

Production of capacitive films from Mn thin films: Effects of current density and film thickness

B. Djurfors^a, J.N Broughton^b, M.J. Brett^b, D.G. Ivey^{a,*}

^a Department of Chemical and Materials Engineering, University of Alberta,
Edmonton, Alta., Canada T6G 2G6

^b Department of Electrical and Computer Engineering, University of Alberta,
Edmonton, Alta., Canada T6G 2V4

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Abstract

Electrochemical oxidation of Mn thin films produces a highly capacitive, porous MnO₂ surface layer. The effects of current density and deposited Mn layer thickness on the morphology of the porous surface layer are quite pronounced. A higher current density results in a much thinner, finer porous layer while thicker deposited Mn films give much thicker porous films. Increasing the current density results in a film with greater hydration and an increase in capacitance. For the films of varying deposited layer thickness, oxidation occurs at a single current density and, as a result, the relative hydration of the film does not change noticeably. Increasing the deposited layer thickness results in a porous surface layer that increases in thickness, but with a constant amount of hydration. This combination of trends results in a significant increase in the areal capacitance of the film but little change in the specific capacitance.

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1. Introduction

Electrochemical pseudocapacitors are used primarily for applications that require a high power output and a high cycle capacity [1,2]. Traditionally, ruthenium oxide has been the material primarily used for these pseudocapacitors and exhibits specific capacitance values of up to 750 F g⁻¹. However, raw material costs and toxicity have made ruthenium difficult to produce as a commercial product [2].

Manganese oxides may provide a lower cost and lower toxicity replacement for ruthenium oxides in capacitor applications [3]. In the past, MnO₂ films have been created through chemical reaction or electrochemical deposition resulting in an amorphous hydrated MnO₂ product or a nanocrystalline hydrated MnO₂ product [3–8]. Brett et al. have used physical

vapor deposition of a manganese layer followed by electrochemical oxidation in a Na₂SO₄ solution to produce a surface film that can develop up to 700 F g⁻¹ in capacitance [9–11,14]. The Mn layer produced by PVD is a two-phase mixture of Mn and MnO [10]. The electrochemical oxidation step produces a highly porous, hydrated, amorphous MnO₂ film [11]. This porous film is the key to developing the high capacitance recorded by these films. Small changes in film morphology and chemistry can significantly affect the resulting capacitance. Preliminary studies about the effects of deposited film thickness on the resulting capacitance [14] have shown an increase in planar capacitance with increasing film thickness; however, there is little corresponding analysis of the films to aid in the explanation of the results. The purpose of this paper is to explore the effects of oxidation current on the resulting porous layer and the effects of the starting film thickness on the porous layer. Ultimately, the effects of the morphology and chemistry of the porous film will be related to the capacitance.

* Corresponding author. Tel.: +1 780 492 2957; fax: +1 780 492 2881.
E-mail address: doug.ivey@ualberta.ca (D.G. Ivey).

2. Experimental procedure

Thin manganese films were fabricated in a sputter deposition system using a 50 mm 99.95% Mn target and a target to substrate distance of 457 mm. The base pressure was 3×10^{-7} Torr and the pressure in the chamber during deposition was 6–7 mTorr. The sputtering gas was argon fed in at a rate of 10 sccm. Sputtering was carried out under constant power operation at 200 W. The manganese was deposited onto a Si substrate coated with a standard Ti/Pt metallization layer (25 nm Ti and 300 nm Pt). Samples with a nominal 50 nm Mn layer thickness were used to study the effect of oxidation current on the capacitance. To study the effect of the PVD manganese layer thickness on the capacitance of the films, samples with Mn layer thicknesses of 25, 60, 110 and 230 nm were used.

Electrochemical oxidation occurred in 1 M Na₂SO₄ electrolyte using a Gamry 750 potentiostat, with an Ag/AgCl reference electrode and a Pt wire as the counter electrode. Samples were electrochemically oxidized by applying a constant anodic current over a specified time period (galvanostatically) until the potential of the film reached 0.9 V (beyond 0.9 V, the film delaminates). A current density of 0.1 mA cm⁻² was used to oxidize the samples of variable thickness (25, 60, 110 and 230 nm). Current densities of 0.2, 0.4, 0.8 and 1 mA cm⁻² were used to evaluate their effect on capacitance. Capacitance was measured using cyclic voltammetry (CV) cycling at a rate of 50 mV s⁻¹ between 0 and 0.9 V. The capacitance was estimated from the current versus time curve. Integrating the area underneath the current versus time curve between 0 and 0.9 V provided an estimate of the total charge capacity of the film. An estimate of the capacitance of the film was then determined by dividing the charge capacity by the change in voltage (0.9 V).

The samples were imaged in a JEOL field emission scanning electron microscope (FE-SEM) at 5 kV without conductive coating. Surface analysis of the films was done by X-ray photoelectron spectroscopy (XPS) using a Kratos AXIS 165 X-ray Photoelectron Spectrometer. A monochromatic Al source was used operating at 210 W with a pass energy of 20 eV and a step of 0.1 eV. The XPS analysis was carried out using a procedure developed by Chigane and Ishikawa [12,13]. The valence of the Mn in the film was determined from the Mn 3s peak splitting widths (Table 1) and the hydration was determined from the de-convolution of the O 1s spectra (Table 2) into the Mn–O–Mn, Mn–O–H and H–O–H components.

Table 1
Mn 3s peak splitting values for various manganese oxides

Sample	Mn 3s splitting width, ΔE (eV)	Valence of Mn
MnO	5.79–5.8	2
Mn ₃ O ₄	5.3–5.50	2, 3
Mn ₂ O ₃	5.2–5.41	3
MnO ₂	4.7–4.78	4

Table 2
O 1s deconvolution energies for different bonds

Bond type	Binding energy (eV)
Mn–O–Mn	529.3–530.0
Mn–O–H	530.5–531.5
H–O–H	531.8–532.8

3. Results/discussion

3.1. Effects of oxidizing current density

PVD deposited manganese films were electrochemically oxidized to a final potential of 0.9 V using varying current densities. The total oxidation time follows an exponential decay trend (Fig. 1). The downward trend is reasonable since higher current densities result in faster oxidation rates and therefore less time required to reach 0.9 V versus Ag/AgCl. The effect of current density on the morphology of the porous layer is quite pronounced. The higher current densities produce a porous layer that is very fine and much thinner (Fig. 2), resulting in an overall reduction in the exposed surface area.

The XPS analysis (Table 3) gives both the valence of the manganese in the porous film and the relative hydration of these films. Using the highest current density results in incomplete oxidation and a two-phase mix of MnO₂ with trace amounts of Mn₂O₃. The most likely explanation for this is that the imposed oxidation rate is too rapid at the higher current density to completely oxidize the porous layer prior to reaching 0.9 V. There is an overall increase in the hydration of the film with increasing oxidizing current density. The result is two competing effects. Film hydration increases with increasing current density, which should have a positive effect on capacitance. Only the hydrated lattice sites are believed to take part in the capacitive process and therefore increased hydration in the structure means more sites are available to contribute to the overall capacitance of the film [1]. There is a simultaneous reduction in the thickness of the porous film and the exposed surface area as well, which will reduce capacitance (Fig. 2).

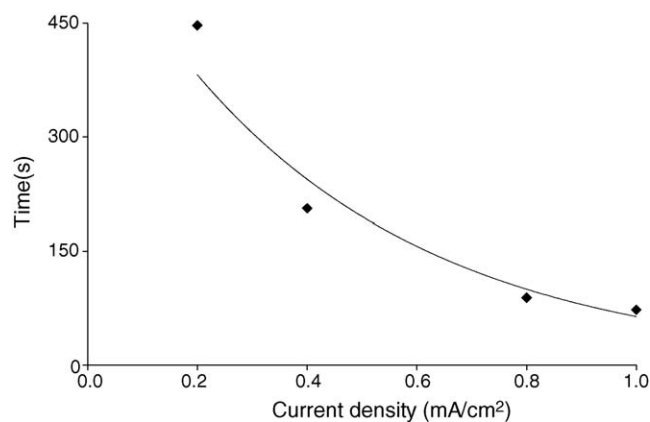


Fig. 1. Oxidation time as a function of current density for 50 nm thick Mn films.

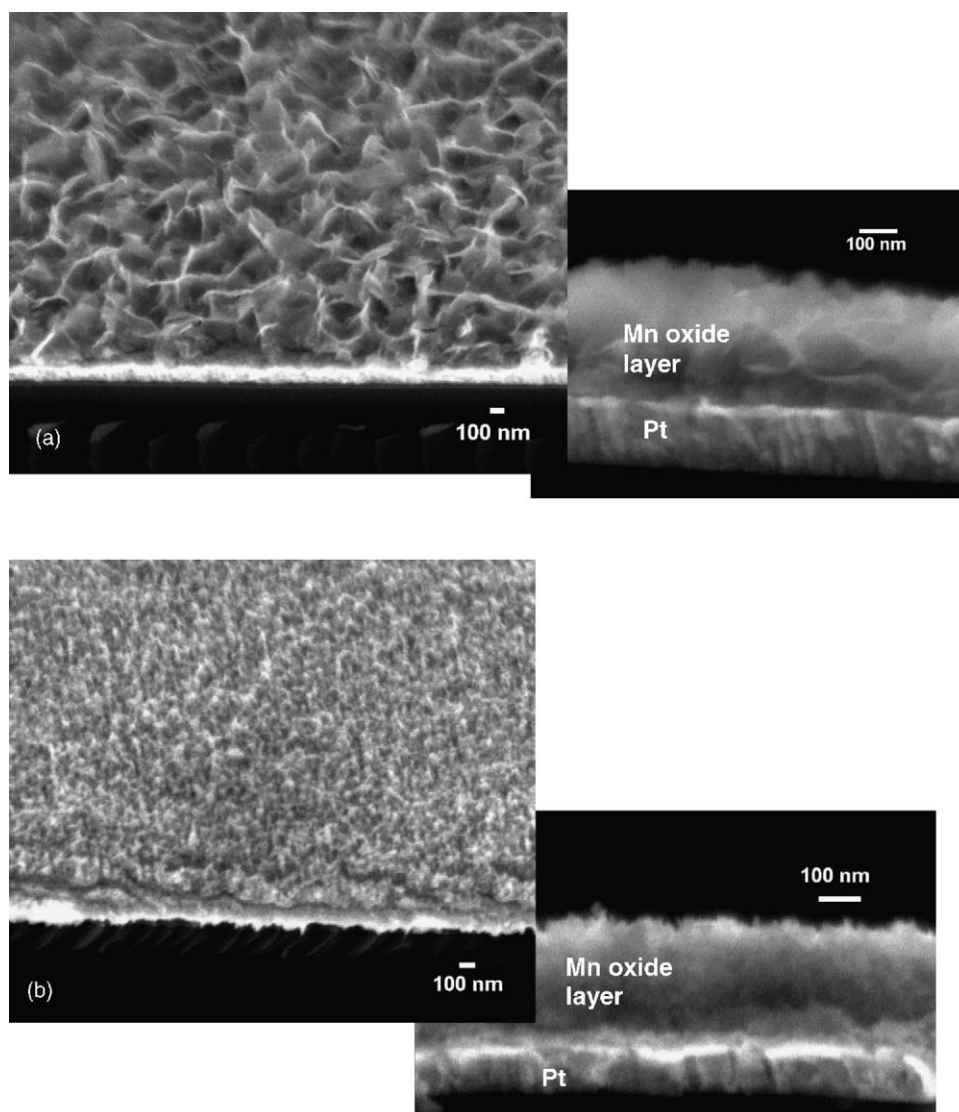


Fig. 2. FE-SEM SE images in oblique view and cross-sectional view of capacitive films produced, from 50 nm deposited Mn layers, at various oxidizing currents: (a) 0.2 mA cm^{-2} , (b) 1.0 mA cm^{-2} .

To determine the relative effects of hydration and surface area, the effect of oxidizing current on the final capacitance was studied (Fig. 3). By overlapping the various CV curves, it is seen that the films oxidized at a higher current density exhibit a CV curve that encloses a greater area and thus these films have larger capacitance values. The relationship between capacitance and oxidizing current density is shown in Fig. 4. The planar capacitance increases with increasing current density.

The increase in capacitance with increasing oxidizing current density is partly due to the increased hydration of the films. Although both the hydration and the capacitance increase with increasing current density, there is not a one-to-one correspondence. The hydration increases $\sim 35\%$ over the range of current densities tested while the capacitance increases only 25%. The increase in hydration occurs mainly on going from 0.8 to 1.0 mA cm^{-2} . The increase in hydration is partially offset by the reduction in exposed surface area

Table 3

XPS Mn 3s splitting width results giving valence of the oxidized samples and O 1s de-convolution results giving hydration

Oxidation current density (mA cm^{-2})	Splitting width (eV)	Valence	Hydration (%)
0.2	4.7	4	25
0.4	4.7	4	28
0.8	4.7	4	27
1	4.9	3,4	34

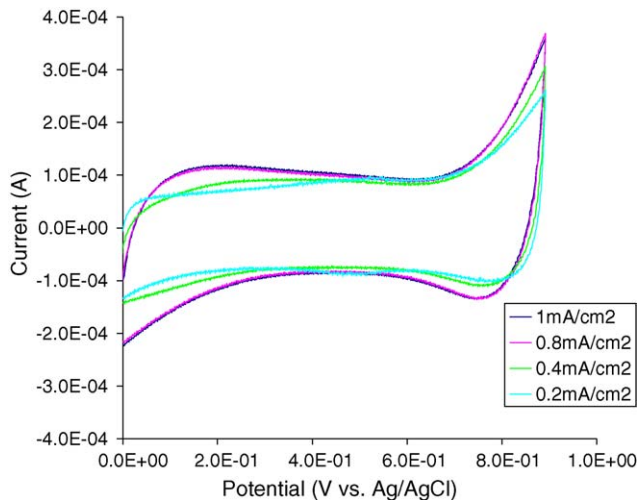


Fig. 3. Current–voltage curves for Mn thin films (50 nm) samples oxidized at various oxidizing current densities (cycle 50).

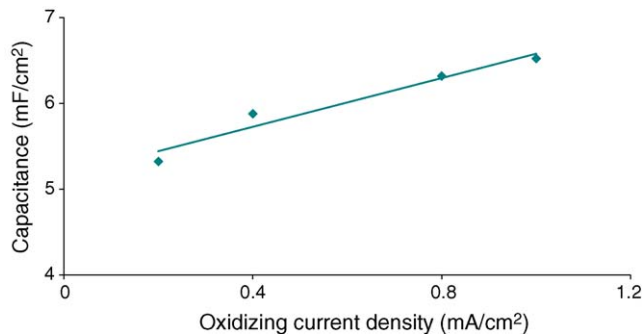


Fig. 4. Plot of planar capacitance for oxidized Mn films (50 nm) as a function of the oxidizing current density.

(Fig. 2). The overall increase in capacitance with increasing current density is an indication that hydration effects outweigh those of surface area.

Overall, the capacitance increases 25%, suggesting that the opposing trends of increased hydration and decreasing film surface area are fairly balanced in these situations, with

more emphasis being placed on hydration. From a manufacturing perspective, it is advantageous to oxidize with a higher current density since it will not only produce better capacitance, but it will also significantly reduce the manufacturing time.

3.2. Effect of starting layer thickness

The effects of starting layer thickness on capacitance have been studied previously for this system [14]. It has been shown that increasing the thickness of the deposited Mn layer results in a significant increase in planar capacitance (from 10 mF cm^{-2} at 0.2 to 50 mF cm^{-2} at 1 mA cm^{-2}). However, if the specific capacitance is examined, there is no significant change over the range of thickness of deposited Mn ($\sim 500 \text{ F g}^{-1}$). The characterization work in this section is used to explain the results previously presented. Samples of different deposited Mn layer thickness were oxidized using a constant current (0.1 mA cm^{-2}) to a potential of 0.9 V versus the Ag/AgCl reference electrode. The oxidation time required to complete the oxidation at each deposited layer thickness is shown in Fig. 5. The time required for complete oxidation is linear with the thickness of the starting layer. A thicker film has more material that needs to be oxidized and therefore more time will be required to complete the oxidation.

The porous layer thickness is a linear function of the starting layer thickness (Figs. 6 and 7). Although there is a relationship between the two quantities, it is not a one-to-one correlation. The 25-nm thick deposited layer produced a porous surface film of 100 nm, four times the size of the starting film. However, the 230 nm thick deposited layer, produced a porous film with a thickness of only 350 nm or approximately 1.5 times the original thickness of the film. The drop in the proportion of porous film with increasing deposited layer thickness is due, at least in part, to an increase in the layer/film thickness which will slow the oxidation process (restrict electron transfer) and, overall, result in a proportionally thinner porous layer being produced.

As previously reported [11], only a certain portion of the film transforms into the porous hydrated structure. A

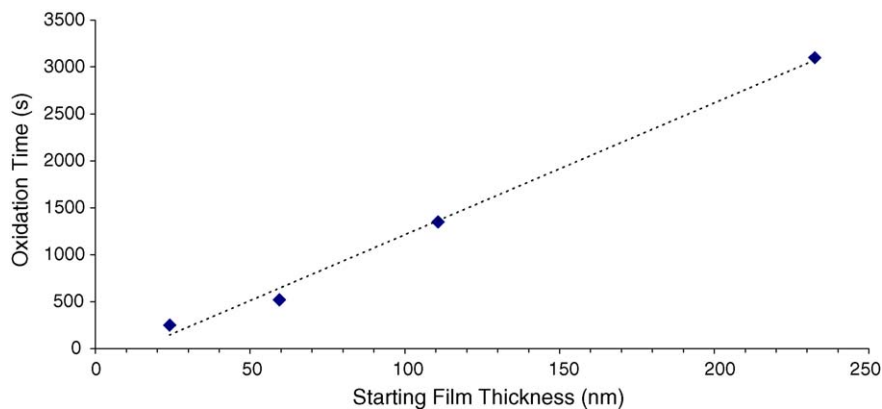


Fig. 5. Plot of the total oxidation time as a function of deposited Mn film thickness. The oxidizing current density was 0.1 mA cm^{-2} .

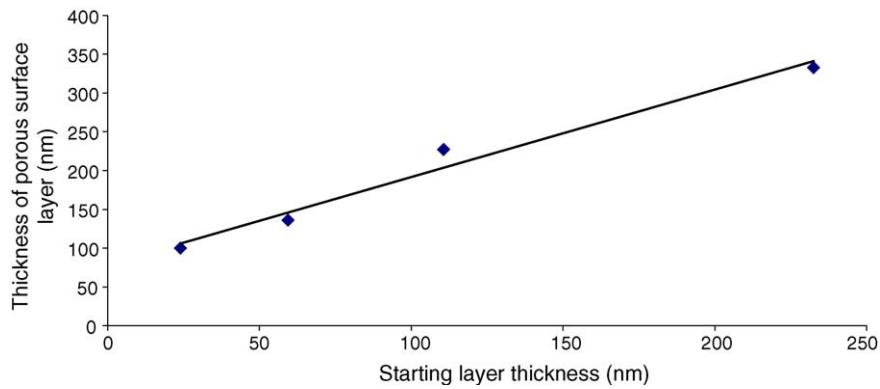


Fig. 6. Effect of the deposited Mn layer thickness on the thickness of the porous surface layer produced during oxidation. The oxidizing current density was 0.1 mA cm^{-2} .

portion of the film remains, morphologically, the same as before the oxidation step. This effect can be seen most clearly in Fig. 7b, where the bottom 200 nm of the deposited film has retained its dense structure during the oxidation process.

If the final thickness of the dense sub-layer is plotted versus the starting layer thickness, a linear relationship is found (Fig. 8). Again, although the relationship is linear, there is not a one-to-one correlation between the two quantities. For instance, the dense under-layer measures 75 nm

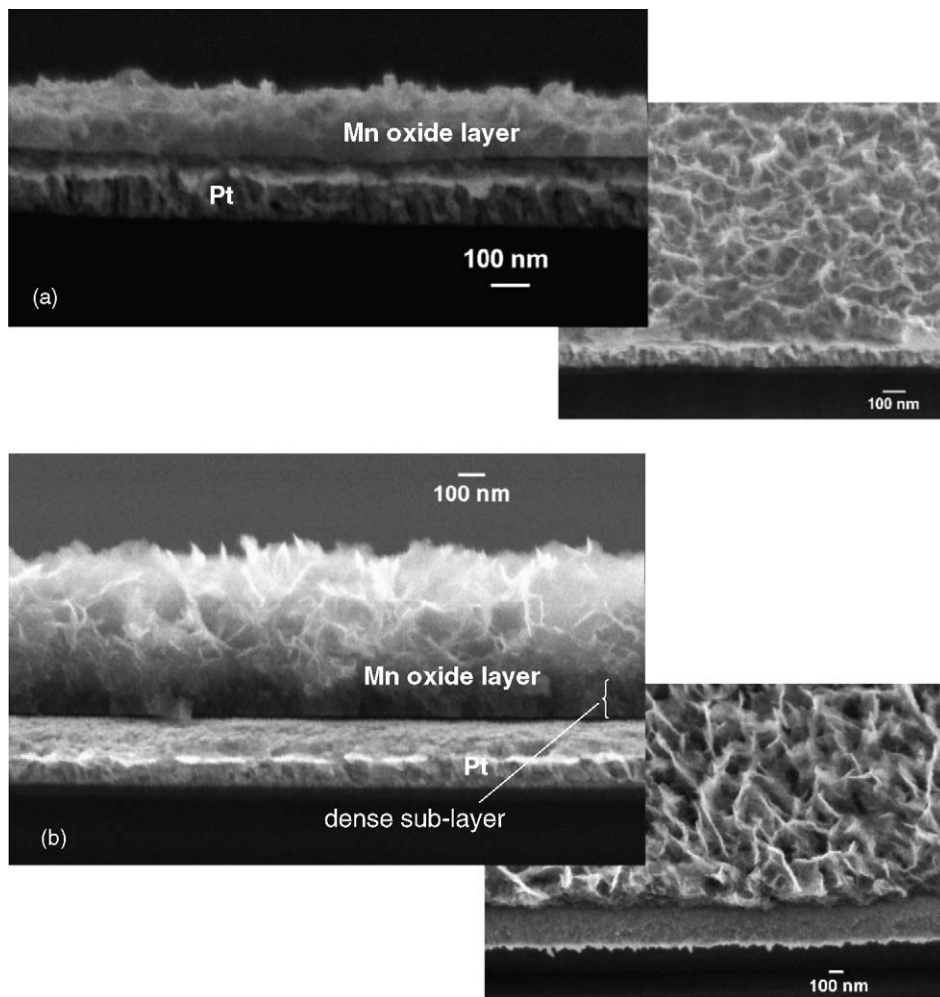


Fig. 7. FE-SEM SE images in the oblique and cross-sectional views for oxidized Mn samples with different deposited film thickness. (a) 25 nm, (b) 230 nm. The oxidizing current density was 0.1 mA cm^{-2} .

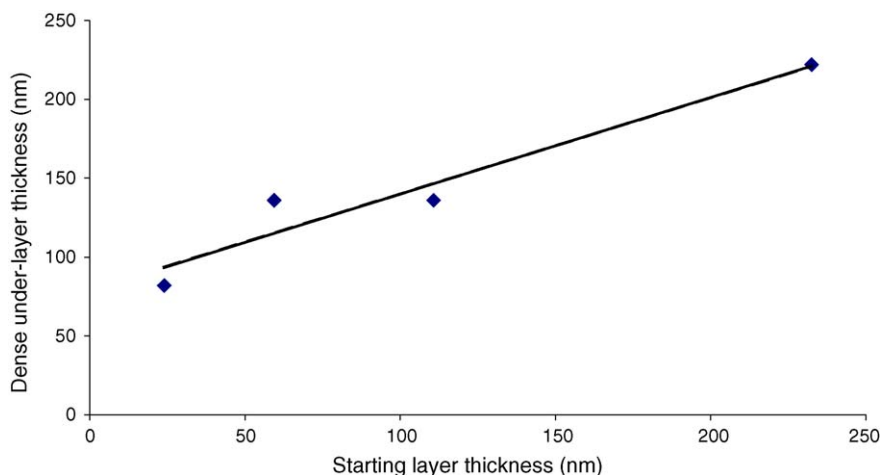


Fig. 8. The effect of deposited Mn layer thickness on the thickness of the dense under layer after oxidation. The oxidizing current density was 0.1 mA cm^{-2} .

for the deposited film with a 25 nm starting thickness (three times the original value). However, in the deposited film with a 230 nm starting thickness, the dense underlayer measures approximately 230 nm. Thus, there is proportionally less dense material being produced as the thickness of the starting layer is increased. The relationships in Figs. 6 and 8 are both linear, but the slope is not the same for the two plots. The slope is twice as great for the porous surface layer plot, indicating the deposited film thickness has a more pronounced effect on the final thickness of the porous layer than on the dense layer beneath the porous layer. This is an advantage for this process since the focus is on obtaining the thickest porous layer.

XPS results (Table 4) confirm that the valence of the manganese in the porous layer is Mn^{4+} at the end of each oxidation process and confirms that the hydration of the porous film, remains relatively constant. The amount of hydration in the sample is a function of the current density used for oxidation rather than the thickness of the deposited film. This is an expected result since the deposited film thickness should not affect the final chemistry of the film, just the final volume of the porous film. Considering that the hydration is independent of the starting deposited film thickness, the thicker film gives better capacitance per planar area due to the increase in thickness of the porous layer that provides more active sites for capacitance [14].

One must also consider, however, not just the final amount of porous layer that can be produced, but also the proportion

of the original film that is converted to porous film. Recall, that thicker deposited films, although they produce thicker porous layers, also leave more “unused” material. Thus, the relative percentage of porous layer produced is the greatest for the thinnest deposited layers, and slowly drops off with increasing deposited layer thickness. From a manufacturing perspective, the thinner deposited layers result in the most efficient use of material, but the thicker layers result in better planar capacitance, which is a more desirable quality. This trend concerning efficient material use is also reflected in the specific capacitance (F g^{-1}) of the film [14]. The specific capacitance is calculated with respect to the total mass of manganese oxide film (including both the porous surface layer and the dense under layer). Within errors, the specific capacitance is independent of the starting film thickness ($\sim 500 \text{ F g}^{-1}$). This effect is quite simple to explain. While the capacitance increases with the deposited layer thickness, the amount of material is also increasing. Therefore, the amount of capacitance developed per gram of manganese oxide material is the same as for the thinner deposited films, which develop less capacitance but also have significantly less mass.

4. Conclusions

The effect of current density on the morphology of the porous surface layer is quite pronounced. A higher current density results in a much thinner, finer porous layer. In addition, the increased current density results in a film with greater relative hydration. The net result is an increase in capacitance with increasing current density. The effect of the deposited layer thickness on the quality of the porous layer produced through electrochemical oxidation is also quite pronounced. As the thickness of the originally deposited layer increases, so does the thickness of the porous layer that is produced during the electrochemical oxidation. The result is a significant increase in the exposed surface area of the porous

Table 4

XPS Mn 3s results giving valence of the samples and O 1s results giving relative hydration for Mn films oxidized at 0.1 mA cm^{-2}

Starting film thickness (nm)	Splitting width (eV)	Valence	Hydration (%)
25	4.6	4	5.0
60	4.5	4	3.4
110	4.7	4	4.7
230	4.6	4	5.5

layer. The oxidation occurs at a single current density and, as a result, the relative hydration of the film does not change noticeably as the thickness of the deposited layer is increased. The ultimate effect of increasing the deposited layer thickness is the production of a porous surface layer that increases in thickness, but with a constant amount of hydration. The combination of variables results in a significant increase in the areal capacitance of the film with increasing deposited layer thickness. The specific capacitance remains relatively unchanged because, although the capacitance for the thinner deposited films is much less, the mass of porous material is much less, resulting in a similar value for specific capacitance. The best possible combination of variables would be a higher current density and a thicker starting film as it will produce the highest possible planar capacitance.

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