Operando Identification of the Point of $[\text{Mn}_2]\text{O}_4$ Spinel Formation During $\gamma\text{-MnO}_2$ Discharge Within Batteries

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Abstract

The rechargeability of γ - MnO_2 cathodes in alkaline batteries is limited by the formation of the $[\text{Mn}_2]\text{O}_4$ spinels ZnMn_2O_4 (hetaerolite) and Mn_3O_4 (hausmannite). However, the time and formation mechanisms of these spinels are not well understood. Here we directly observe γ - MnO_2 discharge at a range of reaction extents distributed across a thick porous electrode. Coupled with a battery model, this reveals that spinel formation occurs at a precise and predictable point in the reaction, regardless of reaction rate. Observation is accomplished by energy dispersive X-ray diffraction (EDXRD) using photons of high energy and high flux, which penetrate the cell and provide diffraction data as a function of location and time. After insertion of 0.79 protons per γ - MnO_2 the α - MnOOH phase forms rapidly. α - MnOOH is the precursor to spinel, which closely follows. ZnMn_2O_4 and Mn_3O_4 form at the same discharge depth, by the same mechanism. The results show the final discharge product, Mn_3O_4 or $\text{Mn}(\text{OH})_2$, is not an intrinsic property of γ - MnO_2 . While several studies have identified $\text{Mn}(\text{OH})_2$ as the final γ - MnO_2 discharge product, we observe direct conversion to Mn_3O_4 with no $\text{Mn}(\text{OH})_2$.

1. Introduction

The oxide γ - MnO_2 , which is a staple of global electrochemical energy storage, shows a high complexity in its structure and discharge mechanism. The mechanism in alkaline electrolyte is often treated in shorthand as a first electron reaction followed by a second electron reaction.[1, 2]

This understanding is true only in limited circumstances. While discharge always begins via the

proton insertion in reaction (1), upon reaction beyond a poorly defined extent various other manganese oxides are observed, including the spinels Mn_3O_4 (hausmannite) and ZnMn_2O_4 (hetaerolite), the latter of which is produced in batteries with zinc anodes. These spinels have low electrochemical activity, and will not recharge to MnO_2 . Despite their importance in keeping γ - MnO_2 batteries from being widely used rechargeably, the reaction mechanisms leading to these spinels are largely unknown, as are their precise points of formation during discharge.

Details from the literature show a strong influence of experimental factors, for example the mass percent of γ - MnO_2 , which must be diluted with a conductive material like carbon. Various dilutions show a range of discharge results, and the studies most cited are difficult to compare directly. In one, constant current discharge at 87.5% mass loading led first to Mn_3O_4 followed by $\text{Mn}(\text{OH})_2$, while in a second, potential scanning at 60% loading led to $\text{Mn}(\text{OH})_2$, which was recharged through γ - Mn_2O_3 , β - MnOOH , and γ - MnOOH , and gave Mn_3O_4 only on the second cycle.[3, 4] In the ensuing years there has been no resolution of this mechanism. A later in situ study at 80% loading showed simultaneous formation of Mn_3O_4 and $\text{Mn}(\text{OH})_2$ at 0.8 extent of reaction (1).[5] Another study at 3% loading showed $\text{Mn}(\text{OH})_2$ with no Mn_3O_4 , suggesting that Mn_3O_4 in earlier reports was a consequence of sample preparation.[6] Addition of a zinc anode has complicated interpretations further. It has been reported that ZnMn_2O_4 was observed in situ during the first electron reaction, and that ZnMn_2O_4 and Mn_3O_4 form at different stages, governed by the cell potential.[6, 7] These variations can also be attributed to data interpretation, as the manganese oxides are difficult to distinguish experimentally. Also in play is the nature of porous electrodes, which almost always display nonuniform reaction rates, especially at high mass loading or high rate. Reaction extents calculated assuming a bulk average will differ from the true values and thus call mechanisms into question.

In this study we target the pathway to and point of spinel formation under the most relevant experimental conditions: those found within commercial γ -MnO₂ batteries. Knowledge of the precise molecular pathway leading to spinel formation may be used to engineer a method to block or reverse this pathway. For practical use, γ -MnO₂ electrodes operate at high mass loading and significant discharge rate. The technique of using photons of high energy and high flux for energy dispersive X-ray diffraction (EDXRD) has been used to track material evolution within electrochemical systems that more resemble actual devices than model systems, which may exclude factors that have a significant impact.[8-11] Thus we use commercial alkaline batteries as the test bed. These have qualities not found in many model systems: ~97% active material loading, thick electrodes, and relatively starved electrolyte. We have previously demonstrated that high energy EDXRD has the sensitivity required to spatially distinguish ZnMn₂O₄ and Mn₃O₄, which have a d-spacing difference of only 0.04 Å, within the sealed steel casing of a battery, using a moderate data collection time of 20 s per location.[12] To account for the distribution of current within the thick electrodes, we use a proven macrohomogeneous battery model to calculate local discharge rates based on the bulk discharge rate. The practical interest in this mechanism is due to the emerging need for inexpensive and safe electricity storage on the scale of the power grid.[13] Because γ -MnO₂ is inexpensive, non-toxic, and non-flammable, it is uniquely suited for massive-scale stationary batteries, fulfilling requirements challenging for other battery chemistries.[14]

2. Experimental

Because the photons used were highly penetrating it was possible to use LR6 commercial alkaline batteries as a test bed, and these were Duracell MN1500 AA with a rated capacity of 2.85 Ah at

0.8 V. The reported specific and volumetric energy densities were 143 Wh kg^{-1} and 428 Wh L^{-1} .

In operando battery discharge was performed using an eight channel MTI battery cycler.

EDXRD experiments were conducted at Brookhaven National Laboratory (BNL) at beamline X17B1 of the National Synchrotron Light Source (NSLS). An incident X-ray beam penetrated the battery, and the diffracted beam was detected at a fixed angle of $2\theta = 3^\circ$. The incident beam was white beam radiation with an energy range of $\sim 20\text{-}200 \text{ keV}$. The diffracted beam intensity was measured using a high resolution germanium detector with a digital signal processor and a 8192-channel multichannel analyzer. The channel number to inverse d-spacing calibration was made using LaB_6 and CeO_2 standards. Diffraction data was smoothed using a Savitzky–Golay filter.

Collimation slits were used to set the sizes of the incident and diffracted beams, and the intersection of the two beam cross-sectional areas defined a gauge volume (GV) in space.[10, 15, 16] By positioning the GV inside the battery, diffraction data was collected at a well-defined spatial location as illustrated in **Figure 1**. Settings were $d_i = 130 \text{ }\mu\text{m}$, $d_s = 100 \text{ }\mu\text{m}$, and width in the x_3 direction of 2 mm . At these conditions the GV was $130 \text{ }\mu\text{m}$ along the radius of the battery. For the 100 mA battery, a larger d_i setting of $300 \text{ }\mu\text{m}$ was used to better resolve the (110) reflection of ramsdellite. Batteries were “mapped” by positioning the GV at the top of the can and moving the battery, using an x - y - z stage, to scan the GV radially inward to the battery center. Data was collected at each point for 20 s . Previously it was found that battery maps collected at different axial or azimuthal locations could be expected to be in general agreement with one another.[11] Axially, the data was collected at the battery half-height. The beam caused no damage to the battery materials on the time scale of the experiments.

Figure 1. (A) Experimental setup showing the EDXRD signal from a GV localized within the battery. (B) Schematic of white beam X-ray diffraction from a gauge volume (GV) inside the battery. The GV size was defined by the collimation slits. The blue color shows the diffracted beam path to the detector. Beam and GV sizes are enlarged many times for visibility.

3. Results

3.1 Battery discharge rates. Batteries were discharged at 400, 143, 100, and 50 mA, as shown in **Figure 2**. Upon reaching 0.02 V the discharge continued at constant potential until the experiment was halted. The gradual drop in cell potential was chiefly due to the γ - MnO_2 cathode material, whose potential drops from its value of $E^0 = 0.26$ V vs. $\text{Hg}|\text{HgO}$ (1.64 V vs. Zn) as it is discharged. The batteries were continually mapped by EDXRD to track the crystal structure of the active material as a function of position inside the battery. EDXRD map times are overlaid on

the potential curves. Other than the 400 mA case, the discharge curves displayed characteristic dips in potential. To make them more visible, the first derivatives of the potential curves dV/dt are shown, and in these the dips appear as points of inflection.

The initial MnO_2 discharge reaction is the proton insertion in Equation (3).

The variable x indicates the number of electron equivalents that have reacted per Mn atom. As the reduction of Mn^{4+} to Mn^{3+} is accompanied by a proton insertion into the MnO_2 tunnel structure, x is also the number of protons inserted. At the endpoint of this reaction $x = 1$ and $\alpha\text{-MnOOH}$ is formed, which has the mineral name groutite. These commercial cells had an extremely high mass loading of MnO_2 in the cathode of 96.8% of total solids.[17] The theoretical capacity of the first electron reaction in Equation (3) was 3.19 Ah. **Table 1** lists times, values of x_b , and relevant EDXRD maps of observed potential dips in the discharge curves.

3.2 Battery modeling. Batteries discharged at these rates were expected to have variable current distributions and concentrations as a function of radius within the cathode, from $r = 4.2\text{-}6.9$ mm. The alkaline battery model of Chen and Cheh was adapted to calculate local values of x at a given radius, x_r . [18] This model was based on the macrohomogeneous theory of porous electrodes, and accounted for diffusion and convection in the electrolyte, changes in porosity and electrolyte composition, ionic migration in concentrated solution, and proton transport in the MnO_2 particles.[19, 20] Details of the model and its solution are discussed in the supporting information. Current distributions in these batteries evolved in diverse ways, and these are plotted in **Figure 3** as volumetric electrochemical reaction rate or transfer current. The initial disparity

between the front and back of the cathode varied from only 13% at 50 mA to 140% at 400 mA.

Figure 2. Discharge curves of 3 AA alkaline batteries. Cell potential is in the top panel, with its first derivative (dotted). Dips in the potential curves are indicated. Current is shown in the bottom panel, with electron equivalents x_b for the bulk-averaged cathodes (dashed). Numbered EDXRD maps are shown on the potential curves. Width of the rectangles represents the actual data collection time.

Figure 3. Battery model calculations for cathodes in the cells discharged in Figure 2. The final time corresponds to observed formation of the α -MnOOH (400) reflection at the separator. Local values for the transfer current j in mA cm⁻³ and x_r are shown. (A) 50 mA; (B) 100 mA; (C) 143 mA; (D) 400 mA.

3.3 Structure of the γ -MnO₂ starting material. The γ -MnO₂ active material has a complex and defect-filled structure that is known to be an intergrowth of two MnO₂ polymorphs. The first is ramsdellite, an orthorhombic material (space group Pbnm) with a 2×1 tunnel structure. The second is pyrolusite or β -MnO₂, a tetragonal material (rutile structure, space group P4₂/mnm) with a 1×1 tunnel structure. The MnO₆ octahedra of these two pure materials are shown in **Figure 4**. γ -MnO₂ can be described by assuming it has a ramsdellite structure affected by two kinds of defects: (i) a stacking disorder in which pyrolusite layers are interspersed within the ramsdellite layers, and (ii) a microtwinning of the ramsdellite lattice.[21] These defects can be quantified with two parameters: defect type (i) by P_r , which is the fraction of pyrolusite layers in the structure; and defect type (ii) by T_w , which is a stacking transition probability in the ramsdellite part of the material.[22] A T_w of 0% is perfect ramsdellite and 100% is maximally twinned. Highly active γ -MnO₂ is highly twinned and incorporates both ramsdellite and pyrolusite into its structure. Bailey and Donne provide examples of a wide range of γ -MnO₂ sample properties.[23]

The γ -MnO₂ used was extensively twinned, $T_w > 80\%$, typical for electrolytic manganese dioxide (EMD). This meant that the orthorhombic ramsdellite structure was not evident from the diffraction pattern. Instead the MnO₂ X-ray reflections were characteristic of a pseudo-hexagonal unit cell, and the material was thus indexed as hexagonal ϵ -MnO₂ (space group P6₃/mc).[24] However as expected, the (110) reflection of an orthorhombic Pbnm space group, indicative of the presence of ramsdellite, was also clearly apparent. From the average of several EDXRD patterns this reflection was located at a value of $0.2488 \text{ \AA}^{-1}$, corresponding to a CuK α 2θ of 22.12° . The method of Chabre and Pannetier was used to calculate P_r , which was 0.39.[22] This was the fraction of pyrolusite layers in the starting material.

Figure 4. Structures of (a) ramsdellite (R-MnO₂, 2 × 1 tunnels) and (b) pyrolusite (β-MnO₂, 1 × 1 tunnels) in the direction along the tunnels. Bottom panels show the corresponding fully proton-inserted structures (c) α-MnOOH and (d) γ-MnOOH. The dotted line shows the incompatibility between groutite, which is inserted, and pyrolusite, which is not.

3.4 Operando EDXRD. Cathode reflections during discharge of the 400 mA battery evolved as a function of position in the battery, as shown in **Figure 5**. Initially the reflections associated with MnO₂ shifted to a lower inverse d-spacing as proton insertion expanded the unit cell. The proton

insertion in Equation (3) begins as a single-phase reaction, with protons inserted into the 2×1 tunnels of ramsdellite.[1, 25] The first evidence of α -MnOOH was due to a diffuse peak corresponding to the (111) reflection and a more pronounced (400) reflection. This (400) reflection rapidly split from the hexagonal (100)_h reflection of ϵ -MnO₂ as it shifted leftward. Immediately following this split, the spinel structure of ZnMn₂O₄ formed directly at the separator. After further reaction, which was at constant voltage in this battery, the other reflections of α -MnOOH became distinct. The α -MnOOH (210) reflection transitioned smoothly from (100)_h of ϵ -MnO₂, and α -MnOOH (211) transitioned from ϵ -MnO₂ (101)_h. An intensifying signal from ZnMn₂O₄ at the separator was accompanied by loss of the α -MnOOH signal, marked by note (c). By the time of map 32, after the experiment was halted and the cell rested, only ZnMn₂O₄ was apparent at the separator, with no trace of α -MnOOH. Finally, the spinel structure of Mn₃O₄ formed throughout the cathode from $r = 4.57$ - 6.55 mm. Mn₃O₄ was accompanied by a related structure labeled *spinel 2*. Traces of Mn₃O₄ and *spinel 2* such as those marked by (a) and (b) intermittently appeared near the detection limit beginning at map 12, with their full patterns forming at map 16.

Localized reflections adjacent to the separator in the 100 mA cell are shown in **Figure 6**. α -MnOOH first became apparent as the diffuse (111) signal at map 23, and this was followed by splitting off of the more intense (400) reflection at map 25. ZnMn₂O₄ then formed suddenly, indicated by the marker (a), with the three sharpest reflections at map 26 and the remainder of the pattern by the next map. This result was general, and it was the case in every battery tested that spinel appeared directly following the α -MnOOH (400) reflection. It was also the case that dips in the cell potential coincided with formation of the α -MnOOH (400) reflection in the cathode adjacent to the separator. Table 1 lists the times of these occurrences to make the connection

clear. Of course with the highest discharge rate of 400 mA no potential dip was seen. Instead the potential fell precipitously at map 6, and this was caused by heavy formation of ZnO at the separator on the anode side. We have previously detailed the growth of such ZnO blocking layers.[11]

Evolution of the 143 mA battery during the end of discharge is shown in **Figure 7**. During the time between maps 18 and 19 the cell potential fell, tripping the constant voltage stage after map 19. At $r = 4.17$ mm the appearance of α -MnOOH (400) occurred at map 16, followed by ZnMn_2O_4 at map 17. Behind this layer, a similar progression was observed in which α -MnOOH (400) was instead closely followed by Mn_3O_4 . The maps of first formation for these materials are listed for each radius in **Table 2**. In some cases there was ambiguity, if only one reflection appeared and was near the noise level of the EDXRD signal, and for these a map range is listed. By map 19 Mn_3O_4 had formed throughout the cathode. As with ZnMn_2O_4 , Mn_3O_4 closely followed the well defined signature of α -MnOOH. We conclude α -MnOOH is the precursor to any spinel structure.

The final calculated times in Figure 3 correspond to the sudden appearance of the α -MnOOH (400) reflection at the separator, and this occurred at $x_r = 0.79$ -0.80. These values are in Table 1. From the model calculation for the 400 mA cell in Figure 3D, α -MnOOH formation at the separator would have occurred just before map 6. However, since maps were collected at the same rate as the other cells despite the much more rapid discharge, this moment was not resolved from that of spinel formation. For the 143 mA cell, cathode utilization values were also calculated beyond this point. While the model did not account for ZnMn_2O_4 formation, this provided good approximations for x_r values during the Mn_3O_4 formation in Figure 7. These are listed in **Table 2** and reveal that α -MnOOH formation in the bulk of the cathode occurred at $x_r = 0.78$ -0.79, similar

to near the separator. Mn_3O_4 formation closely followed, analogous to ZnMn_2O_4 . Thus, the formation pathway of these two spinels is fundamentally the same, following the same chain of events.

Figure 5. Cathode reflections during discharge of the 400 mA battery. Map numbers correspond to the times shown in Figure 2. The section of the cathode nearest the separator was at $r = 4.17$ mm. That nearest the current collector was at $r = 6.55$ mm. This shows the full range of discharge products.

Figure 6. Cathode reflections during discharge of the 100 mA battery from EDXRD maps 19 to 29 near the separator at $r = 4.15$ mm. Details from near note (a) are shown to the right, where the progression to ZnMn_2O_4 formation is clearly apparent. A small ZnO signal was due to the GV overlapping slightly into the separator and anode.

Table 1. Data at dips in cell potential during the battery discharges

Rate (mA)	Dip in cell potential			Map of formation at the separator		Model calculation	
	Time (h)	EDXRD Map	x_b	$\alpha\text{-MnOOH}$ (400)	ZnMn_2O_4	x_r at $r = 4.2$ mm	x_r at $r = 5.0$ mm
400	-	-	-	(6) ¹	6	-	-
143	16.5	16	0.69	16	17	0.79	0.75
100	24.0	25	0.71	25	26	0.79	0.73
50	47.3	48	0.72	48	49	0.80	0.76

1. Data was not collected at map 5 in the 400 mA cell due to an X-ray beam injection

Table 2. Mn₃O₄ formation in the 143 mA cell

radius (mm)	Map of first formation		Model calculation x_r			Spinel (103) reflection d^{-1} (Å ⁻¹), map 19
	α -MnOOH (400)	spinel	map 17	map 18	map 19	
4.17	16	17	0.87	0.91	0.94	0.368 ^a
4.57	16-17	17-18	0.85	0.88	0.92	0.364
4.96	17	18	0.81*	0.86	0.90	0.363
5.36	17-18	18	0.78*	0.83	0.88	0.362
5.76	18	18-19	0.76	0.81*	0.86	0.362
6.16	18	19	0.74	0.79*	0.85	0.362
6.55	18-19	19	0.73	0.78*	0.84	0.361

* First appearance of the α -MnOOH (400) reflection occurred after local state of charge x_r passed ~0.79.

a. This spinel was ZnMn₂O₄.

Figure 7. Cathode reflections during discharge of the 143 mA battery near the end of discharge. The section of the cathode nearest the separator was $r = 4.17$ mm. Formation of Mn_3O_4 begins behind the ZnMn_2O_4 layer and then progress to larger radii. The peaks marked (b) were ZnO reflections from the separator/anode.

4. Discussion

Direct observation showed that $[\text{Mn}_2]\text{O}_4$ spinels formed immediately following appearance of α - MnOOH (400). This transition to the α - MnOOH structure occurred in a tight range of $x = 0.78$ - 0.81 at all locations in all batteries, regardless of local reaction rate. We thus define a single value of state of charge at the phase transition of $x_t = 0.79$, the most common value. The γ - MnO_2 was calculated to have a fraction of 0.39 pyrolusite layers in the crystal lattice, and state of charge to fully insert protons into all 2×1 ramsdellite tunnels was thus

$$x_2 = \frac{(2-2P_r)}{(2-P_r)} = 0.76 \quad (4)$$

This meant the α - MnOOH phase transition occurred universally at 104% capacity required to fill the ramsdellite fraction of the γ - MnO_2 . Ramsdellite and pyrolusite discharge to different polymorphs of MnOOH . [26, 27] α - MnOOH has a 2×1 tunnel structure, corresponding to the fully proton-inserted structure of ramsdellite. γ - MnOOH (manganite) has a 1×1 tunnel structure, corresponding to that of pyrolusite. This relationship between filled and unfilled structures is illustrated in Figure 4. At the phase transition some number of the inserted protons had occupied the tunnels of both ramsdellite and pyrolusite, x_{Rt} and x_{rt} respectively, and $x_{Rt} + x_{rt} = x_t$. The discharge reaction up to the point of α - MnOOH formation can be written:

Pyrolusite domains, which have a rutile structure, are labeled $r\text{-MnO}_2$; ramsdellite domains are labeled $R\text{-MnO}_2$. Here the brackets indicate joined domains in the γ - MnO_2 crystal lattice.

Reaction to x_t caused these domains to be sheared apart due to the lattice mismatch between α - MnOOH and pyrolusite. At this point α - MnOOH became the dominant diffraction signal.

Ripert and co-workers have reported that this lattice shearing occurs after full filling of the ramsdellite domains.[28, 29] Using operando neutron diffraction on γ -MnO₂ with $P_r = 0.3$ and $x_2 = 0.82$, they observed Mn(OH)₂ formation at $x_b = 0.8$ and noted this matched x_2 , suggesting the ramsdellite is filled while the rutile domains remain inactive until shearing. However, this cannot be the case as α -MnOOH reflections shifted leftward after their formation due to continued proton insertion, illustrated by note (b) in Figure 6. Thus the ramsdellite remained incompletely filled and non-stoichiometric immediately upon shearing, with its formula given by $\alpha\text{-MnOOH}_{x_{Rt}}$. This is supported by ²H MAS NMR results of Paik and Grey, who found that the signal from deuterons in 1×1 tunnels was strong during initial discharge.[30] This means $x_{rt} \neq 0$. Because a multitude of materials formed after x_t and the diffraction patterns were not strictly quantitative, it was challenging to calculate x_{rt} with certainty. It was possible to define the bounds $0.03 < x_{rt} < 0.24$, corresponding to α -MnOOH_{0.72} or more filled. However, as no γ -MnOOH signal was detected we assume a value of x_{rt} below 0.12 was more likely, consistent with rutile layers being sheared into isolated surface sites before their half-reduction. This would mean ramsdellite was more filled than α -MnOOH_{0.88} upon shearing.

After α -MnOOH formation and shearing of the lattice, [Mn₂]O₄ spinel building occurs based on whichever complex ion is available to fill the tetrahedral sublattice.

Results above, such as note (c) of Figure 5, demonstrate that spinel formation corresponds to loss of the α -MnOOH signal. The source of $\text{Mn}(\text{OH})_4^{2-}$ ion may be dissolution of Mn^{III} followed by disproportionation, or via an electrochemical reaction. It has been variously suggested that spinel

formation is either by a reaction through the solution or essentially solid state.[31-34] In batteries discharged and rested, ZnMn_2O_4 and Mn_3O_4 were distinguished by their (103) reflections, which when co-located appears as peak splitting.[12] Viewed in operando the (103) reflection showed significant shifting, which was a function of radius or distance from the separator. This is marked in Figure 7 by note (a) and the corresponding values of d^{-1} are listed in Table 2. Since the peak was not split, this shows a single-phase mingling of ZnMn_2O_4 and Mn_3O_4 , with more Zn bringing the d^{-1} value higher. The unknown spinel 2 d-spacing was even smaller than that of ZnMn_2O_4 , and is evidence of partially-formed spinel, for example the $[\text{Mn}_2]\text{O}_4$ spinel framework with the tetrahedral site not yet filled or temporarily filled by a smaller atom. Both ZnMn_2O_4 and Mn_3O_4 have distorted tetragonal spinel structures (space group $\text{I4}_1/\text{amd}$), and spinel 2 appeared analogous to the Mn_3O_4 (112) and (200) reflections. While difficult to identify based on the two visible reflections, spinel 2, as well as the lack of peak splitting, suggest spinel building is slow because the operando results show intermediate species.

The reaction mechanism observed in the current work was at variance with other studies that show $\text{Mn}(\text{OH})_2$ as a discharge product, or as a precursor to Mn_3O_4 formation. In other work with a lower mass loading we have observed $\text{Mn}(\text{OH})_2$ is easily distinguished in EDXRD patterns by reflections at $d^{-1} = 0.348 \text{ \AA}^{-1}$ and $0.407 \text{ \AA}^{-1}$, but was never observed here. Tarascon and co-workers observed $\text{Mn}(\text{OH})_2$ as the final discharge product in their experiments, but the mass loading of $\gamma\text{-MnO}_2$ was 3%, with an extreme excess of carbon.[6] They also observed that ZnMn_2O_4 does not form from MnOOH chemically produced via reduction by hydrazine. From this we conclude that the $\alpha\text{-MnOOH}$ reactants in Equation (6) and (7) must be the electrochemically-produced material, rather than ones chemically synthesized. The results presented here show the final discharge product, Mn_3O_4 or $\text{Mn}(\text{OH})_2$, is not an intrinsic property

of γ - MnO_2 . However, the conversion to α - MnOOH is fundamental, and occurs at a precise and observable point in the discharge reaction.

5. Conclusions

In a discharging γ - MnO_2 electrode, formation of ZnMn_2O_4 and Mn_3O_4 follow the same mechanism, which occurs immediately following the appearance of α - MnOOH as a distinct phase. Time of formation of the α - MnOOH phase is identified by the splitting off of its (400) reflection from the hexagonal (100)_h reflection of ϵ - MnO_2 . After this split, the ϵ - MnO_2 (100)_h reflection smoothly transitions to the α - MnOOH (210) peak upon further discharge. If the electrode is recharged, the ZnMn_2O_4 and Mn_3O_4 materials remain persistent. Because these spinels are electrochemically inactive, their presence in the electrode causes a profound drop in capacity. This means the event that ultimately leads to loss of reversibility for a γ - MnO_2 cathode is the occurrence of well-formed α - MnOOH , after which spinel formation is imminent. Furthermore, this splitting off of the α - MnOOH (400) was observed to always occur at a local value of the state of charge of $x_r \approx 0.79$. This was most likely filling of the ramsdellite tunnels in the γ - MnO_2 corresponding to α - $\text{MnOOH}_{0.88}$ or greater. The first occurrence of α - MnOOH (400) next to the battery separator corresponded to dips in battery potential observable in Zn- MnO_2 discharge curves.

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References

- [1] A. Kozawa, R.A. Powers, J Electrochem Soc, 113 (1966) 870-878.
- [2] A. Kozawa, R.A. Powers, J Electrochem Soc, 115 (1968) 122-126.
- [3] D. Boden, C.J. Venuto, D. Wisler, R.B. Wylie, J Electrochem Soc, 114 (1967) 415-&.
- [4] J. Mcbreen, Electrochim Acta, 20 (1975) 221-225.
- [5] C. Mondoloni, M. Laborde, J. Rioux, E. Andoni, C. Levyclement, J Electrochem Soc, 139 (1992) 954-959.
- [6] R. Patrice, B. Gerand, J.B. Leriche, L. Seguin, E. Wang, R. Moses, K. Brandt, J.M. Tarascon, J Electrochem Soc, 148 (2001) A448-A455.
- [7] Y. Paik, W. Bowden, T. Richards, R. Sirotina, C.P. Grey, J Electrochem Soc, 151 (2004) A998-A1011.
- [8] K. Kirshenbaum, D.C. Bock, C.Y. Lee, Z. Zhong, K.J. Takeuchi, A.C. Marschilok, E.S. Takeuchi, Science, 347 (2015) 149-154.
- [9] K.C. Kirshenbaum, D.C. Bock, Z. Zhong, A.C. Marschilok, K.J. Takeuchi, E.S. Takeuchi, Journal of Materials Chemistry A, 3 (2015) 18027-18035.
- [10] J. Rijssenbeek, Y. Gao, Z. Zhong, M. Croft, N. Jisrawi, A. Ignatov, T. Tsakalakos, J Power Sources, 196 (2011) 2332-2339.

- [11] J.W. Gallaway, C.K. Erdonmez, Z. Zhong, M. Croft, L.A. Sviridov, T.Z. Sholklapper, D.E. Turney, S. Banerjee, D.A. Steingart, *Journal of Materials Chemistry A*, 2 (2014) 2757–2764.
- [12] J.W. Gallaway, M. Menard, B. Hertzberg, Z. Zhong, M. Croft, L.A. Sviridov, D.E. Turney, S. Banerjee, D.A. Steingart, C.K. Erdonmez, *J Electrochem Soc*, 162 (2015) A162-A168.
- [13] J. Eyer, G. Corey, SANDIA REPORT, SAND2010-0815 (2010).
- [14] N.D. Ingale, J.W. Gallaway, M. Nyce, A. Couzis, S. Banerjee, *J Power Sources*, 276 (2015) 7-18.
- [15] M. Croft, V. Shukla, E.K. Akdogan, N. Jisrawi, Z. Zhong, R. Sadangi, A. Ignatov, L. Balarinni, K. Horvath, T. Tsakalakos, *J Appl Phys*, 105 (2009).
- [16] M. Croft, I. Zakharchenko, Z. Zhong, Y. Gurlak, J. Hastings, J. Hu, R. Holtz, M. DaSilva, T. Tsakalakos, *J Appl Phys*, 92 (2002) 578-586.
- [17] W. Luo, A.B. Shelekhin, M. Sylvestre, in: US 6,858,349 B1, The Gillette Company, 2005.
- [18] J.S. Chen, H.Y. Cheh, *J Electrochem Soc*, 140 (1993) 1205-1213.
- [19] J. Newman, W. Tiedemann, *Aiche J*, 21 (1975) 25-41.
- [20] R. Pollard, J. Newman, *J Electrochem Soc*, 128 (1981) 503-507.
- [21] D.E. Simon, R.W. Morton, J.J. Gislason, *Advances in X-ray Analysis*, 47 (2004) 267-280.
- [22] Y. Chabre, J. Pannetier, *Prog Solid State Ch*, 23 (1995) 1-130.
- [23] M.R. Bailey, S.W. Donne, *Electrochim Acta*, 56 (2011) 5037-5045.
- [24] P.M. Dewolff, J.W. Visser, R. Giovanoli, R. Brutsch, *Chimia*, 32 (1978) 257-259.
- [25] A. Kozawa, J.F. Yeager, *J Electrochem Soc*, 112 (1965) 959-963.
- [26] T. Kohler, T. Armbruster, E. Libowitzky, *J Solid State Chem*, 133 (1997) 486-500.
- [27] L.A.H. MacLean, F.L. Tye, *J Solid State Chem*, 123 (1996) 150-160.
- [28] Ripert, Pannetier, Chabre, Poinsignon, *Mat. Res. Soc. Symp. Proc.*, Vol. 210 (1991) 359-365.

- [29] M. Ripert, C. Poinsignon, Y. Chabre, J. Pannetier, *Phase Transit*, 32 (1991) 205-209.
- [30] Y. Paik, J.P. Osegovic, F. Wang, W. Bowden, C.P. Grey, *J Am Chem Soc*, 123 (2001) 9367-9377.
- [31] L.T. Yu, *J Electrochem Soc*, 144 (1997) 802-809.
- [32] D. Im, A. Manthiram, B. Coffey, *J Electrochem Soc*, 150 (2003) A1651-A1659.
- [33] M.M. Thackeray, M.H. Rossouw, R.J. Gummow, D.C. Liles, K. Pearce, A. Dekock, W.I.F. David, S. Hull, *Electrochim Acta*, 38 (1993) 1259-1267.
- [34] W.I.F. David, M.M. Thackeray, P.G. Bruce, J.B. Goodenough, *Mater Res Bull*, 19 (1984) 99-106.

Figure 1. (A) Experimental setup showing the EDXRD signal from a GV localized within the battery. (B) Schematic of white beam X-ray diffraction from a gauge volume (GV) inside the battery. The GV size was defined by the collimation slits. The blue color shows the diffracted beam path to the detector. Beam and GV sizes are enlarged many times for visibility.

Figure 2. Discharge curves of 3 AA alkaline batteries. Cell potential is in the top panel, with its first derivative (dotted). Dips in the potential curves are indicated. Current is shown in the bottom panel, with electron equivalents x_b for the bulk-averaged cathodes (dashed). Numbered EDXRD maps are shown on the potential curves. Width of the rectangles represents the actual data collection time.

Figure 3. Battery model calculations for cathodes in the cells discharged in Figure 2. The final time corresponds to observed formation of the α -MnOOH (400) reflection at the separator. Local values for the transfer current j in mA cm^{-3} and x_r are shown. (A) 50 mA; (B) 100 mA; (C) 143 mA; (D) 400 mA.

Figure 4. Structures of (a) ramsdellite (R-MnO_2 , 2×1 tunnels) and (b) pyrolucite ($\beta\text{-MnO}_2$, 1×1 tunnels) in the direction along the tunnels. Bottom panels show the corresponding fully proton-inserted structures (c) α -MnOOH and (d) γ -MnOOH. The dotted line shows the incompatibility between groutite, which is inserted, and pyrolusite, which is not.

Figure 5. Cathode reflections during discharge of the 400 mA battery. Map numbers correspond to the times shown in Figure 2. The section of the cathode nearest the separator was at $r = 4.17$ mm. That nearest the current collector was at $r = 6.55$ mm. This shows the full range of discharge products.

Figure 6. Cathode reflections during discharge of the 100 mA battery from EDXRD maps 19 to 29 near the separator at $r = 4.15$ mm. Details from near note (a) are shown to the right, where the progression to ZnMn_2O_4 formation is clearly apparent. A small ZnO signal was due to the GV overlapping slightly into the separator and anode.

Figure 7. Cathode reflections during discharge of the 143 mA battery near the end of discharge. The section of the cathode nearest the separator was $r = 4.17$ mm. Formation of Mn_3O_4 begins behind the ZnMn_2O_4 layer and then progress to larger radii. The peaks marked (b) were ZnO reflections from the separator/anode.