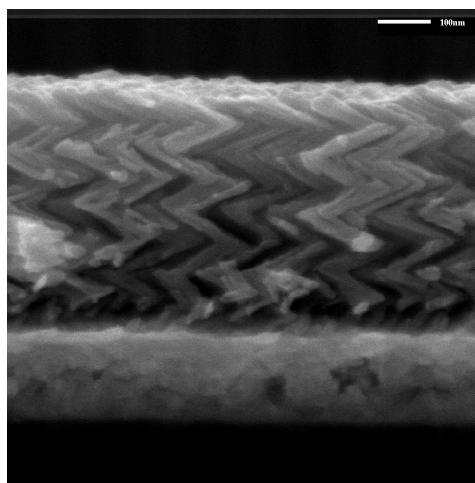


Fig. 2 Nickel film deposited at 82° with a zigzag structure

Fig. 3 Cyclic voltammogram taken from Mn film in Fig. 1