Thermal Treatment Effects on Manganese Dioxide Structure, Morphology and Electrochemical Performance

Wesley M. Dose and Scott W. Donne^{*,z}

Discipline of Chemistry, University of Newcastle, Callaghan, NSW 2308, Australia

Kinetic analysis is used to determine the required isothermal heating time at various temperatures to theoretically completely remove water from an electrolytic manganese dioxide (EMD) sample. The effect of the heat treatment regime on material structure, morphology and composition is investigated using various physical techniques, including X-ray diffraction and gas adsorption. Further, the electrochemical performance of heat treated EMD (HEMD) samples at a range of discharge rates finds that material properties such as retention of the γ - MnO_2 structure and high surface area for the sample heat treated at 250°C, and extensive structural conversion and micro-pore closure in the case of the 350°C material, lead to higher capacity and power output. Conversely, significant amounts of structural water in the 200°C sample, and the compromise in structural rearrangement and surface area loss for the material prepared at 300°C, result in poor electrochemical behaviour, especially at high discharge rates. Particularly evident from this study is the complex interplay between the heat treatment regime, resulting HEMD properties and electrochemical performance.

© 2011 The Electrochemical Society. [DOI: 10.1149/1.3597640] All rights reserved.

Manuscript submitted April 6, 2011; revised manuscript received May 12, 2011. Published June 10, 2011.

General.— The increase in energy consumption by modern society and the desire for portable technologies has increased the demand for improved high power, high specific energy battery systems. The low cost, low toxicity, relative abundance and good electrochemical characteristics of manganese dioxide make it a material of particular interest.¹ While the aqueous Zn/MnO_2 system is the most common battery system, the Li/MnO_2 battery system has found popular application in devices where the high power requirements outweigh the comparatively high cost of the cell.²

The Structure of γ - MnO_2 .—The most commonly used manganese dioxide structure in both the aqueous Zn/MnO_2 system and as a precursor in the non-aqueous Li/MnO_2 system is γ - MnO_2 , primarily because of its relatively high discharge voltage compared to other types of manganese dioxide.³ The γ - MnO_2 structure is built up of edge-sharing MnO_6 octahedra that share corners to create tunnels extending in the c direction through the structure.^{4–6} Within this framework there exists a random microscopic intergrowth of pyrolusite $[1 \times 1]$ tunnels and ramsdellite $[2 \times 1]$ tunnels.⁷ The relative amount of these domains was quantified by De Wolff,⁷ and the fraction of pyrolusite denoted P_r . Further, Chabre and Pannetier⁸ outline a method for the calculation P_r , and introduce the parameter T_w , representing the microtwinning of the (021) and (061) growth planes. Other features associated with the γ - MnO_2 structure include cation vacancies, lower valent manganese cations $[(\text{Mn(III)})]$, and structural water present as protons associated with oxide anions that compensate for the charge deficiency incurred by cation vacancies and Mn(III) ions.^{8–11} Consequently, the chemical composition of γ - MnO_2 has been described as

where x and y represent the mole fraction of cation vacancies ($\square$) and Mn(III) ions, respectively.

γ - MnO_2 thermal characteristics.—Heat treatment of this material at temperatures lower than 400°C results in the loss of structural water and the formation of a more defect free material. Lee et al. identified three types of water^{12,13}; i.e., (i) Type 1 water, which is physisorbed water able to be reversibly removed around 100°C, (ii) Type 2 water, which is comprised of surface bound hydroxyls that are irreversibly removed around 200°C, and (iii) Type 3 water, which are bulk hydroxyl groups removed irreversibly at 300°C. A structural change from the γ -phase to β - MnO_2 (pyrolusite) also

occurs as a consequence of thermal treatment above 150°C, observable from the XRD pattern by an increase in the calculated P_r value.^{8,14} The mechanism for the thermal decomposition of γ - MnO_2 is known to be related to the origin and history of the material, as well as the conditions under which the reduction takes place.^{15–20} For instance, if the heating is carried out in an oxygen containing atmosphere, then oxidation of any Mn(III) present (cf. Eq. 1) will also occur in addition to water loss and the structural transition.

Electrochemistry of γ - MnO_2 in non-aqueous batteries.—Initial efforts to use γ - MnO_2 in non-aqueous lithium batteries proved unsuccessful due to gassing caused by the high moisture content of this material. However, Ikeda et al.²¹ found that heating the manganese dioxide at temperatures above 300°C removed the problematic water content and resulted in an electrochemically active material. In the discharge of this cell lithium ions are inserted into the MnO_2 lattice in a manner analogous to that of the aqueous cathode. They outlined the reaction mechanism for the cathode material to be

Upon discharge the heat treated EMD (HEMD) has been reported to be lithiated in an irreversible process, followed by lithiation in a reversible process.^{22,23} Bowden et al.²³ and Paik et al.²⁴ have investigated the electrochemical lithiation of HEMD using X-ray diffraction (XRD), transmission electron microscopy (TEM) and magic angle spinning (MAS) solid state NMR. It was found that the first irreversible process is the lithiation of pyrolusite domains with a lattice rearrangement to ramsdellite, followed by lithiation of the ramsdellite.

Another attempt to improve the performance of non-aqueous Li/MnO_2 cells involved pre-lithiation of the γ - MnO_2 , as described by Ilchev et al.²⁵ These authors reported that pre-treatment of γ - MnO_2 with a small amount of a lithium source such as LiOH or LiNO_3 prior to heat treatment resulted in partial replacement of protons in the γ - MnO_2 crystal lattice which apparently stabilized the ramsdellite structure during the subsequent heat treatment based on XRD analysis. Cells including this pre-lithiated HEMD had higher average running voltage, enhanced high rate performance (especially pulse discharge) and improved low temperature performance compared to those containing HEMD that had not been pre-lithiated.

This work.—Previously we have applied the incremental isothermal approach to thermogravimetric data to investigate the kinetics of water loss during the heat treatment of a γ - MnO_2 sample. Such an approach to the analysis of manganese dioxide heat treatment has not been reported previously in the literature. Using this analysis, particular heating regimes to prepare materials with a

* Electrochemical Society Active Member.

^z E-mail: scott.donne@newcastle.edu.au

theoretical complete water loss were devised.²⁶ Further, this method of kinetic analysis has been used to determine the influence of the starting material structure, morphology and composition on both the amount of water lost from γ - MnO_2 during thermal treatment, and the activation energy for this process.²⁷ In the work reported here, we take the next logical step in the analysis and we examine the effect of the devised thermal treatment on the material structure, morphology and composition. The electrochemical characteristics of the resulting heat treated EMD samples are investigated and the observed changes in the material properties used to relate the electrochemical performance to the material properties.

Experimental

Preparation of manganese dioxide.—The sample of γ - MnO_2 used in this work was prepared by anodic electrodeposition, and hence given the designation electrolytic manganese dioxide (EMD). For purposes of comparison, the material used here is the same as that used in our previous work investigating the kinetics of water loss from EMD.²⁶ A detailed description of the deposition conditions and material preparation prior to its use here can be found in that work.

Material characterization.—The structure of the material used in this work was confirmed to be γ - MnO_2 by X-ray diffraction using a Phillips 1710 diffractometer equipped with a Cu $K\alpha$ radiation source ($\lambda = 1.5418 \text{ \AA}$) and operated at 40 kV and 30 mA. The scan range was from 10° to 80° 2θ , with a step size of 0.05° and a count time of 2.5 s. Analysis of the diffraction patterns was carried out by fitting a Lorentzian lineshape to individual peaks, with the fitting parameters then used to calculate structural properties such as P_r (as described by Chabre and Pannetier⁸) and the unit cell parameters.

Morphology was examined by gas adsorption using a Micromeritics ASAP 2020 Surface Area and Porosity Analyser. A representative 0.10 g sample of the manganese dioxide material was degassed under vacuum at 110°C for 2 h prior to analysis. An adsorption isotherm was then determined over the partial pressure (P/P_0) range of 10^{-7} –1 using N_2 gas as the adsorbate at 77 K. The specific surface area was extracted from the gas adsorption data using the linearized BET isotherm in the range $0.05 < P/P_0 < 0.30$, while the pore size distribution was determined using a Density Functional Theory-based approach (Micromeritics DFTPlus V2.00).

The composition of the materials was determined using two consecutive potentiometric titrations (Pt indicator and SCE reference electrode) as outlined in Vogel.²⁸ While this procedure has been described in detail in our previous work,²⁶ a brief summary is included here. A blank titration was carried out first in which 25 ml of acidified 0.25 M ferrous ammonium sulphate ($\text{NH}_4\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$, BDH Chemicals, 99%) was titrated with a standardised 0.2 M potassium permanganate solution (KMnO_4 , Ajax Finechem, 99%; standardized using the oxalate method²⁸), and the volume of permanganate added to reach the end point denoted as V_0 . Sample analysis was conducted by digesting 0.100 g of the manganese dioxide being studied to another 25 ml aliquot of the acidified 0.25 M ferrous ammonium sulphate solution. After complete dissolution the resultant solution was then titrated using the same 0.2 M permanganate solution, with the volume to reach the end point recorded as V_1 . For this titration it is important to stop at or just after the end point has been attained. To the solution resulting from the first titration ~ 20 g of tetra-sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, Ajax Finechem, 99%) was added and allowed to dissolve. The pH of this solution was then adjusted to lie within the range 6–7 by the drop-wise addition of ~ 0.20 M sulfuric acid. The second potentiometric titration was performed using the same 0.2 M permanganate solution, and the volume to reach the end point recorded as V_2 . The value for x in MnO_x was then calculated using

$$x = 1 + \frac{5(V_0 - V_1)}{2(V_2 - V_1)} \quad [3]$$

The total manganese content in the sample (%Mn) can be found from the second titration by taking into account the amount of manganese added through the addition of permanganate in the first titration. Using this result, and the dry mass of the manganese dioxide sample, found by subtracting the mass of surface water lost from the sample after heating at 110°C [$\% \text{H}_2\text{O}(<110^\circ\text{C})$] from the original mass, the total manganese content can be found using

$$\% \text{Mn} = \frac{n_{\text{Mn}}}{n_{\text{MnO}_2(\text{dry})}} \times 100 \quad [4]$$

To calculate the relative proportion of manganese (III) and (IV) species (%Mn(III) and %Mn(IV) respectively), we have

$$\% \text{Mn(III)} = (4 - 2x) \times \% \text{Mn} \quad [5]$$

$$\% \text{Mn(IV)} = (2x - 3) \times \% \text{Mn} \quad [6]$$

Finally, the cation vacancy fraction (CVF) can be found by taking into account the percentage structural water (i.e., water removed after heating at 400°C , but above 110°C , ($\% \text{H}_2\text{O}(>110^\circ\text{C})$), found by considering the difference in mass after heating the sample at 400°C for 2 h, and using

$$\text{CVF} = \frac{m}{m + 2} \quad [7]$$

where

$$m = (2 - x) + \frac{M_{\text{Mn}} \times \% \text{H}_2\text{O}(>110^\circ\text{C})}{M_{\text{H}_2\text{O}} \times \% \text{Mn}} \quad [8]$$

and M_{Mn} and $M_{\text{H}_2\text{O}}$ are the molar masses of manganese and water, respectively.

Thermogravimetric analysis (TGA).—TG analysis was conducted using a Perkin Elmer Diamond TG/DTG controlled by Pyris software. Approximately 10 mg of γ - MnO_2 sample was added to an aluminium sample pan and placed into the analyser. The same mass of α - Al_2O_3 in a similar aluminium pan was used as the reference material for DTA measurements. The heating profile applied to the sample under a static air atmosphere was a linear ramp from ambient temperature to 600°C at $1.0^\circ\text{C}/\text{min}$.

Thermal treatment of EMD.—Approximately 10 g of EMD was heated in an alumina boat crucible by a Eurotherm HTC1400 furnace with a static air atmosphere set at the required temperature. After the elapsed isothermal heating time, the sample was removed from the oven and allowed to cool to room temperature.

Electrochemical performance.—The cathode for use in Li/ MnO_2 cells were prepared from HEMD that was thoroughly mixed with graphite and polyvinylidene fluoride, in a 1:8:1 ratio. Around 0.35 g of this mixture was compressed in a 10 mm die press under 1 t of pressure into a disk electrode ~ 1 mm thick. The electrodes were dried at 110°C under vacuum and accurately weighed prior to introduction into the dry box, where cell construction took place.

CR2032 size coin cells were constructed for electrochemical testing. The coin cells were comprised of a HEMD cathode, lithium metal anode, with electrolyte made up from 1 M LiPF_6 (Sigma-Aldrich ($\geq 99.99\%$)) in 1:1 w/w of ethylene carbonate (EC, Sigma-Aldrich 99%) and dimethyl carbonate (DMC, Sigma-Aldrich 99+%). A Celgard 2400 micro-porous separator was used in these cells. After construction, cells were left to equilibrate for 3–4 days before being used for electrochemical testing.

The electrochemical characteristics of the cells prepared were assessed using a Perkin-Elmer VMP multichannel potentiostat/galvanostat on which a modular galvanostatic discharge program was performed at rates of 2, 5, 10 and 20 mA/g of active material.

Results and Discussion

Starting material properties.—The compositional, morphological and structural data for the starting EMD sample are shown in the first row of Table I. While the details of these starting properties and the resulting changes to the measured parameters as a result of heat treatment will be discussed later, we will note here that the EMD chosen for this work is a typical EMD sample. The composition of samples prepared via electrolysis can vary considerably depending on the experimental deposition conditions. We find that the compositional data collected for our starting EMD fit comfortably within the typical range for samples termed EMD.²⁹ The structure of the starting EMD, as measured by XRD, is shown in Fig. 1. The Miller indices for the peaks in the starting EMD pattern are labelled assuming an orthorhombic unit cell.

Analysis of TGA data.—The thermogravimetric (TG) data for the water loss and the corresponding differential thermogravimetric (DTG) plot are shown in Figs. 2 and 3, respectively. The mass loss up to ~110°C is assigned to the removal of physisorbed water adsorbed to the surface of the manganese dioxide. The broad peak shown from ~120–400°C corresponds to the removal of structural water from the material; i.e., protons associated with cation vacancies and Mn(III) ions present in the MnO₂ structure.^{12–15} As such, this region is the focus of this study. The sharp peak at ~500°C is due to the thermal decomposition of β -MnO₂ to Mn₂O₃.³⁰

We have used the incremental iso-conversional approach^{31,32} in order to determine the kinetic parameters with respect to the extent of conversion for the water loss from EMD. Firstly, an exponential background curve was fitted to the broad peak from ~120–400°C in the DTG data (Fig. 3). The resulting curve after background correction describes the process occurring in this region, and is shown in the inset in Fig. 3. The normalised extent of conversion (α) was then found by numerical integration of the background-corrected DTG data, with the normalization being carried out by expressing each point relative to the maximum area determined. A plot of α as a function of temperature is shown in Fig. 4.

Kinetic analysis is based on the following rate equation

$$\beta \frac{d\alpha}{dT} = A f(\alpha) \exp\left(-\frac{E_A}{RT}\right) \quad [9]$$

where A is the pre-exponential factor (min⁻¹), β is the heating rate (°C/min), E_A is the activation energy (J/mol), the term $f(\alpha)$ represents the model chosen to represent the mechanism of thermal decomposition, and all other symbols have their usual significance. In this case we will use $f(\alpha) = 1 - \alpha$ as our decomposition model.

The Runge-Kutta method, an iterative technique for the approximation of ordinary differential equations, was used to solve Eq. 9. This method uses an initial point (α_n, T_n) to approximate the next (α_{n+1}, T_{n+1}), by using the size of the interval between the points (h) and an estimate average of the slopes. This gives rise to a theoretical curve for the extent of conversion against temperature, which can be fitted to the experimental curve using linear least squares regression

Figure 1. XRD pattern of the starting EMD showing the γ -MnO₂ structure, with the corresponding Miller indices indexed using an orthorhombic unit cell, and XRD patterns for the heat treated EMD.

in a restricted range of α (hence employing the incremental integral method), by varying values for the activation energy, E_A , and the pre-exponential factor, A . Figure 5 shows the resultant variation in activation energy as a function of extent of conversion.

Using the values for the pre-exponential factor (A) and activation energy (E_A) with respect to extent of conversion, or temperature, the Arrhenius equation was used to calculate the rate constant at a given temperature. This result was then used to find the isothermal heating time (assuming first order kinetics) required to completely remove structural water from the manganese dioxide. Table II shows the temperatures selected and the corresponding heating time required to produce materials with the same extent of conversion ($\alpha = 1$),

Table I. Composition, morphology and structure of the starting and heat treated EMD samples.

Temperature (°C)	Composition					Morphology		Structure		
	Mn(T) (%)	Mn(IV) (%)	Mn(III) (%)	CVF	%H ₂ O (>110°C)	%H ₂ O (<110°C)	BET SA (m ² /g)	Micro-pore Volume (cm ³ /g)	Meso-pore Volume (cm ³ /g)	P _r
25	58.41	52.64	5.77	0.0764	4.11	2.13	37.22	0.0074	0.0293	0.34
200	59.58	52.90	6.68	0.0401	2.73	1.67	36.68	0.0071	0.0358	0.50
250	60.12	52.60	7.86	0.0130	1.81	1.60	32.46	0.0047	0.0327	0.50
300	60.12	54.76	5.36	0.0133	1.41	1.66	30.67	0.0038	0.0348	0.75
350	60.21	53.99	6.22	0.0000	0.84	0.94	24.90	0.0021	0.0401	1.00
400	61.33	54.98	6.36	0.0000	0.90	1.15	27.49	0.0034	0.0392	1.00

Figure 2. TGA data for the starting EMD sample used in this work recorded at 1.0°C/min.

although as we will see, exhibiting different structural, compositional and morphological properties.

Heat treated material properties.—The XRD patterns for the heat treated MnO_2 samples are shown in Fig. 1. The most obvious changes in these XRD patterns as a result of heat treatment are (i) the merging of the (110) ($\sim 22^\circ 2\theta$) and the (130) ($\sim 36^\circ 2\theta$) lines in the starting EMD to form a single peak at $\sim 29^\circ 2\theta$ in the sample heat treated at 400°C; (ii) clearer separation of the (221) and (240) peaks at $\sim 56^\circ 2\theta$ by 400°C; and (iii) disappearance of the peak at $\sim 68^\circ 2\theta$ and the emergence of two peaks at $\sim 66^\circ 2\theta$ and $\sim 73^\circ 2\theta$.

Figure 3. Differential thermogram (DTG) for the starting EMD sample with background curve and corrected DTG data.

Figure 4. Extent of conversion (α) for the EMD structural water loss process versus temperature.

The extent of conversion from the $\gamma\text{-MnO}_2$ phase, which predominantly displays a ramsdellite composition, to the more thermodynamically stable pyrolusite structure can be determined quantitatively by calculation of the fraction of pyrolusite (P_r) in the samples using the method outlined by Chabre and Pannetier.⁸ This result is listed in Table I. Interestingly, these changes are consistent with literature investigating EMD heat treated at various temperatures for 24 h,^{33,34} indicating a progressive structural conversion with increasing heat treatment temperature. This is despite the largely different experimental heating times used. The similarities indicate

Figure 5. Activation energy for EMD structural water loss versus extent of conversion.

Table II. Temperatures and corresponding heating durations used as heat treatment regimes for EMD in this work.

Temperature (°C)	Heating time (h)
200	31.65
250	11.12
300	5.07
350	1.52
400	0.27

that this conversion is mostly influenced by the thermodynamics of the heating process rather than the kinetics. For instance, samples heated at lower temperatures (i.e., 200 and 250°C) have begun the conversion from $\gamma \rightarrow \beta$ -MnO₂, although this process is clearly retarded by insufficient thermal energy to drive this process to completion. This is further supported by comparing the data recorded for the samples heat treated at 400°C ($P_r=0.92$ in Ref. 33, and $P_r=1.0$ in this work). In both cases the material has essentially been completely converted to pyrolusite, despite the much shorter heating time used here (16 min), suggesting few or no kinetic limitations for this process at the elevated temperature.

The structural changes can be further elucidated by consideration of the unit cell parameters (determined from the XRD patterns of these materials assuming an orthorhombic unit cell) as a function of heat treatment temperature. The unit cell parameters for the starting EMD were $a_0=4.468$ Å, $b_0=9.554$ Å and $c_0=2.833$ Å, which is an expansion in the a - b plane, but a slight contraction in the c direction, compared with ramsdellite.³⁵ The changes in the unit cell parameters with heat treatment temperature are shown in Fig. 6. The decrease shown for both the a_0 and b_0 parameters represents a structural contraction in these directions, while the steady increase in the c_0 parameter indicates lattice expansion in this direction. By considering the differences in the crystal structures of γ -MnO₂ and pyrolusite, it is clear that the main differences are found in the a - b plane. Since the unit cell is found to contract along both these directions, this suggests that Mn(IV) ion movement predominates in these

Figure 6. Changes in the unit cell parameters as a function of heat treatment temperature.

directions during heat treatment. The excess of edge sharing octahedra in a uniform array in the c direction, without any vacancies present to compensate or provide a buffer for the close proximity of the Mn(IV) ions, results in expansion in this direction.¹

The changes in BET surface area for the HEMD samples are shown in Table I. The relatively high surface area for these materials indicates that they are quite porous. Most evident from this data is the general decrease in surface area as temperature increases, barring a slight increase between the 350 and 400°C samples. Given the structural changes occurring during heat treatment, the decreasing surface area suggests that the pores in EMD are removed as Mn(IV) ions diffuse through the structure, creating a more defect free and crystalline material.¹ The slight increase in surface area for the 400°C material is likely to be caused by slow kinetics for this process (relating to the much shorter heating period applied to this material), thus not allowing for the completion of pore collapse. Noticeably, at the lower temperatures (e.g., 200°C), the surface area has not decreased significantly from the original value. This is likely to be connected to insufficient activation energy at the relatively low temperature to drive Mn(IV) diffusion, a factor responsible for pore closure. Table I also lists the changes in micro- (<2 nm) and meso-pore (2–50 nm) structures as a result of heat treatment. Clearly, heat treatment causes the collapse of micro-pores, while an increase in the meso-pore volume was observed. The increase in the micro-pore volume for the 400°C material with respect to the 350°C sample indicates that kinetic limitations in the collapse of these pores is responsible for the increase in BET surface area for this material.

A comparison of how the structural changes relate to morphological changes clearly portrays the key differences in the HEMD materials prepared. Figure 7 compares the changes in the orthorhombic unit cell volume with BET surface area. From this data, it is evident that between the temperatures tested, small changes in BET surface area can relate to large structural changes (e.g., between the standard EMD and 200°C material), or vice versa. Generally, however, the interplay of the thermodynamics and kinetics influencing the variation in these parameters lead to an approximately exponential decrease in unit cell volume with respect to BET surface area. Decreases in the unit cell volume can be attributed to manganese ions within the structure having sufficient thermal energy to move to

Figure 7. Relationship between BET surface area and unit cell volume for heat treated EMD samples.

positions consistent with pyrolusite, thus causing intra-crystallite rearrangement within the material. Conversely, changes in BET surface area relate to either the sintering of crystallites (both intra- and inter-) by joining together across the pores thus resulting in pore closure, or the opening of existing pores. The relationships between the morphological and structural features of the HEMD samples and the subtle differences in these parameters between materials will become especially relevant later when the electrochemical performance of these materials is discussed.

The underlying assumption in the preparation of these samples is that structural water, which is associated with defects (i.e., Mn(III) and cation vacancies), has been completely removed from the material. There is an expectation then that each of the HEMD samples will have no Mn(III), cation vacancies or water removed above 110°C [%H₂O(>110°C)]. However, the compositional data for the HEMD samples (Table I) shows that this is not the case. In light of this, the trends evident in these parameters provide important insights into the kinetic and thermodynamic limitations of the heat treatment under the set conditions and at these temperatures. The data for these samples show that the total manganese content [%Mn(T)] increases with heating temperature. This relates to the rearrangement of Mn(IV) ions to form a more defect free structure as cation vacancies are annealed via loss of structural protons. As a consequence, a steady decrease in the cation vacancy fraction is observed with heating temperature. The gradual decline in this parameter suggests that as the thermal energy required for this process is met by the higher temperatures, vacancy removal is able to proceed to a greater degree. After heat treatment at 350 and 400°C, vacancy defects and associated water have been completely removed from the structure, indicating that these heating regimes have provided sufficient thermal energy to complete this process, without any kinetic limitations.

The oxidation of Mn(III) to Mn(IV) also takes place as a consequence of the oxidising atmosphere present during the thermal treatment. However, complicating the interpretation of these parameters is the increase in %Mn(T), which results in a proportionate increase in both the percentage of Mn(IV) and Mn(III). Therefore, the decrease in Mn(III) caused by oxidation of this ion, and the increase in Mn(III) related to cation vacancy removal, leads to the relatively steady %Mn(III) value observed with respect to heat treatment temperature.

The proportions of water removed above and below 110°C [%H₂O(>110°C) and [%H₂O(<110°C)], further support these findings. The %H₂O(<110°C), which is water adsorbed on the surface of the material, decreases as heat treatment temperature increases, with a slight increase for the 400°C material. Clearly, the amount of water adsorbed to the surface of the material is largely determined by the available surface area and therefore it is no surprise that this result reflects the relative BET surface area for these samples (Table I). The steady decrease in %H₂O(>110°C) (i.e., structural water associated with Mn(III) and vacancy defects) with heat treatment temperature provides a second, independent measure of the extent of structural water removal from the HEMD samples. By 350°C it appears that all structural defects that will be removed in the heat treatment have been, evidenced by the approximately constant %H₂O(>110°C) value for the 350 and 400°C materials.

Electrochemical performance.—Due to the large number of cells tested (i.e., five HEMD materials each discharged at four discharge currents), only the discharge characteristics of each HEMD at 2 mA/g are shown in Fig. 8. The typically flat discharge curve of Li/MnO₂ at 2.8–3.0 V is evident from this plot. The primary discharge capacity for the cells tested was calculated by using the maximum energy produced by the cell (determined from the amount of charge passed during discharge and cell potential), as the cut-off point. This result is shown in Table III. As expected, the capacity of a given material decreases with higher discharge currents. More significantly, the manganese dioxide heat treated at 350°C maintained relatively good capacity at the higher discharge rates, followed closely

Figure 8. Discharge curves for heat treated EMD samples at discharged at 2 mA/g.

by the 250°C material. Also of note is the high capacity of the 300°C material for lower discharge rates, but poor capacity at the higher current drains. It was also observed that materials heat treated at 200 and 400°C exhibited the poorest overall discharge capacity, this being especially noticeable at the higher discharge rates.

Another useful way in which to present the data from these tests is through the use of a Ragone diagram, comparing the relative specific energy of the active material and power output of the materials. Due to the number of cells tested, only the points corresponding to the maximum energy delivered by the cell are shown in Fig. 9. This diagram again clearly shows that the materials heat treated at 350 and 250°C exhibit superior performance at the higher discharge rates compared to the other materials. The other heat treated materials show similar electrochemical behaviour to that already discussed. Furthermore, comparison with literature Ragone diagrams³⁶ the performance of our materials are superior in terms of specific energy, and comparable in terms of specific power.

As the electrochemical behaviour of manganese dioxide is largely dependent on the structure, composition and morphology of the material, the changes in these parameters with heat treatment temperature are invoked in explaining the relative electrochemical performance of these materials. Since the performance is not directly proportional to the heating temperature, it is immediately evident that there are a number of factors influencing material

Table III. Discharge capacity for heat treated EMD samples at various discharge currents (2.0V cut-off).

Temperature (°C)	Capacity (mAh/g)			
	2 mA/g	5 mA/g	10 mA/g	20 mA/g
200	178.9	176.4	80.3	29.1
250	245.6	197.6	170.7	104.4
300	250.3	226.8	169.2	28.9
350	243.0	211.6	216.4	162.1
400	234.0	217.3	67.1	62.0

Figure 9. Ragone diagram showing points corresponding to the maximum energy delivered by the cell and the corresponding power value for the heat treated EMD samples with respect to discharge rates.

performance. From the current understanding of Li/MnO₂ system, these factors may be outlined as follows:

(i) It is well known that the removal of both surface and structural water from the manganese dioxide structure is paramount, and that higher temperatures perform this function most completely and effectively.²¹

(ii) A greater amount of the more electrochemically active Mn(IV) species over Mn(III) is advantageous, and therefore materials in which oxidation of the Mn(III) to Mn(IV) has occurred will exhibit better battery performance. These first two points favour heat treatment at higher temperatures.

(iii) Samples retaining the γ -MnO₂ structure, with larger [1 × 2] tunnels in ramsdellite regions of the structure, are thought to provide both a greater degree of mobility and a larger number of insertion sites for ions introduced into the structure during discharge.³⁷ As the extent of structural conversion from the γ -MnO₂ phase to pyrolusite is related to heating temperature, this factor will likely favour the lower temperature materials.

(iv) The effect of sample porosity on the discharge characteristics of Li/MnO₂ cells remains relatively unknown. However, it has been previously determined³³ that during heat treatment micro-pores within the EMD are sintered shut as a result of manganese ion movement, while the structural contraction connected with the phase transition from $\gamma \rightarrow \beta$ -MnO₂ and the increase in material density, induces cracking. This results in an increase in the number of larger pores. These factors will be especially influential on the rate capabilities and total capacity of the cell.³⁸

In explaining the relative performance of the HEMD tested, each material will be considered separately and the above factors used to explain the resulting electrochemical performance. Some comparison will also be made highlighting differences between materials heat treated at consecutive temperatures and the effect these differences have had on the electrochemical performance. In the proceeding discussion, those materials exhibiting poorest performance will be discussed first, followed by the HEMD samples with better electrochemical characteristics.

From the physical characterisation of the 200°C material, it is clear that it has retained much of its original BET surface area,

experienced some removal of cation vacancies, lost only a small amount of structural water, and maintained to a large extent the γ -MnO₂ parent structure. Of these features, the presence of structural water associated with cation vacancies and Mn(III) is likely to be a limiting factor on the electrochemical performance. The water present evidently makes for poor performance at all discharge rates, highlighting the importance of its removal prior to use in Li/MnO₂ system. Perhaps an additional feature that limits the performance of this material is the relative ease of lithium ion movement in γ/β -MnO₂. While fundamental work has been performed analysing the mechanism and activation energy for proton diffusion in MnO₂ structures,³⁶ these relationships are currently unknown for lithium diffusion in EMD/HEMD.

The performance of the 400°C material is more difficult to explain given that its composition is very similar to the sample heat treated at 350°C; i.e., both samples have had basically all cation vacancies removed, with minor, but similar, amounts of structural water remaining, and both have been essentially been completely converted to pyrolusite. However, an interesting difference is apparent in Fig. 7, when comparing the structural and morphological properties. Here, the sample heated at 400°C has undergone slightly less structural conversion and maintained a higher surface area compared to the 350°C material, most likely as a consequence of the shorter heating time applied to this material. Fascinatingly, this makes the 400°C sample structurally more similar to that of the 300°C sample, a similarity that is reflected in the electrochemical performance of these materials, which both exhibit moderate to high performance at lower discharge rates, but are relatively poor performers at higher current drains (Table III and Fig. 9).

The material heat treated at 300°C was found to contain moderate amounts of defects remaining in the structure, with some conversion from the parent γ -MnO₂ crystal phase to pyrolusite. The compromise between these two factors may explain the electrochemical characteristics of this material. Also of interest is the relationship between the structural and morphological features of the 300°C sample (Fig. 7). This data suggests that this material has undergone significant amounts of structural rearrangement, but maintained a relatively high surface area. The combination of the structural arrangement, composition and surface area for this material has obviously aided discharge at lower rates, but proved disadvantageous for higher rate discharge.

While the material heat treated at 250°C contains significant amounts of structural water associated with both cation vacancies and Mn(III), this material exhibits good electrochemical performance, especially at higher discharge rates. The key differences between this material and its closest counterparts; i.e., the 200 and 300°C materials, can be seen most readily in Fig. 7. Noticeably, while the surface area has decreased somewhat systematically over this temperature region, the 250°C material has a similar structural arrangement to the product from the 200°C heat treatment. The maintenance of the larger unit cell arises from insufficient thermal energy or slow reaction kinetics to move manganese ions through the structure into positions characteristic of pyrolusite. At high discharge rates where the diffusion of the lithium ions through the structure is likely to be a limiting factor, the inhibition of these transitions, when coupled with reasonable amounts of water removal and the particular morphological features of this sample, lead to a high performing material at high discharge rates.

Finally, the 350°C material was found to show superior performance at nearly all discharge rates, but especially at high current drains. Because of this, the differences between the structure of this material and the 300 and 400°C samples either side of it are significant. As already mentioned, the 350 and 400°C materials are very similar in terms of composition, while the sample treated at 300°C is slightly different in that it has slightly less structural conversion to the pyrolusite phase and some retention of defects, and hence water, in the structure. This data again indicates that to obtain a material which performs well at both high and low discharge rates, the removal of water is crucial. Once again, the comparison of the

structural and morphological features (Fig. 7) differentiates the 350°C material from those around it. Markedly, heat treatment at 350°C has caused a greater degree of unit cell change and also significantly lowered the BET surface area. The key difference in BET surface area is a lower volume of micro-pores in the 350°C material relative to the 300 and 400°C materials, and a higher meso-pore volume than the 300°C sample (Table I). This feature aids the discharge of this material since the small micro-pores can only accommodate a limited number of lithium ions. Hence, when the cell is discharged, the few ions in these pores are soon inserted into the structure. The subsequent deficiency of lithium ions in this locality limits the discharge capabilities of the cell. On the other hand, meso-pores are able to contain a large number of lithium ions, so when those closest to the surface are inserted into the structure, remaining ions move to take their place, leading to improved discharge characteristics, especially at higher discharge rates.

Summary and Conclusions

This work has determined the structural, compositional and morphological features of heat treated EMD that lead to superior electrochemical performance in the Li/MnO₂ system at a range of discharge rates. What is especially evident is the complex interplay of these features in determining the electrochemical performance of the material. Specific outcomes of this work include:

(i) Using the incremental iso-conversional approach developed in our earlier work for analysing TGA data, a family of thermal treatment regimes based on heating temperature and time were calculated in order to, in theory, completely remove water from the manganese dioxide structure.

(ii) Characterisation of this family of HEMD samples revealed that materials undergo a mainly kinetically limited thermal conversion from $\gamma \rightarrow \beta$ -MnO₂, in connection with contraction of the lattice structure in the *a-b* plane and expansion in the *c* direction.

(iii) The material surface area also generally decreases with heating temperature, although noticeably, the pore collapse process is thermally limited at lower temperatures, while at the higher temperatures the reaction kinetics dictate the extent to which this process proceeds.

(iv) Despite the theoretical expectation of complete water removal from the EMD, experimental results demonstrate that thermal and kinetic limitations present in these heating conditions prevent the completion of the water loss process. In general, however, as heating temperature increases there is an increase in the Mn(IV) content, while Mn(III) content, cation vacancy fraction and amount of structural water removed above 110°C decrease.

(v) Materials found to exhibit superior electrochemical performance at all discharge rates were distinguished either by (a) retention of the γ -MnO₂ structure and relatively high surface area for the sample heat treated at 250°C, or (b) extensive structural conversion and micro-pore closure in the case of the 350°C material. Conversely, significant amounts of structural water remaining in the 200°C sample, and the compromise in structural arrangement and surface area

for the material prepared at 300°C, result in poor electrochemical behaviour, especially at high discharge rates.

Acknowledgments

The authors would like to acknowledge Ms. Jenny Zobec for her assistance in obtaining the XRD data.

References

1. J. B. Arnott, R. P. Williams, A. G. Pandolfo, and S. W. Donne, *J. Power Sources*, **165**, 581 (2007).
2. D. Linden and T. B. Reddy, *Handbook of Batteries*, 3rd ed., McGraw Hill, New York (2002).
3. C. B. Ward, A. I. Walker, and A. R. Taylor, *Prog. Batt. Batt. Mater.*, **11**, 40 (1992).
4. R. G. Burns and V. M. Burns, *Proc. MnO₂ Symp.*, **1**, 306 (1975).
5. V. M. Burns, R. G. Burns, and W. K. Zwicker, *Proc. MnO₂ Symp.*, **1**, 288 (1975).
6. R. Giovanoli in *Geology and Geochemistry of Manganese*, Vol. 1, I. M. Varentsov and G. Grasselly, Editors, p. 159, Akademiai Kiadó, Budapest (1980).
7. P. M. De Wolff, *Acta Cryst.*, **12**, 341 (1959).
8. Y. Chabre and J. Pannetier, *Prog. Solid State Chem.*, **23**, 1 (1995).
9. P. Ruetschi, *J. Electrochem. Soc.*, **131**, 2737 (1984).
10. P. Ruetschi, *J. Electrochem. Soc.*, **135**, 2657 (1988).
11. P. Ruetschi and R. Giovanoli, *J. Electrochem. Soc.*, **135**, 2663 (1988).
12. J. A. Lee, C. E. Newnham, and F. L. Tye, *J. Colloid Interfac. Sci.*, **42**, 372 (1973).
13. J. A. Lee, C. E. Newnham, and F. L. Tye, *J. Chem. Soc., Faraday Trans.*, **74**, 237 (1978).
14. Y. Paik, W. Bowden, T. Richards, and C. P. Grey, *J. Electrochem. Soc.*, **152**, A1539 (2005).
15. B. D. Desai, J. B. Fernandes, and V. N. K. Dalal, *J. Power Sources*, **16**, 1 (1985).
16. P. R. Skidmore, *Prog. Batteries Sol. Cells*, **9**, 167 (1990).
17. M. I. Zaki, M. A. Hasan, L. Pasupulety and K. Kumari, *Thermochim. Acta*, **303**, 171 (1997).
18. R. Giovanoli, *Thermochim. Acta*, **234**, 303 (1994).
19. C. Gonzalez, J. I. Gutierrez, J. R. Gonzales-Velasco, A. Cid, A. Arranz, and J. F. Arranz, *J. Therm. Anal. Calorim.*, **52**, 985 (1998).
20. A. El-Shobaky, A. M. Ghosza, and H. A. Hassan, *J. Therm. Anal. Calorim.*, **51**, 529 (1998).
21. H. Ikeda, T. Sauto, and H. Tamura, *Proc. of MnO₂ Symp.*, **1**, 384 (1975).
22. J. C. Nardi, *J. Electrochem. Soc.*, **132**, 1787 (1985).
23. W. Bowden, C. Grey, S. Hackney, X.Q. Yang, Y. Paik, F. Wang, T. Richards, and R. Sirotina, *ITE Lett.*, **3**, B1(2002).
24. Y. Paik, Y. Lee, F. Wang, W. Bowden, and C. P. Grey, *Solid State Chem. Inorg. Mater. III*, **658**, GG9.11.1 (2001).
25. N. Itchev, W. Bowden, P. Christian, P. R. Moses, and K. Brandt, *ITE Lett. Batteries, New Technol. Med.*, **2**, B32 (2001).
26. W. M. Dose and S. W. Donne, *J. Therm. Anal. Calorim.*, In press.
27. W. M. Dose and S. W. Donne, *Mat. Sci. Eng. B*, Submitted.
28. A. I. Vogel, *Quantitative Chemical Analysis*, John Wiley & Sons, New York (1989).
29. R. P. Williams, Ph.D. Thesis, University of Newcastle, Australia (1995).
30. B. Liu, P. S. Thomas, A. S. Ray, and R. P. Williams, *J. Therm. Anal. Calorim.*, **76**, 115 (2004).
31. P. Budrugaec and E. Segal, *Int. J. Chem. Kinet.*, **33**, 564 (2001).
32. P. Simon, P. S. Thomas, J. Okuliar, and A. S. Ray, *J. Therm. Anal. Calorim.*, **72**, 867 (2003).
33. J. B. Arnott, R. P. Williams, A. G. Pandolfo, and S. W. Donne, *J. Power Sources*, **165**, 581 (2007).
34. A. P. Malloy, G. J. Browning, and S. W. Donne, *J. Colloid. Interface. Sci.*, **285**, 653 (2005).
35. A. M. Bystrom, *Acta Chem. Scand.*, **3**, 163 (1949).
36. P. Simon and Y. Gogotski, *Nature Mater.*, **7**, 845 (2006).
37. D. Balachandran, D. Morgan, and G. Ceder, *J. Solid State Chem.*, **166**, 91 (2002).
38. T. J. Lee, T. T. Cheng, H. K. Juang, and S. Y. Chen, *J. Power Sources*, **43-44**, 709 (1993).