Electrochemically Deposited Multi-Layered Phosphotungstic Acid – Manganese Dioxide Materials from Square Wave Pulse Deposition for Electrochemical Capacitor Applications

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Electrochemically deposited manganese dioxide thin films have shown promise as the basis for supercapacitor electrodes [1]. Keggin type polyoxometalates have been used to improve the charge storage ability of capacitor materials such as carbon nanotubes, as polyoxometalates have a rich chemistry and are able to undergo multiple fast reversible reduction steps [2]. The inclusion of polyoxometalates into the manganese dioxide structure has the potential to lead to better materials through a synergy between the rich electrochemistry and chemistry of polyoxometalates, combined with the high electrochemical activity of manganese dioxide.

A pulsed chronoamperometric deposition sequence was performed on solutions containing Mn(II) ions and phosphotungstic acid, $H_3PW_{12}O_{40}$ (PW), using a three electrode cell, with a platinum working electrode, graphite rod counter electrode and a saturated calomel reference electrode. From this system, layered materials have been synthesised, as shown in Figure 1, and the capacitance of these has been investigated.

An investigation was also performed on the EQCM, using the same conditions, to qualify the mass change behavior during electrodeposition and to see if there is any continued growth or change during the rest periods of deposition. Results from this investigation, along with a more detailed discussion of the synthesis parameters will be described.

[1] A. D. Cross, A. Morel, T. F. Hollenkamp, S.W. Donne, Journal of the Electrochemical Society, **158,** A1160 – A 1165, 2011.
[2] T. Akter, K. Hu, K. Lian, Electrochimica Acta, **56**, 4966 – 4971, 2011.

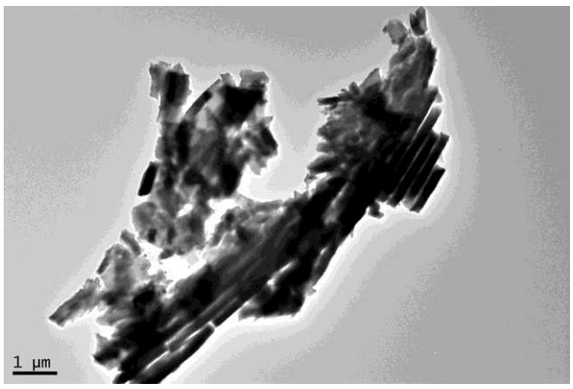

Figure 1: An example of the typical particle morphology, seen under the TEM, of hybrid MnO2 deposited with five 1 min anodic pulses at 1.2 V (vs SCE), with 1 min rest in between pulses. The deposition solution was 0.01 M $MnSO_4$ in the presence of 0.01 M PW, acidified with 0.1 M H_2SO_4. Layering is clearly evident, and with close analysis there appear to be five layers present.