Study on Manganese Dioxide Discharge Using Electrochemical Impedance Spectroscopy

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Electrochemical impedance spectroscopy (EIS) has been used to examine the electrochemical and morphological (porosity) changes that the alkaline manganese dioxide cathode undergoes during reduction. Most significantly, within the EIS data a previously unreported intermediate-frequency (2–50 Hz) inductance loop was observed. This inductance loop, as well as the high (>50 Hz) and low (<2 Hz) frequency EIS data, was able to be interpreted in terms of changes in both the manganese dioxide and electrode porosity, as well as mechanical degradation of the manganese dioxide itself. The key finding was that for compositions more reduced than $\gamma\text{-MnO}_{1.80}$, structural expansion has caused mechanical degradation of individual particles, as well as caused porosity changes within individual manganese dioxide particles and the electrode itself, essentially making them unavailable for discharge (proton insertion). A further implication of this is that the performance of the alkaline manganese dioxide cathode is then predominantly dependent on the geometric surface area and the bulk $\gamma\text{-MnO}_2$ structure.
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Manganese dioxide is the most widely used positive electrode material in battery systems. This popularity can be attributed to a number of material properties, such as an abundance of the raw materials necessary for production, low production costs, low toxicity, and excellent discharge performance under low and moderate discharge rates (i.e., $<50 \text{ mA g}^{-1}$).¹ Because of this widespread usage, manganese dioxide has been studied extensively for many years in both academic and industrial laboratories. Despite this, many fundamental physical and electrochemical properties of the material are not fully understood.

The origin of this lack of understanding lies in the structural complexity of the various manganese dioxide phases that have been identified. Over 30 phases have been identified, each primarily distinguishable in terms of Mn^{4+} ion placement within the octahedral sites of a hexagonal close-packed array of oxide anions.^{2–4} Additional complexity arises as a result of the presence of lower valent manganese ions, cation vacancies, structural water, and various foreign metal ions.^{2–4} The two most fundamental structures are pyrolusite ($\beta\text{-MnO}_2$) and ramsdellite. Pyrolusite can be described as alternating occupied and vacant octahedral sites in the *ab* plane, leading to the formation of $[1 \times 1]$ tunnels in the *c* direction. The result is a tetragonal structure with $a_0 = 4.398 \text{ Å}$ and $c_0 = 2.873 \text{ Å}$.^{2–4} The structure of ramsdellite is similar, except that in the *a* direction there are alternating doubly occupied and unoccupied octahedral sites. Again, tunnels are present in the *c* direction, except now they are $[2 \times 1]$ octahedra in size. Ramsdellite has an orthorhombic unit cell with $a_0 = 4.533 \text{ Å}$, $b_0 = 9.27 \text{ Å}$, and $c_0 = 2.866 \text{ Å}$.^{2–4} Many other materials with larger tunnel sizes have been characterized, e.g., $\alpha\text{-MnO}_2$ with $[2 \times 2]$ tunnels. These structures are somewhat idealized, and in reality it is more common to encounter microscopic intergrowths between these basic structures. The manganese dioxide phase that has been most studied in this regard is $\gamma\text{-MnO}_2$ because it is the preferred phase for electrochemical applications. The structure of $\gamma\text{-MnO}_2$ is believed to be based on an intergrowth between the pyrolusite and ramsdellite forms of manganese dioxide.⁵ In addition, other structural features such as cation vacancies, Mn^{3+} ions, structural water,^{6–8} and microtwinning⁹ have all been associated with this material.

The basis for the discharge mechanism for $\gamma\text{-MnO}_2$ in aqueous alkaline electrolytes was proposed by Kozawa and co-workers as consisting of two stages.^{10–15} The first is a homogeneous reduction process spanning the compositional range MnO_2 to MnOOH , while the second is a heterogeneous process between MnOOH and $\text{Mn}(\text{OH})_2$. This heterogeneous process occurs at low voltages, is

very inefficient, and so contributes little to the electrode discharge. Consequently, our main focus is on homogeneous discharge, which involves electron (from the external circuit) and proton (from water dissociation at the manganese dioxide-electrolyte interface) insertion into the structure, i.e.)

where $0 \leq (r + \Delta) \leq 1$ and $r \approx 0.1$ in an unreduced material. This is the main power generation reaction in an alkaline Zn/ MnO_2 cell. The complexity of this reaction was evident in the work of Chabre and Pannetier,⁹ Swinkels et al.,¹⁶ Donne et al.,^{17–19} Hong et al.,²⁰ and Bowden et al.,²¹ each of which has identified multiple steps during homogeneous reduction. For each of these research efforts the origin of these steps was traced back to the structure of the $\gamma\text{-MnO}_2$. For instance, the higher voltage processes were associated with the reduction of Mn^{4+} ions either in regions near to defects (e.g., cation vacancies) or on the surface. The next step was almost universally assigned to the reduction of Mn^{4+} ions in ramsdellite domains, while the lower voltage step was due to the reduction of Mn^{4+} ions in pyrolusite domains. It is clear from these proposals that the structure of $\gamma\text{-MnO}_2$ has a significant impact on the electrochemical behavior. Nevertheless, while this link between structure and electrochemical discharge does seem logical, it is yet to be confirmed.

The $\gamma\text{-MnO}_2$ used in commercial battery systems is a synthetic form, made typically using electrodeposition (EMD). The EMD grade material is manufactured by anodic electrolysis of aqueous $\text{MnSO}_4/\text{H}_2\text{SO}_4$ solutions and is the preferred type of manganese dioxide for alkaline batteries.²² The structure of EMD has a profound effect on its morphology, and hence on its electrochemical performance. From transmission electron microscopy (TEM) analysis, EMD has been shown to consist of a random agglomeration of roughly spherical grains $\sim 200 \text{ nm}$ in diameter, each of which is composed of crystallites $\sim 10 \text{ nm}$ wide and $50\text{--}200 \text{ nm}$ in length.²³ This collection of crystallites and grains results in a relatively large quantity of voids, creating a high level of accessible porosity within the material. The porosity which exists within particles (described as intraparticle porosity, as separate from interparticle porosity which is the void between particles) can be divided into three categories: macropores greater than 500 Å , mesopores within the range $20\text{--}500 \text{ Å}$, and micropores less than 20 Å . This porosity leads to a typical commercial EMD having a surface area of $20\text{--}50 \text{ m}^2 \text{ g}^{-1}$, although it can lie outside of this range depending on the electrolysis conditions used.

This paper characterizes the porosity of a manganese dioxide sample over the complete reduction range using electrochemical impedance spectroscopy (EIS). The intent is to develop a model for interpreting EIS data in terms of manganese dioxide electrode porosity and then evaluate how this porosity changes during discharge.

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Figure 1. Schematic of the cell used for electrochemical experimentation.

Experimental

Electrode material.—The EMD starting material was supplied by Delta EMD Australia, Pty, Ltd. It was prepared by the anodic electrolysis of a hot (90–98°C) acidic (H_2SO_4) aqueous solution of MnSO_4 (acid to Mn molar ratio of ~ 0.4). This resulted in deposition of the EMD onto titanium anodes, which after sufficient deposit had accrued, was mechanically removed and milled into a fine powder ($\sim 105 \mu\text{m}$). The EMD was neutralized washed to remove any remaining electrolyte, and dried before being ready for use.

The electrode was prepared by thoroughly mixing the EMD with graphite (Timrex SFG6) in a 1:10 ratio. The resulting mixture was then combined with the electrolyte solution (37% KOH) using a mortar and pestle to form a moist paste. The mixture was left to equilibrate in an airtight container overnight before it was loaded into the electrochemical cell.

Electrode preparation and the electrochemical cell.—A schematic of the electrochemical cell employed in this study is displayed in Fig. 1. Cell assembly involved placing an appropriate amount of sample mixture corresponding to 0.020 g of EMD into a Teflon-lined, Au-coated C-size battery can. After the inside of the sleeve was brushed to remove any attached particles, the mixture was covered with three separator papers and pressed under 1 ton using a stainless steel piston. A perforated Perspex separator disk was placed on top of the electrode and a cylindrical stainless steel counter electrode slid on top of the disk. The chamber of the cell was filled with $\sim 15 \text{ mL}$ of electrolyte solution. The cell was mounted on top of a brass current collector between two Perspex plates and then secured by three bolts tightened to a torque of 0.75 c Nm, ensuring uniform pressure. A Hg/HgO reference electrode was inserted into the top of the cell. The constructed cell was left to equilibrate for 6 h before electrochemical testing was performed.

Discharge regime.—EIS measurements were performed using a Princeton Applied Research 273A potentiostat/galvanostat coupled with a Solartron 1253 gain-phase analyzer controlled by ZPlot software. Starting at the open-circuit voltage of the cell an EIS spectrum was recorded. The EMD electrode voltage was then stepped cathodically 10 mV and allowed to equilibrate for 2 h, during which time the current flowing was recorded. Integration of the current with time allows determination of the charge passed during discharge, and hence, the composition (average oxidation state) of the EMD. After this time another EIS spectrum was recorded. Equilibration for 2 h was deemed sufficient because after this time the current flowing matched that of the background (negligible). This process was

repeated until the EMD electrode voltage was below -0.4 V . For the EIS experiments a 5 mV root-mean-square signal was used between the frequency limits of 0.1 Hz and 20 kHz.

Results and Discussion

EIS data.—Typical EIS data recorded at different depths of EMD discharge are shown in Fig. 2. First, Fig. 2a shows the EIS spectrum (Nyquist plot) of the initial unreduced EMD electrode. At high frequencies the EIS data shows the expected semicircular arc due to the parallel arrangement of a charge-transfer resistance and a double-layer capacitance. Similarly, at low frequencies the observed EIS results were expected, i.e., a somewhat linear response reflecting diffusional processes within the electrode. However, what is of particular significance is the presence of an inductance loop at intermediate frequencies. This result has not been observed before in previous EIS studies on battery materials. In the previous works, if inductance was present it was only observed at high frequencies, in which case its presence was most likely due to the use of unshielded cables and not the electrode itself. To demonstrate the reproducibility and origin of this inductance loop, separate cells with the same working electrode composition were subjected to the same discharge and EIS protocol with no apparent change in EIS response. Similarly, separate cells with no working electrode present (i.e., just the current collector) or just the graphite component of the cathode were also examined with no evidence of any inductance, suggesting that the EMD was the source.

Another significant feature of the observed inductance loop is that it apparently disappears as the electrode is reduced, as indicated by the remaining Nyquist plots in Fig. 2. Clearly this inductance loop is related to a physical process within the electrode that changes as discharge proceeds. To assist with the interpretation of the EIS data, three frequency ranges were identified, as shown in Fig. 2a. These include (i) a high-frequency range (A–B) from 20 kHz to $\sim 20 \text{ Hz}$, (ii) an intermediate-frequency range (B–C) from ~ 20 to $\sim 2 \text{ Hz}$ that encompasses the inductance loop, and (iii) a low-frequency range (C–D) from ~ 2 down to 0.1 Hz. An equivalent circuit was devised to model each section, after an understanding of the physical processes associated with the electrode and the individual electrochemical processes was established. Fitting of an appropriate equivalent circuit to the experimental was achieved using complex nonlinear least-squares regression, as defined by Boukamp.²⁴

High frequency (A–B) EIS data.—Within this frequency range we have interpreted the EIS data in terms of the equivalent circuit shown in Fig. 3a, which is a modified Randles circuit for the interface.²⁵ Here R_s represents the uncompensated solution resistance from the reference electrode to the current collector for the EMD electrode. In the parallel branches of the circuit, R_{CT} represents the resistance to charge transfer at the EMD–electrolyte interface and provides us with an indication of the kinetics of charge transfer. In another branch of the circuit we have used a constant phase element (CPE) to account for nonfaradaic charging of the double layer at the EMD–electrolyte interface. The impedance of a CPE (Z_{CPE}) can be described by

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

where σ is the CPE prefactor, m is the exponent, ω is the angular frequency (rad s^{-1}), and j is the imaginary number. Note that if $m = 1$ in Eq. 2, then the impedance becomes that of an ideal capacitor (Z_C), i.e.

$$Z_C = -\frac{j\sigma}{\omega} \Rightarrow \sigma = \frac{1}{C} \quad [3]$$

We have used a CPE to describe the interfacial capacitance so as to take into account contributions from surface roughness and its subsequent effect on intersecting double layers. In terms of the EIS

Figure 2. Typical EIS data at various depths of EMD discharge.

data, inclusion of the CPE compensates for the depressed arc at high frequencies that would otherwise be semicircular if an ideal capacitor was used. In the final branch of the equivalent circuit we have included another capacitor (C_C) to represent the contribution from double-layer buildup at the graphite-electrolyte interface. The electrode used in this study was composed of a substantial proportion of graphite, the surface of which needs to be accounted for in the EIS analysis. As part of our efforts to identify the source of inductance, an electrode containing only graphite was examined. The corresponding EIS results indicate that not only was the graphite not the source of inductance, but the nonfaradaic capacitive contribution to the overall impedance is insignificant compared to what is occurring at the EMD-electrolyte interface. Hence, this branch of the high-frequency equivalent circuit has been ignored.

Figure 4 shows the individual fitted parameters as a function of x in MnO_x , which was determined by numerical integration of the current density-time data resulting from the step potential portion of the experiment. The uncompensated resistance (R_s) in Fig. 4a shows a slight downward trend with x in MnO_x , although it does not amount to a substantial change. A relatively constant R_s value was to be expected given the relatively large proportion of conductor (graphite) within the electrode, and the excessive amount of electrolyte in the cell, which when combined ensures little change in composition, and hence resistivity, occurs due to reduction.

As described in the Introduction, discharge of the $\gamma\text{-MnO}_2$ electrode involves concerted proton (from H_2O decomposition at the solid-electrolyte interface) and electron (from the external

Figure 3. Equivalent circuits used model the frequency ranges of (a) A–B, (b) B–C, and (c) C–D; (d) an example of the goodness of fit using the circuits in (a) and (c).

circuit via the conductor within the cathode) insertion into the host γ - MnO_2 structure. The charge-transfer resistance (R_{CT}) reflects the facility of this process. Figure 4b shows that there is significant variation in R_{CT} as the EMD electrode is reduced, going from $\sim 0.38 \Omega$ in the starting material to at most $\sim 0.99 \Omega$ at a composition of $\text{MnO}_{1.779}$. This variation reflects the equilibrium composition of the EMD surface and the ease with which charge can pass through this interface. Numerous previous works on the electrochemical discharge of γ - MnO_2 , employing such techniques as step potential electrochemical spectroscopy (SPECS), voltammetry, etc., have demonstrated the existence of distinctly separate reduction processes within the overall homogeneous reduction range.^{16–21} There is agreement that these processes represent the reduction of different

domains within the γ - MnO_2 structure, e.g., ramsdellite, pyrolusite, etc., although there still exists some debate as to which structural domain corresponds to which electrochemical process. Figure 5 shows the low-rate (0.02 mV s^{-1}) voltammetric discharge of the EMD used in this study, and as expected, it shows the homogeneous reduction of various structural domains. Because this is solely an electrochemical study, we cannot add to the debate as to the origin of the various homogeneous reduction processes, but what we can comment on is their facility to charge insertion.

Clearly, at the start of discharge, for compositions less reduced than $\sim \text{MnO}_{1.87}$, R_{CT} is relatively low, i.e., 0.38 – 0.49Ω . In this compositional range, which previous authors have referred to as the reduction of higher energy surface sites and/or defect regions, charge transfer is easy because these domains are readily accessible and unencumbered by the presence of already occupied sites, i.e., Mn^{3+} and hydroxyl groups. It is important to remember at this stage that the EIS measurements were conducted on an electrode at equilibrium, i.e., at each composition the appropriate structural domains are uniformly occupied throughout each particle. At $\sim \text{MnO}_{1.87}$ R_{CT} increases dramatically from ~ 0.49 to $\sim 0.99 \Omega$. According to our insertion model, this is most likely due to complete occupancy of the higher energy, accessible structural sites forcing charge transfer to occur through another slightly lower energy domain. It also implies that if the first γ - MnO_2 reduction process is indeed associated with the reduction of higher energy surface sites and defects, then quite possibly these are already occupied at this degree of reduction, meaning that there may be very few locations on the solid surface through which proton and electron insertion may occur. If this is the case then it is highly likely that R_{CT} will increase dramatically at this composition. For compositions more reduced than $\sim \text{MnO}_{1.77}$, R_{CT} does drop slightly, although it does remain elevated at $\sim 0.91 \Omega$. The fact that R_{CT} remains high suggests that for the remainder of homogeneous reduction, charge transfer occurs through the same surface sites, which when the EIS spectra are recorded, remain unsaturated at equilibrium.

In terms of the capacitive branch of the modified Randles circuit shown in Fig. 3a (CPE), the value of σ drops quite dramatically as discharge proceeds, as shown in Fig. 4c. Perhaps more relevant to this discussion is $1/\sigma$ (also shown in Fig. 4c; cf. Eq. 3), because in this form we have a first approximation of the EMD–electrolyte double-layer capacitance, albeit not a direct link because there is a dependence on the exponent m . The first possible explanation for the observed behavior is that the intrinsic nature of the EMD surface is changing so as to increase its ability to store surface charge. This possibility is consistent with the R_{CT} data discussed previously, in the sense that if charge transfer at the solid–electrolyte interface was becoming more difficult, then it is logical to expect that the capacitance should increase. Another likely cause of the decreasing σ values (increasing $1/\sigma$) is that the available interface between the EMD and electrolyte is increasing. If this is the case, then there has been a increase in the surface area over a narrow composition range, with $1/\sigma$ increasing from 0.001 to $0.07 \Omega^{-1} (\text{rad s}^{-1})^m$ by $\sim \text{MnO}_{1.80}$, i.e., increasing by almost 2 orders of magnitude. At more reduced compositions $1/\sigma$ remains essentially constant. If we presume that the intrinsic interfacial capacitance per unit area does not change with depth of discharge, then changes in $1/\sigma$ can potentially be used to predict the relative EMD surface area during discharge. Given that the surface area of the EMD used in this work was $52.4 \text{ m}^2 \text{ g}^{-1}$ [N_2 adsorption at 77 K and using the Brunauer, Emmett, and Teller method (BET) isotherm], we can therefore predict that by a composition of $\text{MnO}_{1.80}$ the surface area has apparently increased substantially (possibly 2 orders of magnitude if a direct correlation is assumed). While this prediction may seem extreme, certainly the predicted trend in surface area changes is explainable. Let us consider the nature of γ - MnO_2 structural changes that occur upon reduction. With proton and electron insertion into the structure and the subsequent formation of OH^- and Mn^{3+} , the structure swells because both these species are larger than their respective parent ions.

Figure 4. Fitted EIS parameters arising from the modified Randles circuit.

In actuality, using the unit cell parameters for ramsdellite and its reduced structural analogue groutite (α - MnOOH),²⁻⁴ we can predict that the unit cell will swell by $\sim 18\%$. This swelling of the structure could very well lead to mechanical degradation of individual particles, hence exposing a greater surface area to the electrolyte. The fact that the apparent maximum surface area, or minimum σ value, is reached at a composition of $\sim \text{MnO}_{1.80}$ does indicate that only a fraction of this structural expansion is necessary to cause degradation. Competing with mechanical degradation is the possibility that structural expansion will cause pores within the particles to close. The extent of closure will depend on pore size, particularly if the pores are small. While this proposal is contrary to the observed data, we expect that both mechanisms will be occurring in tandem, hence mediating the overall change in electrochemically active surface area.

Figure 4d shows the change in the CPE exponent (m) as a function of depth of discharge. While an empirical value, m can still provide us with information on the solid-electrolyte interface. For instance, when $m = 1$ the CPE behaves like an ideal capacitor, and

so deviations from this value indicate nonideal behavior such as nonparallel or intersecting charge planes due to surface roughness. In Fig. 4d, m quite closely mimics the behavior of σ , as shown in Fig. 4c; however, there is some lag apparent in the m data set. The initial rapid drop in m from ~ 0.84 to ~ 0.64 at $\text{MnO}_{1.80}$ indicates that there has been a considerable deviation from ideal capacitor behavior. Beyond this composition the value of m remains essentially constant. This data trend can be interpreted in terms of the mechanical breakdown of particles and the shrinking pore model described above. In the unreduced EMD the majority of the solid-electrolyte interface is associated with pores. Therefore, running down a pore we have opposing layers of charge building up on either side of the pore. More ideal capacitive behavior would be encountered if the pores were straight and slit-shaped, because in these instances the extent of charge plane intersection would be minimal. With a starting m value of ~ 0.84 , this description of the EMD surface would seem reasonable. As reduction proceeds the EMD structure swells and, as we have discussed above, causes mechanical breakdown and possibly pore closure. The solid-electrolyte

Figure 5. (a) Low-rate (0.02 mV s^{-1}) voltammetric discharge of the EMD used in this study, 1:10 EMD:SFG6 graphite; 37% KOH electrolyte; and (b) the corresponding compositional data.

interface is now mainly concerned with the geometric size and shape of the macroscopic EMD particles, which given the rough surface morphology of the particles, would mean that there would be a relatively large number of intersecting charge planes. Hence, as the solid-electrolyte interface becomes more dependent on the geometric surface area, the value of m drops as shown in Fig. 4d. At compositions more reduced than $\text{MnO}_{1.80}$, m is relatively constant, meaning that mechanical breakdown is essentially complete, leaving the geometric surface area for either charge transfer or double-layer charge buildup.

Intermediate frequency (B-C) EIS data.— Within this intermediate frequency range our focus has been on the inductance loop, its origin, and its subsequent disappearance as reduction proceeds. Evidence of induction in EIS typically occurs at high frequencies where the use of unshielded cables introduces the effects of stray electric fields generated in the laboratory. However, at intermediate frequencies there must be some more localized source of electric field causing inductance to be observed, which in itself disappears during the course of an experiment. Based on our preceding discussion concerning changes in EMD porosity with depth of discharge, we have attempted to explain this inductance behavior in terms of changing electrode porosity.

Consider an unreduced electrode in which the EMD has a full complement of pores. For an electrode such as this at rest, electrolyte has penetrated all the pores, filling them completely, as shown

Figure 6. Schematic representation of depletion layers in EMD pores.

in Fig. 6a. Now at high frequencies above 20 Hz, electrode behavior can be described by the modified Randles circuit, as shown in Fig. 3a and discussed above. Under these conditions charge transfer and double-layer formation are very localized at the solid-electrolyte interface due to the high frequency used, i.e., depletion of the electrolyte (H_2O consumption) during the cathodic portion of the applied sinusoidal signal does not penetrate substantially into the electrolyte (Fig. 6b). Clearly, as the frequency decreases, electrolyte depletion progresses further from the interface. As the frequency drops, a point is reached where the electrolyte depletion layer on opposite sides of pores collides (Fig. 6c). When this occurs the electrolyte within the pore has a need for lateral mass transport, i.e., along the axis of the pore, rather than perpendicular mass transport, because the bulk electrolyte now resides outside the pore instead of at the center of the pore. When this happens during the cathodic part of the sinusoidal signal, OH^- ions have to diffuse out of the pore and H_2O has to diffuse in to allow for the pore surfaces to continue to play a part in the electrochemical reaction. It is this lateral movement of the OH^- ions along the pore axis that we believe causes an induction loop to be observed. In effect, the scenario we have here is similar to passing a current through a wire and observing the induced field that is generated. Instead of electrons passing through a wire, we have the similar situation of OH^- ions diffusing along a pore. As a result of this ion movement, proton and electron movement is most likely induced in the solid surrounding the pore, thus giving rise to the induction loop. As the frequency continues to drop, the importance of lateral $\text{OH}^-/\text{H}_2\text{O}$ movement becomes greater, up until the point where the porosity is not large enough to support the increasing amount of charge transfer. Under these conditions the pore essentially becomes saturated with OH^- , effectively eliminating it from participating in charge transfer (Fig. 6d). Here, lateral OH^- ion movement is either no longer possible due to saturation, or is at least very slow, which would cause induction to cease. Any current flowing in the electrode at lower frequencies then becomes dependent on mass transport in the bulk of the electrolyte, i.e., outside of the pore, to the geometric solid-electrolyte interface. The implication of this model is that under the dc conditions that a commercial cathode is subjected to, the majority of charge transfer occurs through the geometric solid-electrolyte interface, simply because mass transport into or out of pores in the EMD is not possible under these conditions.

As the electrode is reduced using the SPECS protocol, Fig. 2 clearly shows that the inductance loop vanishes. According to our model, disappearance of the inductance loop must be due to the closing of pores in the electrode, which, as we have discussed previously, is possibly due to structural expansion. Another important

consequence of this is it again reinforces the idea that porosity plays little part in EMD reduction. If it were not for the pores being made unavailable by OH^- saturation, then certainly it would be the case as a result of either mechanical particle breakdown or pore closure due to structural swelling.

We are now in a position to be able to attempt an estimate of the EMD electrode porosity by considering the frequency range over which the inductance loop was observed. Using the cell impedance at a particular frequency (when inductance was present), and from that the impedance modulus ($|Z|$) and phase angle (ϕ), the ac current flowing was determined. For the cathodic half of the sinusoidal wave an average current was determined. The average current was used for the sake of simplicity; first, solving Fick's second law (Eq. 4) under ac current conditions (using appropriate boundary conditions) is not possible because there is no net polarization of the electrode, and hence, no net change in concentration profile with time. Second, using an average current, while of course not strictly correct for the cathodic portion of the sinusoidal wave, does simplify the analysis immensely because a constant current can be used. Therefore, solving Fick's second law in one dimension

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} \quad [4]$$

using the initial and semi-infinite boundary conditions for planar diffusion

$$t = 0 \quad \text{all } x \quad C(x,0) = C_0 \quad [5]$$

$$t > 0 \quad x = 0 \quad \frac{\partial C(0,t)}{\partial x} = \frac{I}{nFAD} \quad [6]$$

$$t > 0 \quad x = 0 \quad \lim_{x \rightarrow \infty} C(x,t) = C_0 \quad [7]$$

where $C(x,t)$ is the electrolyte concentration (mol m^{-3}) at any location perpendicular to the solid surface (x) and time (t), C_0 is the initial concentration (mol m^{-3}), I is the current (A), and the other symbols have their usual significance. Under these conditions the solution of Eq. 4 is

$$C(x,t) = C_0 - \frac{I}{nFAD} \left\{ 2 \left(\frac{Dt}{\pi} \right)^{1/2} \exp\left(-\frac{x^2}{4Dt}\right) - \text{xerfc}\left(\frac{x}{2(Dt)^{1/2}}\right) \right\} \quad [8]$$

Typical values for the included parameters include $C_0 = 9000 \text{ mol m}^{-3}$ (37% KOH), $A = 1.05 \text{ m}^2$ as determined from the BET surface area ($52.4 \text{ m}^2 \text{ g}^{-1}$) and the mass of active EMD used in the electrode, and $D = 5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, which is a typical diffusion coefficient for OH^- ions in aqueous solutions.²⁶ Now, as an example, consider the impedance of the unreduced electrode at 50.2 Hz where the duration of half a cycle is $9.96 \times 10^{-3} \text{ s}$ (t), and from the impedance the mean current flowing is $2.91 \times 10^{-3} \text{ A}$ (I). Under these conditions, the change in OH^- concentration moving away from the EMD surface is as shown in Fig. 7. What is immediately apparent is that the predicted rise in OH^- concentration is very small relative to C_0 . Given the duration over which the cathodic portion of the sinusoidal wave is applied, the mean current that is flowing, as well as the large electrolyte concentration, this relatively small increase appears reasonable. However, the predicted rise in OH^- concentration is essentially constant out to $\sim 100 \text{ nm}$ from the surface. According to most EMD porosity distribution data (most often from gas adsorption), this is considerably larger than the biggest EMD pores,²⁷ which in itself suggests that either there is a uniform rise in OH^- concentration across the breadth of the pore (not physically reasonable) that it is not specifically the EMD porosity itself we are examining here, or that the model may be incompatible with the system being considered. With regard to the latter point, the model described in Eq. 8 is typically used to explain diffusional behavior after longer times, using more dilute solutions,

Figure 7. OH^- concentration profile away from the EMD surface.

and at distances considerably larger than molecular dimensions away from the electrode surface. Therefore, it is possible that the model data may not be correct for small distances and times. However, at more reasonable distances away from the electrode surface (micrometer scale) and longer times we should expect to be able to reliably predict behavior.

Let us consider the possibility that the inductance loop is due to lateral mass transport in electrode pores rather than EMD pores. Our model concerning porosity changes is still valid because not only may the EMD structure swell to close internal pores, but it may also swell to close off pores between particles within the electrode as a whole. Therefore, from the data in Fig. 7, for a particular frequency, we are looking for the furthest point away from the electrode where there is an appreciable increase in OH^- concentration, and for our purposes we have specified that as a change greater than $1 \mu\text{mol m}^{-3}$. This corresponds to the pore radius or half the pore diameter. Table I shows the range of pore radii determined in such a way using Eq. 8 for all electrode compositions and frequencies that were affected by inductance. The predicted pore radius ranges from ~ 10 to $\sim 189 \mu\text{m}$, and as reduction proceeds it is these pores within the electrode that are being closed down.

Low frequency (C-D) EIS data.—In many studies that utilize equivalent circuit modeling of EIS data, a Warburg impedance is often used to characterize either finite or semi-infinite planar diffusion within the system. However, this process is not applicable in this instance because of surface roughness and any residual porosity remaining in the manganese dioxide electrode at the relevant low frequencies. As in many previous studies,²⁸⁻³⁰ we have again used a CPE, the mathematical expression for which is shown in Eq. 2, to model the low-frequency EIS data of our electrode, and hence compensate for nonideal behavior. Note that if $m = 0.5$ in Eq. 2, then the impedance of the CPE becomes identical to that of a Warburg element, i.e.

$$Z_W = \frac{\sigma}{\sqrt{2\omega}}(1 - j) \quad [9]$$

A number of other approaches, mainly based on distributed circuit elements, have also been used to model low-frequency EIS data for porous electrode systems.³¹⁻³⁷ Application of these models to our

Table I. Pore radii (μm) as a function of electrode voltage (composition) at frequencies affected by inductance.

Frequency/Hz	Electrode voltage/V vs Hg/HgO (x in MnO_x)									
	0.13 (1.960)	0.12 (1.957)	0.11 (1.952)	0.10 (1.946)	0.09 (1.940)	0.08 (1.934)	0.07 (1.927)	0.06 (1.920)	0.05 (1.912)	0.04 (1.903)
200	9.8	9.8	9.8	9.8	9.8	9.7	9.7	9.7	9.6	9.7
158.9	14.1	14.3	14.3	14.3	14.1	13.9	13.8	13.7	13.7	13.8
126.2	16.8	16.9	16.9	16.8	16.8	16.7	16.6	16.5	16.5	16.6
100.2	18.2	18.2	18.2	18.2	18.2	18.1	18.1	18.0	18.0	18.0
79.6	19.1	19.1	19.1	19.1	19.1	19.0	19.0	19.0	19.0	19.0
63.2	19.8	19.8	19.8	19.8	19.8	19.7	19.7	19.7	19.7	19.7
50.2	24.2	24.4	24.4	24.4	24.2	24.0	23.8	23.8	23.7	23.8
39.91	27.6	27.6	27.6	27.6	27.5	27.4	27.3	27.3	27.3	27.3
31.7	29.4	29.5	29.5	29.5	29.4	29.4	29.3	29.3	29.3	29.3
25.18	34.6	34.7	34.7	34.7	34.5	34.3	34.1	34.0	33.9	34.0
20.0	38.6	38.6	38.6	38.6	38.5	38.4	38.3	38.3	38.2	38.3
15.89	44.0	44.1	44.1	44.1	43.9	43.6	43.3	43.2	43.1	43.2
12.62	49.2	49.2	49.2	49.2	49.1	48.9	48.8	48.7	48.7	48.7
10.02	56.7	56.7	56.7	56.7	56.5	56.2	56.1	55.9	55.8	55.9
7.96	64.2	64.2	64.2	64.2	63.9	63.5	63.2	63.0	62.8	62.9
6.32	72.4	72.5	72.5	72.5	72.2	71.6	71.2	71.0	70.8	70.9
5.02	82.2	82.3	82.3	82.3	82.0	81.3	80.9	80.6	80.4	80.5
3.991	93.5	93.8	93.7	93.7	93.4	92.8	92.3	92.1	91.8	92.0
3.17	135.0	136.3	136.0	136.1	134.3	131.4	128.8	127.6	126.6	127.0
2.518	174.4	175.0	175.0	174.9	174.1	173.1	172.1	171.5	171.2	171.4
2.0	188.5	188.7	188.7	188.7	188.4	187.9	187.5	187.3	187.0	187.1

EIS data is, however, beyond the scope of the current work, but will be the subject of a future communication.

Figure 8 summarizes the fitted parameters (σ' and m') determined from the low-frequency EIS data. Clearly, both data sets show variation as a function of composition which, as before, is dependent on electrode morphology and electrochemical behavior of the EMD. The CPE prefactor (σ') in this case can be used as an indicator of how substantial an impact mass transport has on the electrode impedance; i.e., those conditions where the electrode requires a substantial contribution from mass transport to function will have a large impedance. Under these circumstances, the large increase in σ' at a composition of $x = 1.78$ (-0.07 V vs Hg/HgO) would suggest that mass transport is very significant at this stage. This composition (voltage) corresponds to the current maximum observed in the low-rate linear sweep voltammogram (Fig. 5). It is pertinent at this point to discuss the nature of the diffusing species because there are a number of possibilities. First, because water is a reactant in the reduction reaction, there is a need for it to be present at the EMD-electrolyte interface so that reduction can proceed. In the 9 M KOH electrolyte used here the amount of "free" uncoordinated water would be relatively small, and so there is the possibility that it could be the limiting diffusing species. This is especially true because the water molecules have to pass through the surface layer

of electrogenerated OH^- at the surface, and also if water transport has to occur through the EMD porous structure, although as discussed above, this may not be relevant. The alternative diffusing species is the hydrogen (H^+/e^- pair) inserted into the EMD structure. Because proton conductivity in EMD has been shown to be less than electron conductivity³⁸ for the majority of the composition range, it is the proton component of the pair that is the limiting species. Overall, when comparing the two possible diffusing species (H^+ in the solid or H_2O in the electrolyte), it is more likely that solid-state diffusion is the mass-transport-limiting phenomena. Therefore, from the EIS data, when there is a substantial current flowing across the EMD-electrolyte interface, and when substantial demands are being placed on the solid EMD to diffuse the inserted hydrogen away from the interface, σ' becomes large. From Fig. 8a, at the more oxidized compositions (from $x = 1.960$ to 1.934), the small drop in σ' from 0.61 – $0.45 \text{ } \Omega(\text{rad/s})^{-m'}$ may be the result of pore closure, hence making mass transport easier, especially because little current is flowing through the interface at this composition. Over the subsequent composition range from $x = 1.934$ to 1.894, σ' remained relatively constant at $0.45 \text{ } \Omega(\text{rad/s})^{-m'}$. Here again the current flow through the interface was relatively small, and at these more oxidized compositions the EMD structure was

Figure 8. Fitted parameters arising from the low-frequency EIS data interpreted using a CPE.

able to adequately diffuse the protons away from the surface. From $x = 1.894$ to 1.779 the value of σ' increased dramatically from 0.45 to $2.61 \Omega(\text{rad/s})^{-m'}$. In this composition range the current flow through the interface was substantial, indicating that the demands on mass transfer were growing and also that the structure could not as easily remove the inserted hydrogen from the surface. The subsequent drop in σ' from 2.61 to $0.95 \Omega(\text{rad/s})^{-m'}$ at $x = 1.636$ again reflects the drop in current passing through the interface, placing less of a demand on mass transport. At compositions more reduced than $x = 1.636$ the steady rise in σ' is most probably due to the decreasing ability of the EMD to remove species from the surface into the bulk solid.

The variation of m' with composition (Fig. 8b) is more difficult to explain. First, a CPE can be used as a substitute for a capacitor, Warburg diffusion element, or a resistor, depending on the value of m' ; i.e., 1 , 0.5 , or 0 , respectively. Therefore, in this particular case where we are using a CPE to simulate a diffusion element, even a qualitative description of the variation in m' with composition will be speculative. In general, m' varies between 0.40 and 0.79 . For those compositions where m' is near 0.5 (0.50 ± 0.05) we might expect behavior approaching planar semi-infinite diffusion. Interestingly, this occurs in the compositional range from $x = 1.862$ to 1.688 , which corresponds to a large value of σ' , or the point where the electrode is dependent on mass transport. It also suggests that the diffusional aspects of the electrode at these compositions approximates planar semi-infinite diffusion, i.e., nonporous EMD particles. In the remaining compositional ranges ($x = 1.960$ – 1.873 and $x = 1.679$ – 1.503) m' is substantially larger than 0.5 . In the more oxidized composition range this may be due to electrode porosity, which becomes unavailable abruptly at $x = 1.873$ due to pore closure, whereas in the more reduced compositional range, the increasing value of m' is probably due to a preferential buildup of charge (OH^-) at the electrode surface (rather than undergoing charge transfer), forcing capacitive behavior. This is most probably due to the relatively high charge-transfer resistance in this composition range.

Conclusions

In this study EIS at various depths of discharge has been used to examine the electrochemical and morphological behavior of the alkaline manganese dioxide electrode. Key features of the work include:

1. EIS data has been collected over the complete range $[\text{Mn(IV)} \rightarrow \text{Mn(III)}]$ of alkaline manganese dioxide electrode compositions.

2. The EIS data has been divided into three frequency ranges. At high (20 kHz – 50 Hz) and low ($< 2 \text{ Hz}$) frequencies the expected electrode behavior was observed, i.e., at high frequencies a parallel arrangement of charge-transfer resistance and interfacial capacitance, while at low frequencies diffusional contributions to the impedance were observed. However, at intermediate frequencies a previously unreported inductance loop was observed. Within each individual frequency range a suitable equivalent circuit model was devised and used to interpret electrode behavior.

3. Overall, the EIS data in all frequency ranges can be interpreted in terms of a combination of mechanical breakdown of particles and a shrinking pore model, both of which occur as a result of γ - MnO_2 structural expansion. This was also suggested to cause interparticle porosity as a whole to decrease. During the initial stages of discharge, electrode porosity is anticipated to be freely available for

charge transfer; however, by a composition of $\sim \text{MnO}_{1.80}$, the EIS data suggests that significant mechanical breakdown has occurred, causing a loss of porosity.

4. The implications of this are that the behavior and performance of the alkaline manganese dioxide electrode is dependent primarily on the geometric surface area of the particles rather than the porous surface area. Furthermore, the crystal structure of the bulk manganese dioxide is then most significant in determining electrochemical performance.

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