Electrochemical Characterization of Proton Diffusion during Discharge and Cycling of γ -MnO₂

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In this work step potential electrochemical spectroscopy (SPECS) and electrochemical impedance spectroscopy (EIS) are used to examine the γ -MnO₂ electrode and provide two distinct measurements of proton diffusivity during the discharge and cycling of γ -MnO₂. This is carried out by modeling the electrochemical data assuming solid-state spherical diffusion (in the case of SPECS) and by using an equivalent circuit approach (in the case of EIS). In both cases an outline of the model employed and the details of the fitting process are included. The resulting $A\sqrt{D}$ values are then considered and any changes noted during discharge or cycling, along with the variation observed between the two techniques, are explained in terms of the structural and morphological changes which the material undergoes. A key finding from these studies is that SPECS characterizes bulk diffusional processes, while EIS focuses on near-surface (<1 nm deep) processes.

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Manuscript submitted August 8, 2013; revised manuscript received September 12, 2013. Published October 1, 2013.

Electrochemical energy storage.— The alkaline Zn-MnO₂ system retains a prominent place in the global battery market, occupying ~80% of the total number of batteries manufactured in the US, and with over 10 billion units manufactured worldwide.¹ The widespread use of electrolytic manganese dioxide (EMD) in alkaline battery cathodes arises from an abundance of its raw materials,² low production costs, low toxicity, and excellent performance under low and moderate discharge rates. These factors drive continued research on the alkaline manganese dioxide cathode, with current research directed toward better understanding the link between material structure, morphology and electrochemical performance.

Structure and electrochemistry of γ -MnO₂.— EMD has the γ -MnO₂ structure which is built up of edge- and corner-sharing [MnO₆] octahedra in a manner consistent with a random microscopic intergrowth of pyrolusite (1 × 1) and ramsdellite (2 × 1) forms of MnO₂.³ Its structure has been considered in depth by Chabre and Pannetier,⁴ who outlined a method for the calculation of the pyrolusite content (denoted P_r), and the level of microtwinning (denoted T_w) present in the (021) and (061) growth planes. Other key features associated with the γ -MnO₂ structure include cation vacancies, lower valent manganese cations (Mn³⁺), and structural water present as protons associated with the oxide anions that compensate for the charge deficiency incurred by Mn³⁺ ions and cation vacancies.^{5–7}

The discharge mechanism of electrolytic manganese dioxide in an alkaline environment was proposed originally by Kozawa et al.,^{8,9} and later refined by others.^{10–12} For the single electron reduction to δ -MnOOH, the model consists of a homogeneous process based on concerted electron-proton insertion into the host γ -MnO₂ structure; i.e.,

The inserted electron originates from the external circuit, passing through the conductive pathway in the electrode to be inserted into the manganese dioxide structure to reduce a Mn⁴⁺ ion to Mn³⁺. This process occurs in tandem with water decomposition at the manganese dioxide-electrolyte interface, leading to proton insertion into the γ -MnO₂ structure, with the remaining OH[−] ion staying in the electrolyte. Protons and electrons then diffuse through the structure, via movement between adjacent oxide or manganese sites, tending toward a uniform distribution of inserted species.

Proton diffusion mechanism in γ -MnO₂.— The diffusion of protons and electrons through the γ -MnO₂ structure is of particular importance for the performance of the alkaline manganese dioxide cathode.

Previous work has shown that proton diffusion is rate limiting,¹³ when compared to electron mobility, for the majority of the discharge process. The location and movement of protons within the pyrolusite and ramsdellite sub-units of γ -MnO₂ has been previously considered by Balachandran et al.,¹⁴ who reported a first principles computational study on proton intercalation. By determining the energy barriers for proton diffusion along different paths in the materials, the authors were able to show that the lowest energy diffusion path (~200 meV) for a proton in the ramsdellite structure consists of hops between pyramidal oxygen ions on opposite sides of the (2 × 1) tunnel. This was found to occur via a rotation-and-jump mechanism, whereby a proton attached to a pyramidal oxygen site rotates prior to hopping to the opposite oxygen site.

In contrast, the lowest energy pathway in pyrolusite was observed to be from an oxygen site on one side of the (1 × 1) tunnel to an oxygen site on a neighboring side. The movement between oxygen sites without rotation results in an activation barrier much higher in pyrolusite (575 meV) when compared to ramsdellite (~200 meV). As a result it was implied that the presence of de Wolff defects would inhibit proton diffusivity and hence limit performance under rate limited conditions. Finally, the effect of twinning on the diffusion process was studied by considering proton diffusion through the α -PbO₂ structure, the 100% twinned equivalent of pyrolusite. The activation barrier for the lowest energy transition was found to be ~1.2 eV, suggesting that twinning dramatically reduces the rate of proton diffusion through the material.

This work.— In this work we will make use of step potential electrochemical spectroscopy and electrochemical impedance spectroscopy to examine the γ -MnO₂ electrode and provide two distinct measurements of proton diffusivity during the discharge and cycling of γ -MnO₂. In each case analysis of the electrochemical data will be combined with an appropriate model to allow values for proton diffusion to be determined. The resulting values, and the models which were developed in each case, will then be compared and any variation considered in terms of the structural changes γ -MnO₂ undergoes during discharge and cycling.

Experimental

Materials and characterization.— The EMD used in this work was provided by Delta EMD Australia, Pty Limited. It was prepared by the electrolysis of a hot (~98°C), acidic (H₂SO₄) solution of MnSO₄ (acid:Mn ratio of ~0.4) resulting in deposition of the manganese dioxide onto a titanium anode. Following deposition, the EMD was mechanically removed from the anode, milled into a ~105 μm powder (mean particle size of ~45 μm), neutralized and washed to remove entrained electrolyte, and then dried before being ready for use. Using standard analytical techniques it was determined that the EMD

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employed possessed a γ - MnO_2 crystal structure,⁴ had an x in MnO_x value of 1.97,¹⁵ a cation vacancy fraction of 0.07–5–7 and a BET surface area (N_2 adsorption at 77 K) of 30.0 m^2/g .¹⁶

To assess the changes this material undergoes during reduction a series of partially reduced materials was prepared by reaction with 2-propanol. The structure of each of these materials was determined by X-ray diffraction using a Phillips X'Pert MPD diffractometer equipped with a Cu $K\alpha$ radiation source ($\lambda = 1.5418 \text{ \AA}$) operated at 40 kV and 30 mA. The scan range was from 10° to $90^\circ 2\theta$, with a step size of $0.007^\circ 2\theta$ and a scan time of 1 h. The morphology of selected materials was also investigated using a JEOL JEM-2100 electron microscope with a LaB_6 source operating at 200 kV.

Electrochemical cell construction.— The EMD working electrode used in this study was prepared by mixing together EMD (0.200 g), Timcal SFG 6 graphite (2.000 g) and 9 M KOH ($\sim 0.25 \text{ g}$) using a mortar and pestle. Cell assembly involved placing 0.200 g of the blackmix into a Teflon-lined Au-coated C-size battery can. After covering with three separator papers, the electrode was compacted under 1 t for $\sim 2 \text{ min}$. A perforated Perspex separator disk was then placed onto the electrode and a stainless steel counter electrode sleeve slid into place. The chamber was then filled with $\sim 15 \text{ mL}$ of electrolyte, sealed with Parafilm-M (SPI Supplies) and mounted between a Perspex cover and base-plate. The cell was held in place with three securing bolts that were each tightened to a torque of 75 cN.m to ensure a uniform pressure. Finally, a Hg/HgO reference electrode was inserted into the cell, which was then allowed to equilibrate for 60 min prior to cycling. A schematic of an assembled electrochemical cell can be seen in Ref. 17.

Electrochemical protocol.— The electrochemical behavior of this electrode was investigated via step potential electrochemical spectroscopy (SPECS), and the combination of SPECS with electrochemical impedance spectroscopy (EIS). Briefly, both techniques involved stepping the potential in 25 mV increments from 0.1 V to an upper limit of 0.3 V, down to a lower limit of -0.3 V , and then back up and down, giving a total of two charge-discharge cycles. At each step the electrode was allowed to equilibrate and the current response recorded over a 60 min interval. An impedance spectrum was then measured using the frequency range 20 kHz to 0.1 Hz with a 10 mV (AC) excitation signal. In this way a series of current decay curves and impedance spectra were gathered over the two charge-discharge cycles examined.

Results and Discussion

SPECS characterization and analysis.— The chronoamperometric response of the manganese dioxide electrode at set potentials during discharge is shown in Figure 1. It was observed that as the potential was made more cathodic, the current increased due to the enhanced reduction of manganese dioxide. As expected, the current response was observed to vary significantly depending on the applied potential. By integrating the current-time response the charge passed during each potential step could be quantified. As shown in Figure 2, this process provides similar information as to that which can be obtained via slow-scan cyclic voltammetry; except that in this case the peak positions are shifted toward their thermodynamic potentials due to the nature of the SPECS experiment. In the initial charging half-cycle, carried out to ensure the EMD is fully oxidized prior to use, evidence of oxygen evolution is apparent at potentials above 0.25 V. This feature is also evident in the second charging half-cycle, and likely arises from sitting the electrode at high anodic potentials for substantial periods of time. During the discharge half-cycles we observe behavior typical of EMD,^{8–12} with reduction of surface states observed at $\sim 0.1 \text{ V}$ and bulk EMD reduction occurring below 0.0 V. Discharge capacities of 218 mAh/g and 193 mAh/g were obtained for the first and second half-cycles, with the $\sim 10\%$ decrease in discharge capacity in line with previous findings for cycling of EMD.¹⁷

Figure 1. Chronoamperometric data recorded during discharge of the EMD electrode, with the inset showing an example of the fitting process applied to each data set.

The SPECS data shown in Figure 1 can also be analyzed further to gain insight into the kinetics, rather than the thermodynamics, of the reaction taking place at each potential step. Numerous models have been used to interpret chronoamperometric data, with the most well known being the Cottrell equation developed for planar semi-infinite diffusion in a bulk electrolyte.¹⁸ Given the present electrode system, where diffusion in approximately spherical crystallites in the solid-state rather than in a bulk electrolyte gives rise to the current response, the boundary conditions employed for deriving the Cottrell equation cannot be reasonably applied. A more appropriate model

Figure 2. Variation in incremental capacity with applied potential and cycle number for the EMD electrode.

Table I. Fitted parameters and composition changes for selected potentials during the first and second discharge half-cycles.

Potential (V vs. Hg/HgO)	Cycle 1			Cycle 2		
	MnO _x	P1	P2	MnO _x	P1	P2
0.300	1.990	0.100	7.580	1.985	0.150	8.000
0.200	1.984	0.252	7.583	1.984	0.045	2.500
0.100	1.970	0.103	0.781	1.961	0.052	0.107
0.000	1.925	0.076	0.192	1.906	0.056	0.129
-0.050	1.887	0.060	0.088	1.868	0.036	0.035
-0.100	1.821	0.019	0.004	1.806	0.019	0.005
-0.150	1.727	0.021	0.003	1.739	0.019	0.005
-0.200	1.658	0.015	0.004	1.689	0.030	0.017
-0.250	1.608	0.012	0.003	1.655	0.034	0.043
-0.300	1.577	0.006	0.002	1.627	0.021	0.025

based on solid-state spherical diffusion was proposed and applied to the manganese dioxide electrode by Hong et al.¹¹ The model assumes the following initial and boundary conditions:

$$\text{Initial: } C(x, t) = C_0 \quad \text{for all } x \text{ when } t = 0 \quad [2]$$

$$\text{Boundary: } C(x, t) = C_1 \quad \text{for all } x \text{ when } t = 0 \quad [3]$$

$$\text{Boundary: } \frac{\delta C(x, t)}{\delta x} = \frac{i(t)}{nFAD} \quad \text{for } x = 0 \text{ and } a \text{ when } t > 0 \quad [4]$$

Under these conditions, Fick's Second Law of Diffusion can be solved to yield

$$i = \frac{2FAD\Delta C}{a} \sum_{n=1}^{\infty} \exp\left(-\frac{n^2\pi^2 Dt}{a^2}\right) \quad [5]$$

where i is the current density (A/g), A is the electrochemically active surface area (m²/g), D is the diffusion coefficient (m²/s), ΔC is the change in hydrogen concentration in the host manganese dioxide structure over the potential step ($= C_1 - C_0$; mol/m³), a is the particle radius (m) and t is the time (s). By combining constants in Eq. 5 two fitting parameters P_1 and P_2 can be produced; i.e.,

$$i = P_1 \sum_{n=1}^{\infty} \exp(-n^2 P_2 t) \quad [6]$$

where

$$P_1 = \frac{2FAD\Delta C}{a} \quad [7]$$

and

$$P_2 = \frac{\pi^2 D}{a^2} \quad [8]$$

P_1 and P_2 can then be determined using linear least squares regression by fitting a curve (or curves) defined by Eq. 6 to the experimental data.

An example of this fitting procedure carried out to the experimental data is shown inset in Figure 1, and the resulting parameter values for selected potentials are shown in Table I. As is evident in this figure, a good fit is obtained over the course of the experiment with the deviation in the modeled current response less than 0.02 A/g, with a percentage variation <4%, over the range examined. Importantly, we have chosen to model the electrode response with a single process, rather than including multiple processes as has been previously carried out.^{19,20} The use of multiple processes to model the electrode response arises from the attempt to characterize energetically different sites within the EMD electrode. However, by modeling the data using a single curve, fitting parameters can be obtained which represent a weighted average of electrode response during each potential step, while maintaining a good fit to the experimental data. Analyzing the

Figure 3. XRD patterns recorded for the series of partially reduced EMD materials, with the values assigned to each pattern reflecting the composition (as x in MnO_x).

experimental data in this way allows for a more direct comparison to be made between the SPECS data modeled here, and the EIS data to be analyzed in the following section.

In this way, the fitted parameters can then be combined with the change in proton concentration over the respective potential step to calculate a single, average value for $A\sqrt{D}$; i.e.,

$$A\sqrt{D} = \frac{\pi}{2F\Delta C} \sqrt{\frac{P_1^2}{P_2}} \quad [9]$$

However, to accurately determine how the solid state proton concentration changes during the reduction process, it was first necessary to characterize how the structure of the EMD material, in particular its unit cell volume, changes during proton insertion.

To examine these changes a series of partially reduced materials was prepared from the starting material and their structure determined via powder XRD. A comparison of the XRD patterns for these materials, including the assignment and shift of the key (110), (021), (121), (221, 240) and (002, 061) reflections is presented in Figure 3. As reduction proceeds, the overall trend is a peak shift toward lower 2θ angles, consistent with anisotropic expansion of the underlying lattice. As the depth of reduction exceeds MnO_{1.60}, the peaks in the region 30–45° 2θ were observed to lose intensity and being to separate, reflecting a loss of underlying symmetry beyond this point. Upon complete reduction, five distinct peaks were observed in this region, along with a broad (130) reflection shifted slightly to lower angles. The loss of order in the structure beyond this depth of discharge is particularly important for the cyclability of the material, with previous studies clearly illustrating that cycling which is carried out beyond this composition results in a steady decline in rechargeable capacity.²¹ Additional features which arise include an increased separation of the

Table II. Compositional and structural properties of partially reduced materials.

Composition			Structure				
x in MnO _x	%Mn(IV) _T	%Mn(III) _T	a ₀ (nm)	b ₀ (nm)	c ₀ (nm)	Volume (nm ³)	[H ⁺] (mol. m ⁻³)
1.970	52.6	5.8	0.445	0.963	0.281	0.121	3307
1.894	46.0	12.4	0.446	0.962	0.280	0.120	11705
1.859	41.9	16.5	0.450	0.965	0.281	0.122	15338
1.803	35.4	23.0	0.455	0.974	0.285	0.126	20713
1.753	29.6	28.9	0.456	0.979	0.285	0.127	25766
1.672	20.1	38.3	0.455	0.991	0.286	0.129	33741
1.651	17.6	40.8	0.456	0.991	0.288	0.130	35633
1.583	9.7	48.7	0.456	0.998	0.291	0.132	41907
1.554	6.3	52.1	0.457	0.998	0.292	0.133	44439
1.510	1.2	57.2	0.457	1.004	0.294	0.135	48320

(221) and (240) reflections, and a merging (and subsequent exchange of positions) for the (002) and (061) peaks. Orthorhombic unit cell parameters were subsequently determined from the positions of the (021), (200), (121), (140), (221), and (240) reflections, in accordance with the method outlined by Chabre and Pannetier.⁴ Using these parameters the proton concentration was determined for each material and is presented alongside unit cell parameters in Table II. The relationship between proton concentration and material composition (expressed as x in MnO_x) was then modeled with a quadratic equation, yielding the following expression describing the change in [H⁺] (mol/m³) with x in MnO_x:

$$[H^+] = -24114 x^2 - 13694 x + 123979 \quad [10]$$

By combining the compositional change during each potential step with Eq. 10, accurate values for the change in proton concentration (ΔC) were obtained. In this manner, values for $A\sqrt{D}$ during the first and second discharge half-cycles were obtained and the results are presented in Figure 4. It was observed that $A\sqrt{D}$ changed from $4.80 \times 10^{-10} \text{ m}^3 \cdot \text{s}^{-1/2} \cdot \text{g}^{-1}$ initially, up to a maximum of $7.45 \times 10^{-9} \text{ m}^3 \cdot \text{s}^{-1/2} \cdot \text{g}^{-1}$ when discharge began, and then decreased slowly to a minimum of $1.35 \times 10^{-9} \text{ m}^3 \cdot \text{s}^{-1/2} \cdot \text{g}^{-1}$. Given that only minimal changes in composition occur above 0.2 V, the values obtained in this region do not give an accurate representation of solid-state diffusion

($A\sqrt{D}$) and are included here only for the sake of completion. However, as the potential becomes increasingly cathodic and the current response increases, modeling of the electrode response becomes far more reliable and here the changes in $A\sqrt{D}$ fit with expectations. The decrease in $A\sqrt{D}$ as the level of reduction increases occurs as the $\gamma\text{-MnO}_2$ lattice undergoes expansion (see Figure 3), making the hop distance for proton diffusion larger thus slowing diffusion.¹⁴ It is interesting to note that a minimum in $A\sqrt{D}$ occurs at around -0.1 V, with calculated values relatively stable beyond this potential. During the second discharge half-cycle the behavior mirrors that of the first, suggesting that under these conditions the material has reverted to a structure very similar to that present initially. Despite the material showing a decrease in discharge capacity from 218 to 193 mAh/g, indicating the structural transitions occurring during cycling are not completely reversible,^{17,21} the stability in proton diffusion values is significant for the use of $\gamma\text{-MnO}_2$ in rechargeable applications.

EIS characterization and analysis.— A second series of experiments was carried out using electrochemical impedance spectroscopy, and an example of the resulting electrode response during discharge is shown in Figure 5. In contrast to the SPECS experiment, which characterizes how the material changes during each potential step, the EIS

Figure 4. Variation in $A\sqrt{D}$ values calculated from SPECS data during first and second discharge half-cycles.

Figure 5. Nyquist plots of EIS data at selected potentials during discharge of the EMD electrode. The inset shows the equivalent circuit model employed during the fitting process.

response characterizes the charge transfer and/or transport processes which occur in the electrode after equilibration at a set potential. The Nyquist plots for the EMD electrode all exhibit a single semicircular arc at high to mid-frequencies, followed by a low-frequency diffusion tail. Comparing these spectra it is evident that as discharge proceeds the width of the semicircular arc decreases, while the magnitude of diffusion tail is enhanced. To understand these changes in a more quantitative manner, it is first necessary to develop an appropriate model to interpret the data.

To quantitatively understand the results of an EIS experiment, an equivalent circuit approach is commonly employed. Here, this was carried out by taking into account the various paths charge may move through the electrode, including both charge buildup at the interface and the act of charge transfer, and an understanding of the reactions which occur within the electrode. To begin, the movement of charge to the surface of the active EMD needs to be considered. Primarily this occurs by charge transport through bulk electrolyte (R_e), in combination with a solid state contribution due to charge transport within the porous electrode (R_m). Overall, this process can be represented by a series resistance (R_s) and can be measured directly in the EIS response at the high frequency limit; i.e., at the x-intercept at the beginning of the semicircular arc. As this is the only path available for charge transport it was placed first in the equivalent circuit, in series with all the other circuit elements.

Once the ionic charge in the electrolyte reaches the EMD surface, one of two options become available. Firstly, charge transfer can take place, such that during the cathodic portion of the applied ac signal the homogenous reduction of EMD occurs. The details of this process have been described earlier, but it is important to note that for meaningful data to be obtained charge transfer needs to be reversible over the 10 mV potential window imposed by the ac signal. In the case of the EMD electrode employed, with its large excess of electrolyte and conductive graphite, this assumption is reasonable and allows the charge transfer process to be represented by a second resistor (designated R_{ct}) in the circuit model.

The alternative process, modeled in parallel with R_{ct} , is for ionic charge in the electrolyte to remain at the interface and contribute to the establishment of a double-layer capacitance. In the case of EMD, with its combination of variable surface composition, roughness and porosity, the formation of numerous intersecting double layers is expected. As a result, different regions of the EMD surface will have different intrinsic capacitances, resulting in a distribution rather than a single capacitance value. To account for this non-ideal capacitance, a constant phase element (Z_{CPE}) is commonly employed;^{22,23} i.e.,

$$Z_{CPE} = \sigma \omega^{-m} \left\{ \cos\left(\frac{m\pi}{2}\right) - j \sin\left(\frac{m\pi}{2}\right) \right\} \quad [11]$$

where σ is the CPE pre-factor (Ω), m the exponent, j an imaginary number, and ω the angular frequency (rad/s). Once protons and electrons have been inserted into the EMD structure, a diffusional aspect to their behavior must also be considered, with this becoming most evident at low frequencies. Specifically, during the impedance measurement a frequency is reached where the kinetics of mass transport are the limiting factor in the impedance response. As a means of accounting for this, a second constant phase element (CPE2) was employed in series with R_{ct} , giving rise to the equivalent circuit shown inset in Figure 5. The development of this equivalent circuit model accounts for the single semicircular arc, with a low-frequency diffusion tail, observed in the recorded data, and is consistent with our understanding of the electrochemical processes which occur within the electrode.

To obtain the optimized values for the equivalent circuit components compared to experimental data a complex non-linear least squares (CNLS) regression technique was employed. This method was proposed initially by Boukamp,^{24,25} and involves simultaneously fitting the real and imaginary components of the impedance, predicted

from the equivalent circuit, using the expression

$$S = \sum_i w_i [\{Z'_i - Z'_i(\omega)\}^2 + \{Z''_i - Z''_i(\omega)\}^2] \quad [12]$$

where S is indicative of the divergence between experimental and predicted data, $Z_i^* = Z'_i + jZ''_i$ is the measured data set, $Z_i^*(\omega) = Z'_i(\omega) + jZ''_i(\omega)$ is the predicted data set, and w_i is a weighting factor for each data point inversely proportional the square of the modulus of the measured data set; i.e.,

$$w_i = \frac{1}{|Z_i^*|^2} \quad [13]$$

The fitting procedure involved optimizing the equivalent circuit parameters such that S was minimized. In all cases the fitting between the model and experimental data was very good, meaning that S was always small, with an error associated with each of the parameters <5%.

Each of the fitted parameters could then be considered in terms of the changes which occur to the electrode during discharge and cycling. Firstly, a stable series resistance of $0.61 \pm 0.04 \Omega$ was observed experimentally across all potentials and this verified that any variation in equivalent circuit components could be confidently assigned to changes in the active material rather than any limitations in electrode construction. The next two circuit elements, R_{ct} and CPE1, reveal how charge behaves upon reaching the EMD surface, and hence reflect both changes in this process and the surface itself. The changes observed for these circuit elements are shown in Figure 6, wherein the double layer capacitance was calculated from CPE1 pre-factor σ and exponent m .¹⁸ The key features observed for the charge transfer resistance were: (i) the decrease in R_{ct} during discharge, correlating to the onset of the bulk reduction process; and (ii) the increase and peak in R_{ct} during the second charging half-cycle, indicating that oxidation results in an altered material when compared to that employed initially. In terms of the double layer capacitance, it was observed that the capacitance generally increases during the later stages of each half-cycle and is higher during the second charge and discharge half-cycles when compared to the first. The first feature can be attributed to kinetic limitations associated with the charge transfer process, with charge anticipated to buildup rather than enter/exit the structure in

Figure 6. Variation in the charge transfer resistance (R_{ct}) and double layer capacitance as a function of cycling. Half-cycles are denoted C1 and C2 for charging, and D1 and D2 for discharging.

the potential region after the bulk reduction/oxidation process has occurred. The second feature indicates that the nature of the EMD surface had been irreversibly altered by the redox process, resulting in a greater buildup of charge and suggesting a breakdown of constituent particles.

The final circuit element, CPE2, was employed to characterize the diffusional characteristics of the active material observed under low frequency conditions. By combining the impedance response in this region with the effective solid-state proton concentration at each potential (Eq. 10), values for $A\sqrt{D}$ were determined as follows:¹⁸

$$A\sqrt{D} = \frac{RT}{\sigma F^2 \sqrt{2} C} \quad [14]$$

where A is the electrochemically active surface area (m^2), D is the proton diffusion constant (m^2/s), R is the standard gas constant, T is the temperature, σ is the CPE2 pre-factor (Ω), F is Faradays constant, and C is the effective solid-state proton concentration (mol/m^3).

The change in $A\sqrt{D}$ values during the first and second discharge half-cycles is shown in Figures 7a and 7b, respectively. During primary discharge it was observed that $A\sqrt{D}$ was highest initially, decreased steadily down to -0.1 V, after which it dropped off sharply. In contrast, during the second discharge half-cycle $A\sqrt{D}$ was significantly lower initially, remaining relatively stable around $5 \times 10^{-9} \text{ m}^3 \cdot \text{s}^{-1/2} \cdot \text{g}^{-1}$, and then dropping off sharply after 0.0 V. Also shown in Figure 7 are the corresponding $A\sqrt{D}$ values determined via SPECS. Focusing on primary discharge it is apparent that both data sets show similar behavior from 0.3 V to -0.1 V, with proton diffusivity decreasing steadily as the structure expands during electron-proton insertion. However, beyond this potential the data sets diverge, with the EIS data suggesting that the material is undergoing significant changes in this region which result in poorer measured proton diffusivity. Given that this potential aligns with the mid-point in reduction (c.f. Figure 2), dissolution of Mn(III) from the host structure, along with subsequent disproportionation, can be expected to occur in this region.²⁶⁻²⁸ These processes result in the formation of a K-rich birnessite phase on the surface of the EMD and provide a likely reason for the marked decrease in $A\sqrt{D}$ in this region.²⁶⁻²⁸ During the second discharge half-cycle the divergence occurs right from the start, with the EIS data suggesting the presence of a poorer performing electrode material resulting from intervening redox processes. The relationships between the electrochemical technique employed, calculated proton diffusivity, and the redox reactions occurring within the electrode are considered in more detail in the following section.

Variation in $A\sqrt{D}$ and its relationship to material structure.—The two electrochemical methods employed to determine proton diffusivity vary significantly in the time constraints surrounding data collection and this has important implications for the calculated $A\sqrt{D}$ values. In the case of the SPECS experiment the applied potential is stepped 25 mV each hour, during which the current response peaks and then slowly decays as the electrode tends toward an equilibrium state. As a result of these experimental conditions, protons (and electrons) can diffuse throughout the bulk of active material and the calculated $A\sqrt{D}$ values reflect this movement. However, in the EIS experiment diffusion-limited conditions are observed as the frequency shifts toward its lower limit (0.1 Hz) and the corresponding time period (5 s for a cathodic/anodic wave) is much shorter. The shorter time period means that the EIS response is more sensitive to changes in the surface of the active material, whereas SPECS provides greater insight into changes in the bulk.

By combining the calculated $A\sqrt{D}$ values for each technique with the BET surface area and time period for each experiment, the penetration depth for protons at any stage during discharge can be estimated by adapting the Einstein-Smoluchowski equation,²⁹ i.e.,

$$D = \frac{\lambda^2}{2\tau} \quad [15]$$

Figure 7. Variation in $A\sqrt{D}$ values calculated from SPECS and EIS data during (a) first and (b) second discharge half-cycles.

where D is the diffusion coefficient (m^2/s), λ is the penetration depth (m), and τ is the time period (s) during which diffusion can occur.

Using this equation the penetration depth at a number of points during discharge was calculated and these values are reported in Table III. Importantly, these values rely on the use of the BET surface area as an approximation for the electrochemically active surface area, which, while being a reasonable assumption, likely overestimates the active surface area and hence underestimates the penetration depth. This arises because the BET surface area is determined by the adsorption of N_2 gas which varies significantly in terms of its properties (size, polarity, etc.) when compared to electroactive water in alkaline electrolytes. In spite of this, it is readily apparent from these values

Table III. Effect of depth of discharge on $A\sqrt{D}$ values and penetration depth during SPECS and EIS experiments.

x in MnO_x	BET S. A. ($\text{m}^2\cdot\text{g}^{-1}$)	SPECS			EIS		
		$A\sqrt{D}$ ($\text{m}^3\cdot\text{s}^{-1/2}\cdot\text{g}^{-1}$)	D ($\text{m}^2\cdot\text{s}^{-1}$)	λ (nm)	$A\sqrt{D}$ ($\text{m}^3\cdot\text{s}^{-1/2}\cdot\text{g}^{-1}$)	D ($\text{m}^2\cdot\text{s}^{-1}$)	λ (nm)
1.970	30.0	3.31×10^{-9}	1.01×10^{-20}	8.52	2.13×10^{-9}	4.18×10^{-21}	0.20
1.803	23.2	1.35×10^{-9}	3.40×10^{-21}	4.95	2.95×10^{-10}	1.62×10^{-22}	0.04
1.753	22.3	1.27×10^{-9}	3.24×10^{-21}	4.83	1.50×10^{-10}	4.55×10^{-23}	0.02
1.651	16.6	1.40×10^{-9}	7.12×10^{-21}	7.16	9.85×10^{-11}	3.52×10^{-23}	0.02
1.583	15.8	1.84×10^{-9}	1.36×10^{-20}	9.90	6.07×10^{-11}	1.48×10^{-23}	0.01

that the time period of the SPECS experiment allows protons to diffuse much further into the material at any stage during discharge. It is also clear that the EIS response is limited to changes in the surface layers of the material, allowing the significantly lower $A\sqrt{D}$ values determined using this technique to be confidently assigned to changes at the EMD surface.

As a means of relating the penetration depth to the underlying structure of EMD particles, high resolution transmission electron microscopy (HRTEM) investigations were carried out. In agreement with previous HRTEM studies in the literature,^{30,31} these revealed that the larger 45 μm particles were built up of smaller nanoporous grains with dimensions 100–200 nm, and these were in turn made up of smaller ellipsoidal crystallites with dimension ~ 10 –25 nm. These underlying crystallites, which agglomerate together to give the bulk EMD structure, can be observed readily in Figure 8. Importantly, if we compare the penetration depth for the SPECS experiment (5–10 nm) with the size of the crystallites (~ 10 –25 nm) it follows that spherical diffusion would result in the movement of protons through the entire crystallite. Given the porous nature of EMD particles, which allows electrolyte to penetrate into the depth of each particle, this would result in proton movement through most of the particle. In contrast, the EIS experiment is limited to surface layers (< 1 nm) and as such the calculated $A\sqrt{D}$ values are strongly influenced by changes in this region. Specifically, the surface changes brought about by dissolution-disproportionation reactions at the EMD surface^{26–28} provide an explanation for the large decrease in $A\sqrt{D}$ during discharge. Thus, the changing $A\sqrt{D}$ values shown in Figures 7a and 7b provide insight into both bulk and surface changes, resulting from the corresponding SPECS (bulk) and EIS (surface) experiments.

Conclusions

In this work two electrochemical techniques, SPECS and EIS, were used to characterize the behavior of the alkaline $\gamma\text{-MnO}_2$ electrode during discharge and cycling. In both cases this involved a consideration of the change in electrochemical behavior at each potential step, the development of an appropriate model to quantify these changes, and the calculation of proton diffusivity ($A\sqrt{D}$) values. For the SPECS experiment, the current response during each step was observed to vary considerably over the potential range examined and these changes were first quantified by integrating the current response to yield the charge passed during each potential step. The resulting variation in incremental capacity with applied potential revealed the thermodynamic peak potentials for each of the underlying redox reactions which occurred during the two charge/discharge cycles examined.

To characterize the change in proton diffusivity, a solid-state spherical diffusion model developed by Hong et al.¹¹ was outlined and then applied to the SPECS data. Importantly, here the fitting was carried out using a single process, as opposed multiple underlying processes,^{19,20} and this allowed the calculation of a single, average $A\sqrt{D}$ value at each potential step. During the first discharge half-cycle the $A\sqrt{D}$ values were observed to peak at $7.45 \times 10^{-9} \text{ m}^3\cdot\text{s}^{-1/2}\cdot\text{g}^{-1}$ and then decrease slowly to a minimum of $1.35 \times 10^{-9} \text{ m}^3\cdot\text{s}^{-1/2}\cdot\text{g}^{-1}$. The decrease in $A\sqrt{D}$ was noted to be consistent with the well characterized expansion of the $\gamma\text{-MnO}_2$ lattice upon reduction,^{4,10,11,14} increasing the hop distance protons must undergo to diffuse through the material. During the second discharge half-cycle the behavior mirrored that of the first, suggesting that despite reduction and re-oxidation the structure is similar to that employed initially.

Figure 8. HRTEM imaging of the EMD material employed in this study showing its underlying lattice structure.

For the EIS experiment, the electrode response was modeled using an equivalent circuit approach which accounts for the movement of charge in the electrode at high, mid and low frequencies. The change in the circuit parameters representing charge transfer (R_{ct}) and charge buildup (CPE1) revealed that the surface of the active material is irreversibly altered by charge/discharge cycling. This was particularly evident during the second charging half-cycle; where higher charge transfer and capacitance values indicate that movement of charge into (and/or out of) the material is inhibited. Proton diffusion ($A\sqrt{D}$) values were then determined from the EIS response and shown to vary significantly when compared to those determined via SPECS. While a similar decreasing trend was observed until -0.1 V, beyond this point the values diverged significantly. In the case of the EIS values, a sharp decrease in $A\sqrt{D}$ occurred as the applied potential decreased and this was assigned to dissolution and the subsequent formation of a K^+ -rich birnessite phase on the γ - MnO_2 surface.

By adapting the Einstein-Smoluchowski equation, the penetration depth for protons in each technique was then estimated at selected points during discharge. By comparing these values with the nanostructure of the material, imaged via HRTEM, it was shown that $A\sqrt{D}$ values determined via SPECS represent the movement of protons through the bulk of the material, whereas EIS values focus on diffusion localized at the surface (penetrating <1 nm into the material). Each set of values thus provides keys insight into different aspects of the material; with the former suggestive of stability in the bulk of the material and the latter indicative of degradation of the surface through dissolution and undesirable surface layer formation.

Acknowledgments

The authors acknowledge the contributions made by Dr. Sing Wei Wong from the University of Newcastle Electron Microscopy and X-Ray Facility. MRB acknowledges the University of Newcastle for the provision of a PhD scholarship.

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