Electrochemical Quartz Crystal Microbalance and Rotating Ring Disk Electrode Analysis of Manganese Dioxide Electrodeposition for Thin Film Electrochemical Capacitors

A. D. Cross,^a I. Olcomendy,^b M. Drozd,^c A. F. Hollenkamp,^d and S. W. Donne^{a,*}

^aDiscipline of Chemistry, University of Newcastle, Callaghan NSW 2308, Australia

^bUniversité de Poitiers, 86022 Poitiers Cedex, France

^cÉcole Polytechnique de l'Université de Nantes, Nantes Cedex 3 44306, France

^dCSIRO Division of Energy Technology, Clayton South VIC 3169, Australia

This work compares the electrodeposition behavior of thin films of manganese dioxide produced from solutions of four commonly available Mn(II) salts; namely, sulfate, chloride, nitrate and acetate, as well as their corresponding acids. The deposition behavior is investigated in terms of the masses of the thin films produced, calculated by integration of charge current during deposition, and by the electrochemical quartz crystal microbalance (EQCM). Generally, it was shown that EQCM masses deviated from the mass expected from current integration, with increases ranging from 14–40%, depending on the anion. The most notable deviations from this trend were the high-acid (0.1 M) and low-Mn(II) (0.01–0.001 M) solutions where MnCl₂ and HCl were used. This difference is discussed in terms of the deposition mechanism, and in particular, complexation of the Mn(III) intermediate with excess chloride in solution, accounting for any anomalous behavior. This claim is further corroborated through rotating ring disk electrode (RRDE) data, which was used to detect any Mn(III) that would be lost to the solution after an initial oxidation. Their behavior as supercapacitor electrode materials has also been compared.

© 2012 The Electrochemical Society. [DOI: 10.1149/2.067302jes] All rights reserved.

Manuscript submitted August 28, 2012; revised manuscript received November 26, 2012. Published December 20, 2012.

Energy storage.— With the world population increasing, and expected to continue to grow to 10–11 billion by 2050,¹ so too do we expect to see an increase in global power demand. This demand is expected to reach 28 TW annually by the same year.¹ As such, the need for renewable energy sources such as solar, wind and geothermal will increase, given the finite nature of currently used fossil fuels. This in turn will require energy storage systems during periods of increased production to compensate for periods when, say, overcast weather or night-time renders solar panels ineffective, or when wind is unavailable to power turbines. Energy storage systems are also essential for consumer electronic devices, and are also an emerging technology in transportation. Even in this domain, power demands are increasing, placing greater stress on existing power sources. Given these factors, the development of energy storage devices that are capable of storing considerable amounts of energy, delivering that energy in an appropriate timeframe, and with the ability to sustain many charge and discharge cycles will be essential to maintain the anticipated energy demands facing the world.

Manganese dioxide in energy storage systems.— Manganese dioxide has an extensive history in various energy storage systems, and in particular as the cathode material in alkaline and Leclanche batteries. The basic structural building block of manganese dioxide is the [Mn(O²⁻, OH⁻, H₂O)₆]⁴⁺ octahedral unit (abbreviated as [MnO₆]), the arrangement of which is capable of forming many differing structures, with over 30 synthetic and natural structures currently classified.^{1–3} Edge and/or corner sharing between these [MnO₆] octahedra allows for the formation of materials with one-, two- or three-dimensional tunnels. The most common phases contain tunnel structures with dimensions [n×m], where n and m represent the number of octahedral subunits in the a-b plane. Typical structural varieties include the stoichiometric pyrolusite (β-MnO₂, [1×1] tunnels) and ramsdellite ([1×2] tunnels) structures, γ-MnO₂, which is best defined as a random intergrowth of the [1×1] and [1×2] tunnel structures, with larger tunnels, such as α-MnO₂ ([2×2]), λ-MnO₂, which has a spinel structure, and in the extreme case, birnessite (δ-MnO₂; [2×∞]) which is composed of flat sheet-like layers of edge sharing [MnO₆] octahedra.

Manganese dioxide can be produced from a variety of synthetic methods, including thermal, chemical or electrochemical means. Specific approaches include reduction of Mn^{5+/6+/7+},^{4,5} oxidation of

Mn²⁺,^{6–8} as well as disproportionation of Mn(III) species. Despite this variety, anodic electrodeposition of manganese dioxide from an acidic Mn²⁺ solution is the most commonly used method for commercial applications.

The use of MnO₂ as a supercapacitor electrode material was first reported by Lee and Goodenough in 1999, describing the pseudocapacitive behavior of amorphous MnO₂, and giving a specific capacitance of 200 F/g.⁹ While not performing as well as the then prototypical metal oxide capacitor material, amorphous hydrated ruthenium dioxide (α-RuO₂·xH₂O with a specific capacitance >700 F/g¹⁰) it was advantageous in many areas, particularly when taking into account the cost of ruthenium-based materials, due to its scarcity when compared to more abundant metals such as manganese. The work by Lee and Goodenough, and indeed the vast majority of work in the area of MnO₂ capacitors, typically involves producing an electrode film via affixing high-surface area MnO₂ powders to the substrate using a polymer binder. This typically yields an electrode with a specific capacitance of 125–250 F/g,^{9,11} though some work describing the use of electrodeposition was also published in subsequent years, giving specific capacitances of approximately 400 F/g.¹² Electrodeposition offers advantages in the formation and processing of electrode films, and also removes the requirement for binding additives in the electrode film.

The focus of work by the authors in recent years has been on the use of electrodeposition as a means of producing thin films of manganese dioxide for supercapacitor applications. These studies have included (i) the effect of H₂SO₄ and Mn²⁺ concentration in the depositing solution, as well as how the deposition potential and deposition time affect the resulting specific capacitance,¹³ (ii) the effect of constant current versus constant potential during deposition,¹⁴ and (iii) evaluating a number of methods for accurately estimating the mass of a thin film of manganese dioxide produced by electrodeposition.¹⁵ Here, it was found that a combination of high acid concentration, low manganese concentration, and lower (i.e. mass transport-limited) deposition potentials were the most advantageous, routinely giving specific capacitances >2000 F/g.

Manganese dioxide electrodeposition mechanism.— The current understanding of the manganese dioxide electrodeposition mechanism by oxidation of acidic Mn²⁺ solutions has found that two main pathways are possible, dependent on the acid concentration of the solution from which deposition occurs.^{16–20} As such, these two pathways have been termed the high-acid and low-acid paths. Both of these paths are summarized in Figure 1.

*E-mail: scott.donne@newcastle.edu.au

Figure 1. Summary of manganese dioxide electrodeposition mechanism pathways, showing the low-acid (A) and high-acid (C) cases, as well as the direct two-electron oxidation (B).

Irrespective of the path, the first step in the process is the single-electron oxidation of Mn^{2+} to soluble Mn^{3+} . In the low-acid path (A) this is then followed by hydrolysis of Mn^{3+} to form solid MnOOH on the electrode surface. The final step is the solid-state oxidation of MnOOH to MnO_2 . The high-acid path (C) differs somewhat in that after the initial oxidation two Mn^{3+} ions disproportionate to form Mn^{2+} and Mn^{4+} , the latter of which is then hydrolysed to form solid MnO_2 on the electrode surface. The direct pathway (B), while theoretically possible, has not been reported in the literature as of the writing of this paper.

This work.— The work presented here aims to build upon information obtained from previous studies made by the authors. Here, using the electrochemical quartz crystal microbalance (EQCM) and rotating ring-disk electrode (RRDE), we will characterize the electrodeposition of manganese dioxide from solutions of various Mn(II) salts and their corresponding acids. The aim is to explain any differences in the deposition mass and resulting performance as a supercapacitor electrode of the films produced from these various anionic solutions in terms of the anion properties and any interactions with the $\text{Mn}^{2+/3+/4+}$ ions in solution.

Experimental

Materials. Manganese dioxide deposits were prepared from solutions of a Mn(II) salt and the corresponding acid. The manganese salts were sourced from $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (Sigma-Aldrich; $\geq 99\%$),

$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich; 96.0–101%), $\text{Mn(NO}_3)_2$ (Sigma-Aldrich; $>97\%$) and $\text{Mn(CH}_3\text{COO)}_2 \cdot 4\text{H}_2\text{O}$ ($\geq 99\%$; Acros Organics). The corresponding acids used in these experiments were H_2SO_4 (Ajax Finechem; 98%), HCl (Ajax Finechem; 32%), HNO_3 (BDH Chemicals; 69–71%) and CH_3COOH (Sigma-Aldrich; $\geq 99.99\%$). The electrolyte used for performance evaluation as a supercapacitor electrode was a solution of 0.5 M Na_2SO_4 (Sigma-Aldrich; $\geq 99\%$). All solutions were made using ultra-pure Milli-Q water (resistivity $>18.2 \text{ M}\Omega \cdot \text{cm}$). Electrodeposition of manganese dioxide was carried out using a matrix of solutions containing 0.001–0.1 M acid solution together with 0.001–0.1 M of the Mn(II) salt. In total the matrix consisted of nine different solutions for each individual anion.

Electrodeposition method.— The electrodeposition cell consisted of a 250 mL beaker, which contained the platinum working electrode in the electrochemical quartz crystal microbalance (EQCM; Stanford Research Systems QCM200) crystal housing (working electrode area $= 1.325 \text{ cm}^2$), a graphite rod serving as the counter electrode (area $= 6.3 \text{ cm}^2$), and a saturated calomel reference electrode (SCE), against which all potentials were measured and reported.

The appropriate deposition potential for this work was determined by first performing a linear sweep voltammetry experiment, by measuring the current when the potential was swept from the open-circuit potential to 1.6 V versus SCE at a rate of 5 mV/s (Perkin-Elmer VMP II controlled by EC-Lab software (BioLogic, V6.80)). From these experiments, both non-diffusion and diffusion-limited potentials were selected for chronoamperometric electrodeposition from each solution. Table I summarizes the deposition conditions, including the deposition potentials used.

For electrodeposition, the working, counter and reference electrodes were placed in the cell and attached to the potentiostat, as in the linear sweep experiments. The software was configured so as to step the potential of the working electrode surface to the deposition potential determined from linear sweep voltammetry. The potential was held at this value for 30 s, after which the electrodes were washed thoroughly with Milli-Q water and transferred to a solution of 0.5 M Na_2SO_4 for cyclic voltammetry, the conditions of which will be outlined later.

The mass of manganese dioxide produced by electrodeposition was calculated from numerical integration (using the trapezoidal rule) of the current with respect to time during the chronoamperometry experiments. It is then assumed that all of the charge passed during chronoamperometry was involved in the two-electron oxidation of

Table I. Summary of the data collected in this work for the (a) sulfate, (b) chloride, (c) nitrate and (d) acetate electrolytes.

(a) Sulfate data							Specific Capacitance ($\text{F/g} \cdot \text{cm}^2$)	
$[\text{H}_2\text{SO}_4]$ (M)	$[\text{MnSO}_4]$ (M)	Deposition Potential (V vs SCE)	Integrated Mass ($\mu\text{g}/\text{cm}^2$)	EQCM Mass ($\mu\text{g}/\text{cm}^2$)	% Mn(III) Lost (RRDE)		Integrated Mass	EQCM Mass
0.1	0.1	1.200	15.1	20.5	10.1		294	216
		1.500	8.3	7.5			363	402
	0.01	0.900	0.5	1.9	2.7		2503	663
		1.100	0.6	2.2			2140	617
		0.900	0.5	0.4	6.4		4082	5381
		1.100	0.8	0.3			2944	6750
0.01	0.1	1.000	2.3	4.1	0.5		600	340
		1.200	4.2	6.1			532	364
	0.01	1.100	2.5	4.2	0.6		1385	826
		1.400	2.3	2.5			434	383
		0.900	0.5	1.9	0.8		1703	451
		1.100	0.8	1.7			1094	500
0.001	0.1	0.900	2.0	4.8	0.1		813	337
		1.100	6.3	10.8			645	377
	0.01	1.000	2.7	5.1	0.3		388	205
		1.200	5.5	9.9			575	322
		1.100	1.1	2.4	<0.1		646	292
		1.200	1.3	1.4			530	497

Table I. (Continued)

(b) Chloride data

[HCl] (M)	[MnCl ₂] (M)	Deposition Potential (V vs SCE)	Integrated Mass (μg/cm ²)	EQCM Mass (μg/cm ²)	% Mn(III) Lost (RRDE)	Specific Capacitance (F/g/cm ²)	
						Integrated Mass	EQCM Mass
0.1	0.1	1.150	37.4	48.2	47.8	382	297
		1.250	52.1	52.4		257	256
	0.01	1.250	30.7	3.1	29.3	139	1381
		1.450	20.6	3.2		261	1684
	0.001	1.250	28.4	0.7	92.0	35	1340
0.01		1.400	20.8	0.4		254	14026
	0.1	1.100	40.5	44.9	5.0	316	285
		1.350	66.5	82.4		352	284
	0.01	1.050	4.0	14.8	0.2	625	169
		1.130	10.1	17.5		535	309
0.001	0.001	1.060	1.3	2.6	0.5	724	352
		1.120	1.8	1.7		736	777
	0.1	1.100	41.6	45.5	0.5	311	284
		1.350	66.4	77.3		289	248
	0.001	1.100	7.4	13.1	0.2	509	287
		1.320	13.8	18.2		353	268
	0.001	0.900	1.1	0.6	1.2	988	1906
		1.100	2.0	4.3		483	229

(c) Nitrate data

[HNO ₃] (M)	[Mn(NO ₃) ₂] (M)	Deposition Potential (V vs SCE)	Integrated Mass (μg/cm ²)	EQCM Mass (μg/cm ²)	% Mn(III) Lost (RRDE)	Specific Capacitance (F/g/cm ²)	
						Integrated Mass	EQCM Mass
0.1	0.1	1.125	6.9	13.1	0.3	302	159
		1.275	20.7	31.3		275	182
	0.01	1.200	5.4	13.1	2.1	245	101
		1.300	4.5	5.6		257	206
	0.001	0.925	0.3	0.4	7.3	3291	2468
0.01		1.125	0.6	0.3		1891	3782
	0.1	1.050	12.6	14.8	<0.1	315	269
		1.250	37.0	35.9		167	173
	0.01	1.100	2.5	7.6	0.1	383	126
		1.200	3.4	6.3		296	160
0.001	0.001	1.060	1.2	5.1	0.9	952	225
		1.120	1.1	3.9		1040	287
	0.1	0.850	1.8	7.6	<0.1	551	131
		1.100	18.8	28.0		364	244
	0.001	1.050	2.9	8.3	0.4	424	148
		1.250	6.7	13.3		344	174
	0.001	0.950	0.8	3.7	0.4	1400	303
		1.125	1.4	5.8		519	125

(d) Acetate data

[CH ₃ COOH] (M)	[Mn(CH ₃ COO) ₂] (M)	Deposition Potential (V vs SCE)	Integrated Mass (μg/cm ²)	EQCM Mass (μg/cm ²)	% Mn(III) Lost (RRDE)	Specific Capacitance (F/g/cm ²)	
						Integrated Mass	EQCM Mass
0.1	0.1	0.850	5.8	10.2	<0.1	901	640
		1.050	7.7	12.5		578	445
	0.01	0.950	5.4	3.0	<0.1	3546	8000
		1.250	4.5	6.4		304	268
	0.001	1.000	0.8	0.2	<0.1	1575	7875
0.01		1.200	1.9	1.9		533	666
	0.1	0.650	11.8	10.5	<0.1	764	859
		0.770	20.7	22.7		959	1052
	0.01	0.950	8.2	13.7	2.0	398	298
		1.200	12.2	18.7		363	296
0.001	0.001	0.950	0.9	2.6	6.6	1823	800
		1.150	1.1	3.5		1857	728
	0.1	0.900	27.5	39.9	<0.1	295	254
		1.100	35.5	48.6		301	275
	0.001	0.750	2.3	7.2	5.8	1236	490
		1.150	6.8	10.3		665	551
	0.001	0.800	0.8	5.1	4.7	890	175
		1.100	1.9	6.8		661	231

Mn^{2+} in solution to MnO_2 , giving a number of moles and hence mass of MnO_2 deposited. This is calculated by

$$m = \frac{QM}{nF} \quad [1]$$

where Q is the charge passed (C), M is the molar mass of MnO_2 (86.9368 g/mol), n is the number of electrons involved in this process ($n = 2$) and F is the Faraday constant (96486.7 C/mol).

Electrochemical quartz crystal microbalance (EQCM).— EQCM offers the ability to track changes in electrode mass over time by detecting changes in the resonant frequency of a quartz piezoelectric crystal on which the electrode is mounted, according to the Sauerbrey equation;²¹ i.e.,

$$\Delta m = -\frac{\Delta f}{C_f} \quad [2]$$

where Δm is the change in mass ($\mu\text{g}\cdot\text{cm}^{-2}$), Δf is the change in frequency (Hz), and C_f is the sensitivity factor of the quartz crystal. The value of C_f has been previously determined to be $56.6 \text{ Hz}\cdot\text{cm}^2\cdot\mu\text{g}^{-1}$ by the deposition of Cu metal from an acidified (1 M H_2SO_4) solution of CuSO_4 (10 mM).

Cyclic voltammetry.— After electrodeposition of MnO_2 onto the working electrode surface via chronoamperometry, the working, reference and counter electrodes were transferred to a cycling solution of 0.5 M Na_2SO_4 . This cell was cycled between 0–0.8 V vs SCE at a rate of 5 mV/s for 50 cycles. While it is typical to conduct supercapacitor electrode cycling over more cycles, we have seen in previous work that cycling at a low rate for limited cycles is more demanding on pseudo-capacitive electrode materials.^{13,22} Capacity was calculated from the charge passed during the discharge (cathodic) portion of the cycle, which was then used to determine the capacitance by dividing by the potential window during cycling (i.e., 0.8 V). Specific capacitance (SC) was then calculated by dividing the capacitance by the mass of electroactive manganese dioxide calculated from either the electrodeposition current or EQCM analysis, i.e.,

$$\text{SC} = \frac{Q}{VM} \quad [3]$$

where Q is the cathodic capacity (C), V is the potential window used during cyclic voltammetry (V), and M is the mass (g).

Rotating ring-disk electrode (RRDE) voltammetry.— Similarly to the EQCM analysis, the three electrodes (Pt working (Pine Instruments in the F4 series quick change electrode holder; 5 mm diameter), graphite counter and saturated calomel reference electrodes) were placed in a five-necked 250 mL round bottom flask. All the electrodes were connected to the appropriate channels of a Pine Instrument Company bipotentiostat (model AFCBP1), with the working electrode connected via an analytical rotator (Pine Instrument Company, model AFMSRXE). To perform the experiment, the platinum disk potential was set to sweep from the open circuit potential to 1.6 V versus SCE, while the ring potential was set at 0.6 V versus SCE. This ring potential, when combined with electrode rotation, which was set at 500 rpm, allowed for any soluble Mn(III) intermediate produced during deposition to be swept away from the disk surface to the ring where it was reduced back to Mn(II) at its potential. The collection efficiency of this process (N_D) was calculated by

$$N_D = -\frac{i_R}{i_D} \times 100\% \quad [4]$$

where i_R is the ring current and i_D is the disk current. The collection efficiencies were compared to the well behaved $\text{Fe(CN)}_6^{3-/4-}$ system, which has a measured collection efficiency of 23.43% for this electrode system, to determine a percentage of Mn(III) that remains in some soluble form during deposition (% Mn(III) Lost). That is, the measured collection efficiency for the manganese dioxide electrodeposition experiment ($N_D(\text{MnO}_2 \text{ Deposition})$) was compared to that of the

Figure 2. Current and mass versus time for chronoamperometry of a solution containing 0.001 M MnSO_4 + 0.1 M H_2SO_4 . Chronoamperometry step-potential was set at 0.900 V vs SCE for 30 s.

ideal, completely soluble $\text{Fe(CN)}_6^{3-/4-}$ system ($N_D(\text{Fe(CN)}_6^{3-/4-})$), expressed as a percentage; i.e.,

$$\% \text{Mn(III) Lost} = \frac{N_D(\text{MnO}_2 \text{ Deposition})}{N_D(\text{Fe(CN)}_6^{3-/4-})} \times 100\% \quad [5]$$

Results and Discussion

Electrodeposition.— Electrodeposition of manganese dioxide has in our previous studies been primarily achieved using solutions of MnSO_4 and H_2SO_4 , and as such, all results from this study on properties such as deposition potential, deposition mass and percentage of recovered Mn(III) will be compared to samples deposited from MnSO_4 + H_2SO_4 solutions. Typical chronoamperometry (i vs t), and mass versus time data, from such a deposition are shown in Figure 2. As expected, the chronoamperometric data showed a pulse in current at the onset of the applied potential, followed by a steady decrease in current due to the consumption of Mn(II) species at the electrode surface, with its subsequent replenishment due to diffusion and migration.

EQCM data.— Electrodeposition experiments were performed using all solutions, with the compiled data for all solutions shown in Figure 3. As can be seen, there is a strong linear trend between the masses determined by EQCM when compared to the mass calculated by current integration. It is generally seen that the EQCM masses are larger than the integrated current masses, with this increase varying between 14% in the case of chloride, 27% for sulfate, 34% for acetate, and 40% for nitrate anion solutions (percentage increases determined by linear sum of least squares analysis). This linear relationship was shown to hold for masses ranging from $<1 \mu\text{g}/\text{cm}^2$, through to the upper end where masses were calculated to be $\sim 66 \mu\text{g}/\text{cm}^2$ by integration and $77\text{--}82 \mu\text{g}/\text{cm}^2$ by EQCM in the case of diffusion-limited electrodeposition from solutions of low concentrations of HCl and high concentrations of MnCl_2 .

The most notable exception was the chloride data series, specifically those solutions based on the 0.1 M HCl solution, where the current resulting from chronoamperometric deposition

Figure 3. Combined EQCM data for all solutions used to electrodeposit manganese dioxide in this study. Electrodeposition solutions were based on sulfate, nitrate, chloride and acetate salts of Mn(II) (0.001–0.1 M concentration), combined with the corresponding acid solution (0.001–0.1 M). Electrodeposition was via chronoamperometry (30 s deposition) at a range of different potentials. The working electrode was Pt (1.325 cm²), reference electrode was SCE, and the counter electrode a graphite rod (6.3 cm²). The diagonal line indicates direct correlation, while the inset figure employs a logarithmic scale to provide more detail on the low mass samples prepared.

suggested that masses of manganese dioxide should equal 30.7 and 28.4 $\mu\text{g}/\text{cm}^2$ for mass transport-limited conditions (0.01 M and 0.001 M MnCl_2 , respectively). If EQCM masses were to follow the trend of an increase of 14% over integral masses, as shown by other chloride electrodeposition data, we should expect masses of 34.9 and 32.3 $\mu\text{g}/\text{cm}^2$, respectively, when in fact a comparison instead shows that masses of only 3.1 and 0.7 $\mu\text{g}/\text{cm}^2$ were obtained. This then suggests that for 0.01 M MnCl_2 only 10% of the charge passed contributed to oxidation of Mn(II) to manganese dioxide, while in the case of 0.001 M MnCl_2 , only 2.6% of the charge passed contributed to electrodeposition. This behavior is also seen in the diffusion-limited cases, where, given that we see masses calculated from integrating the current passed during deposition equalling 20.6 and 22.1 $\mu\text{g}/\text{cm}^2$ for 0.01 and 0.001 M MnCl_2 , respectively, we would expect, based on the trend shown in other chloride-based depositions, masses equal to 26.2 and 28.1 $\mu\text{g}/\text{cm}^2$. As with the non-diffusion limited cases, we see masses much lower than this expected result, with the EQCM masses equalling 3.2 and 0.4 $\mu\text{g}/\text{cm}^2$, suggesting that for these deposition conditions, only 16 and 2% of the charge passed during chronoamperometry is actually involved in the deposition of the MnO_2 product.

This behavior in the chloride-based electrolytes is attributable to enhanced stabilization of the soluble Mn(III) intermediate, most likely through complexation of the manganese ions with chloride anions in solution. The fact that we only see this type of behavior in high acid concentration solutions, which is dependent on the disproportionation of Mn(III) (refer to Section 1.3) can give clues as to the factors that contribute to this behavior. As this is dependent on the interaction between Mn^{3+} ions in solution, it would stand to reason that the frequency of this disproportionation would be lower in solutions that contain lower concentrations of Mn(II); i.e. 0.01 and 0.001 M MnCl_2 . As these solutions are also high in acid (0.1 M HCl), the chloride is far in excess of the Mn(III), in ratios of approximately 10:1 and 100:1. Therefore, a combination of the relatively long lifespan of

Figure 4. Comparison between the (a) mass versus time and (b) mass versus charge chronoamperometric deposition data for 0.1, 0.01 and 0.001 M MnCl_2 in 0.1 M HCl. The step potential was 1.250 V versus SCE.

the Mn(III) intermediate in high acid and high chloride conditions would most likely lead to the formation of a complex species such as $[\text{Mn}(\text{OH}_2)_6\text{Cl}_4]^{3-}$.

The electrodeposition mass (obtained via EQCM) versus time data for this chloride system can possibly give some insight into the deposition mechanism. If we directly compare deposition data for 0.1, 0.01 and 0.001 M MnCl_2 in 0.1 M HCl in the mass transport-limited case, as shown in Figures 4a and 4b, the differences are readily highlighted. In Figure 4a we have plotted deposit mass versus deposition time, while in Figure 4b we have plotted deposit mass versus charge passed. For 0.1 M MnCl_2 in Figure 4a, there appears to be an induction time of ~ 1 s, where the Mn^{2+} has begun approaching the electrode surface,

Figure 5. Revised electrodeposition mechanism.

but has not gained a critical amount to be hydrolysed or disproportionate, and thus be deposited, but after this period electrodeposition begins, and the mass increases in a steady fashion approximately proportional to that expected from the current. The 0.01 M and 0.001 M MnCl_2 solutions, however, present a less straightforward case. Both show a maximum in electrode mass at short times, corresponding to the same amount of charge passed, as seen in Figure 4b, followed by an increase in mass, which is more pronounced in the 0.01 M MnCl_2 case. The implication with a constant amount of charge passed to achieve the same process is that the process must involve some critical concentration level. This process can possibly be explained in terms of the deposition mechanism previously outlined in this work, with this new process summarized in Figure 5.

After the potential step is applied to the electrode and the surface becomes polarized, the Mn^{2+} will begin to diffuse to the electrode surface where it is oxidized to Mn^{3+} (Step 1). After this, the Mn^{3+} can either diffuse out into the bulk solution, or undergo hydrolysis, leading to the deposition of MnOOH (Step 2), which is able to undergo a final solid-state oxidation to MnO_2 . The Mn^{3+} intermediate is also capable of disproportionating with another Mn^{3+} ion, giving Mn^{2+} and Mn^{4+} (Step 3), the latter of which then undergoes hydrolysis to form manganese dioxide. From the deposition mass versus time data shown in Figure 4, it appears that the 0.1 M MnCl_2 solution undergoes electrodeposition of MnO_2 via Steps 1, 2 and 3. For the 0.01 M MnCl_2 , it would appear that we see an initial fast deposition, most likely of the first deposition product, MnOOH . After this, it would appear that for a short period of time, there is a close competition between two processes, the first of which is dissolution of MnOOH , as evidenced by the slight decrease in mass, and after a period where the ions have reached a saturation point, the further deposition of both MnOOH and MnO_2 in some proportion, which after a sufficient period of time dominates over the dissolution. This would also appear to be the case for 0.001 M MnCl_2 ; however, as the increase in mass is not as significant; i.e., from $0.16 \mu\text{g}/\text{cm}^2$ at the minimum, to $0.22 \mu\text{g}/\text{cm}^2$ at 30 s, as opposed to the 0.01 M electrolyte where the minimum is $\sim 0.06 \mu\text{g}/\text{cm}^2$, and increases to $3.4 \mu\text{g}/\text{cm}^2$ at the completion of deposition. This would suggest that the 0.001 M MnCl_2 solution is close to the equilibrium concentration of the deposition/dissolution of the MnOOH .

This behavior was also observed for the diffusion-limited cases, where the difference between higher (0.1 M MnCl_2) and lower (0.01 and 0.001 M MnCl_2) concentrations is considerable. As before, the 0.1 M MnCl_2 shows a brief (~ 1 s) induction time, after which the deposition continues in a steady manner, and achieves a mass of $\sim 52 \mu\text{g}/\text{cm}^2$ after 30 s. 0.01 and 0.001 M MnCl_2 , also show electrodeposition behavior similar to the mass transport-limited case observed before, in that after initial increases in mass, corresponding to saturation of the electrode surface by Mn^{2+} , a decrease in mass, indicative of competition between dissolution of MnOOH and deposition of $\text{MnOOH}/\text{MnO}_2$, is observed. 0.01 M MnCl_2 shows an increase in mass after the minimum mass has been achieved, suggesting that the conditions during deposition are more favorable toward the deposition, rather than dissolution, of mass on the electrode, whereas the 0.001 M solution, shown to have a relatively constant mass after the initial increase, is more toward the equilibrium between dissolution and deposition of product. Mass versus time for these non-diffusion limited cases are shown in Figure 4. It should also be noted that the phenomena of induction times for electrodeposition were observed only in chloride-based solutions, further suggesting that, of the studied anions, the Mn(III) intermediate is only stabilized by chloride anions in solution.

RRDE analysis.— To further support the new deposition mechanism, RRDE was used to determine the percentage of Mn(III) lost to the solution during electrodeposition. An example of the typical disk and ring currents are shown in Figure 6, and the compiled collection efficiency data for all anions, concentration of acid and concentration of Mn(II) salt are shown in Table I.

It is shown that the percentage of Mn(III) is typically below 10%, and in the cases of 0.01 and 0.001 M H_2SO_4 , HCl and HNO_3 , generally $<1\%$, excluding 0.01 M $\text{HCl} + 0.1$ M MnCl_2 case. An interesting feature in the SO_4^{2-} , Cl^- and NO_3^- series is the consistent trend of the 0.1 M acid solutions showing collected Mn(III) percentages that are at least one order of magnitude larger than the lower acid concentrations, most likely due to the high-acid dependence of the Mn^{3+} disproportionation reaction during deposition, as well as the relatively long lifetime of the Mn(III) intermediate.^{16–20}

Figure 6. Typical RRDE data for 0.01 M $\text{MnSO}_4 + 0.001$ M H_2SO_4 , with both disk and ring currents shown.

The most interesting feature of this data is the 0.1 M HCl series, which showed Mn(III) percentages ranging from 29–92%, which is at least a three-fold increase when compared to the highest Mn(III) content found in the sulfate series, and similarly, a four-fold increase when compared to the nitrate solution that exhibited the highest amount of Mn(III). The 0.1 M HCl + 0.001 M MnCl₂ depositions in particular, with a recovered Mn(III) content of 92%, may also explain the large discrepancy between masses calculated by EQCM and charge integration, and lends credence to the earlier inference regarding the enhanced stability of the Mn(III) intermediate during the deposition process.

Supercapacitor electrode performance.— Cycling for all deposits is typical for previously observed conditions, with typical voltametric data for sulfate, chloride, nitrate and acetate data shown in Figure 7a, with the corresponding cycling performance shown in Figure 7b. As with previous studies,¹³ the best-performing electrodes tend to be those electrodeposited from a solution containing a high concentration of acid (0.1 M), a low concentration of Mn²⁺ (0.01–0.001 M), and from non-diffusion or mass transport limited deposition potentials (varies depending on the solution, but generally 0.9–1.25 V versus SCE). The specific capacitance will of course vary depending on whether or not the normalizing factor; i.e., mass, is calculated via the current passed during deposition, or the mass measured from the EQCM data – this difference is obviously the difference between the mass from integration and EQCM (cf. 14% for chloride, 27% for sulfate, 34% for acetate, and 40% for nitrate) and is especially noticeable in the 0.1 M HCl series, where specific capacitances vary between 35 F/g for charge-derived mass, as opposed to 4670 F/g for EQCM calculated mass. Compiled specific capacitance data for all anions, acid concentrations, Mn²⁺ concentrations and deposition potentials are shown in Table I. It is important to note that, as has been described in our previous work,¹³ some of the specific capacitances obtained from this study were above the theoretical specific capacitance for manganese dioxide (1386 F/g). As described in our previous work,¹³ we believe this is due to a combination of both pseudo-capacitive behavior and double layer charging.

Discussion.— The combination of integrating chronoamperometric current, EQCM and RRDE presents an interesting picture. Comparison of masses derived from integration of current during electrodeposition and EQCM show that the EQCM-calculated masses are generally greater than masses derived from the amount of charge passed during deposition. This increase ranges from 14–40% depending on the anion. The order of observed increase in mass by EQCM is chloride (14%), sulfate (27%), acetate (34%) and nitrate (40%). This trend of greater mass from EQCM when compared to current integration would suggest that the factors that would increase mass, such as the inclusion of water or the deposition anion into the electrodeposited structure, have a more appreciable effect on the mass of the electrode film. This is also correlated with the percentage of Mn(III) detected by RRDE, which shows that for the most part, the factor that would contribute the greatest toward the loss of electrode film mass at these deposition potentials; i.e., the loss of soluble Mn(III) species to the electrolyte, as opposed to O₂ evolution, is less than 10%. The most noteworthy exception to this are the solutions containing 0.1 M HCl, and in particular, the lower concentrations of the Mn(II) salt; i.e., 0.01 and 0.001 M. As previously observed, the percentage of Mn(III) detected by RRDE was found to be in the range 29–92%, with the mass calculated from EQCM accounting for only 10% and 2.6% of the mass that would be expected from integrating the charge passed during deposition. The reasons for this can be explained in terms of the complexation of Mn(III) with the various anions.

Previous examples in the literature have shown that while certain anionic ligands such as sulfate can stabilize the Mn(III) state in solution, they undergo slow decomposition. Manganic (Mn(III)) acetate has also been previously described to as an oxo-centered [Mn^{III}O(μ-O₂CMe)₂]⁺, and often referred to as Mn(OAc)₃·2H₂O or Mn₂O(OAc)₄·HOAc.²¹ Nitrate-based ligands have also been

Figure 7. Cycling performance data on the manganese dioxide electrodes prepared using the various anion containing solutions. (a) Sample cyclic voltammetry data (0.1 M acid + 0.01 M Mn²⁺ electrolyte; 50th cycle) and (b) specific capacitance as a function of cycle number for the corresponding samples.

described;²⁴ however, it is reasonable to assume that oxygen would be the electron pair donor rather than the nitrogen, and thus it is expected that it would behave more like an oxygen ligand such as sulfate, acetate, oxalate, etc., rather than a ligand that donates an electron pair from the nitrogen, such as an amine, amide or azide. Halides, particularly chloride ligands, have been reported in many complexes with Mn(III), such as the [MnCl₅]²⁻^{25,26} anion in the form of (Et₄N)₂MnCl₅,²⁷ bipyridine ([MnCl₃(bipy)]_n),^{28,29} and complexes with imides such as MnCl(NBu)₃,³⁰ and also the ion [MnCl₆]³⁻,²⁶ in addition to the myriad of methods of synthesizing MnCl₃.^{31–37}

The combination of the relatively longer lifetime of the Mn(III) intermediate in the second step of the high-acid deposition

mechanism; i.e., disproportionation of Mn^{3+} ion as opposed to hydrolysis, the relative concentrations of the Mn(III) , and the chloride in solution, and selectivity for chloride complexes with Mn(III) would explain the lower than expected EQCM masses for solutions containing high concentrations of HCl (0.1 M) and low concentrations of MnCl_2 (0.01 and 0.001 M). From mass versus time data, it can also be inferred that for these lower concentrations of MnCl_2 , there appears to be an induction time associated with reaching a critical amount of Mn^{2+} in solution to begin electrodeposition, and after which, a competition between the dissolution of the deposited MnOOH and deposition of MnOOH and/or MnO_2 takes place. 0.001 M MnCl_2 + 0.1 M HCl in particular, due to the slightly increasing mass versus time after the induction time, is particularly representative of the equilibrium between this dissolution/deposition, with these conditions slightly favoring the deposition. In these conditions, however, the vast majority of charge that is passed during chronoamperometry is presumably going to the oxidation of Mn^{2+} to Mn^{3+} , which then undergoes complexation with chloride in solution, rather than deposition of MnOOH and subsequent oxidation to MnO_2 .

Conclusions

This work has detailed the similarities and differences in thin-films of manganese dioxide electrodeposited from four salts of Mn(II) and their corresponding acids. Comparisons were made between the electrode mass calculated via integration of current during chronoamperometric electrodeposition or using EQCM, calculation of the proportion of soluble Mn(III) by RRDE, as well as performance evaluations using cyclic voltammetry. Notable findings include:

- (i) The EQCM mass ranged from 14–40% higher than that calculated from current integration. This difference was dependent on the anion. This suggests that any mass difference was due to the inclusion of water or foreign cations and anions from the deposition solution rather than any other competing processes that would lower the mass, such as O_2 evolution or soluble Mn(III) loss.
- (ii) The most noteworthy exception was deposition of manganese dioxide from solutions of 0.1 M HCl , particularly with 0.01 and 0.001 M MnCl_2 . Here the EQCM mass was only 2.6–10% of the mass expected from current integration. This is due to the stability of Mn(III) in high-acid electrolytes, and the presence of excess complex forming chloride ions in the electrolyte. Evidence of competition between MnOOH dissolution, and deposition of MnOOH and MnO_2 is also shown for these solutions.
- (iii) RRDE experiments support the previous point, where the percentage of soluble Mn(III) lies between 29–92%, whereas for all other solutions it was less than 10%, and often less than 1%.
- (iv) Better electrochemical performance as a supercapacitor electrode was achieved with (a) activation limited deposition potentials, (b) higher concentrations of acid, and (c) lower concentrations of Mn(II) .

Acknowledgments

AC wishes to acknowledge funding provided by the CSIRO Division of Energy Technology, as well as the University of Newcastle to undertake this research.

References

1. R. M. McKenzie, *Mineral. Mag.*, **38**, 493 (1971).
2. R. G. Burns and V. M. Burns, *Proc. Manganese Dioxide Symp.*, 1975.
3. V. M. Burns, R. G. Burns, and W. K. Zwicker, *Proc. Manganese Dioxide Symp.*, 1975.
4. O. Glensier, G. Gattow, and H. Meisiek, *Z. Anorg. Allg. Chem.*, **309**, 1 (1961).
5. E. Narita and T. Okabe, *Bull. Chem. Soc. Jpn.*, **53**, 525 (1980).
6. W. Feitknecht and W. Marti, *Helv. Chim. Acta*, **28**, 149 (1945).
7. W. Feitknecht and W. Marti, *Helv. Chim. Acta*, **28**, 129 (1945).
8. B. M. Tebo, R. A. Rossen, and K. H. Nealson, *NATO ASI Ser., Ser. C*, **351**, 1/3 (1991).
9. H. Y. Lee and J. R. Goodenough, *J. Solid State Chem.*, **144**, 220 (1999).
10. J. P. Zheng, P. J. Cygan, and T. R. Jow, *J. Electrochem. Soc.*, **142**, 2699 (1995).
11. H. Y. Lee, S. W. Kim, and H. Y. Lee, *Electrochem. Solid-State Lett.*, **4**, A19 (2001).
12. T. Shinomiya, V. Gupta, and N. Miura, *Electrochim. Acta*, **51**, 4412 (2006).
13. A. Cross, A. Morel, A. Cormie, T. Hollenkamp, and S. Donne, *J. Power Sources*, **196**, 7847 (2011).
14. A. D. Cross, A. Morel, T. F. Hollenkamp, and S. W. Donne, *J. Electrochem. Soc.*, **158**, A1160 (2011).
15. A. Cross, A. Morel, M. Druzd, I. Olcomendy, T. Hollenkamp, and S. Donne, *Electrochimica Acta*, **88**, 133 (2013).
16. C. J. Clarke, G. J. Browning, and S. W. Donne, *Electrochim. Acta*, **51**, 5773 (2006).
17. M. Fleischmann, H. R. Thirsk, and I. M. Tordeillas, *Trans. Faraday Soc.*, **58**, 1865 (1962).
18. W. H. Kao and V. J. Weibel, *J. Appl. Electrochem.*, **22**, 21 (1992).
19. R. L. Paul and A. Cartwright, *J. Electroanal. Chem. Interfacial Electrochem.*, **201**, 123 (1986).
20. R. L. Paul and A. Cartwright, *J. Electroanal. Chem. Interfacial Electrochem.*, **201**, 113 (1986).
21. G. Sauerbrey, *Zeitschrift für Physik*, **155**, 206 (1959).
22. A. Cross, A. Cormie, A. F. Hollenkamp, and S. W. Donne, Performance of manganese dioxide-based electric double-layer capacitors, in: *ISEE/Cap09*, Nantes, France, 2009.
23. K. D. Donnelly, W. E. Fristad, B. J. Gellerman, J. R. Peterson, and B. J. Selle, *Tetrahedron Lett.*, **25**, 607 (1984).
24. Y. A. Simonov, A. A. Dvorkin, V. F. Shul'gin, O. V. Konnik, and V. Y. Chirva, *Koord. Khim.*, **17**, 1384 (1991).
25. G. A. Barclay, R. S. Vagg, and E. C. Watton, *Acta Crystallogr., Sect. B*, **B33**, 3777 (1977).
26. C. E. Bell and D. N. Waters, *J. Inorg. Nucl. Chem.*, **39**, 773 (1971).
27. C. Bellitto, A. A. G. Tomlinson, and C. Furlani, *J. Chem. Soc. A*, 3261 (1971).
28. K. Dehnicke, H. Prinz, W. Kafilz, and R. Kujanek, *Liebigs Ann. Chem.*, **20** (1981).
29. H. A. Goodwin and R. N. Sylva, *Aust. J. Chem.*, **20**, 629 (1967).
30. A. A. Danopoulos, G. Wilkinson, T. K. N. Sweet, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 937 (1995).
31. G. Aromi, M. J. Knapp, J.-P. Claude, J. C. Huffman, D. N. Hendrickson, and G. Christou, *J. Am. Chem. Soc.*, **121**, 5489 (1999).
32. P. V. Nhat, N. T. Cuong, P. K. Duy, and M. T. Nguyen, *Chem. Phys.*, **400**, 185 (2012).
33. C. Paun, V. Parvulescu, O. Seicaru, I. Dumitru, and G. Simion, Manganese ammonium phosphate-based cosmetic pigment manufacture by oxidation of manganese sulfate or chloride, in: *Institutul de Cercetare, Inginerie Tehnologica, Proiectare si Productie pentru Industria Anorganica si Metale Neferoase*, Rom., 1991, pp. 3.
34. K. Pradhan, G. L. Gutsev, C. A. Weatherford, and P. Jena, *J. Chem. Phys.*, **134**, 234311/234311 (2011).
35. M. Barber, J. W. Linnett, and N. H. Taylor, *J. Chem. Soc.*, 3323 (1961).
36. A. Chretien and G. Varga, *Bull. Soc. Chim. Fr., Mem.*, **3**, 2385 (1936).
37. J. H. Krepelka and J. Kubis, *Collect. Czech. Chem. Commun.*, **7**, 105 (1935).