Role of Titanium Dioxide in Enhancing the Performance of the Alkaline Manganese Dioxide Cathode

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In this work the role of TiO₂ in improving cathode performance has been investigated through the use of electrode imaging, porosity changes, electrochemical characterisation and changes in the chemical composition of constituent γ-MnO₂ particles. Time-of-flight secondary ion mass spectrometry studies revealed that TiO₂ is mobile in the electrolyte and associates itself with the porous γ-MnO₂ surface. This association gives rise to improved electrode performance by allowing electron/proton pairs to more easily (de)intercalate into the MnO₂ structure. Depth profiling confirmed that upon cycling surface TiO₂ becomes incorporated into the bulk γ-MnO₂ structure inhibiting proton diffusion.

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Electrochemical energy storage.— With the increased prevalence of portable electronic devices a higher demand is being placed on the both the performance and efficiency of their electrochemical power sources. With global sales exceeding \$10 billion per year, batteries are the power source of choice due to their portability, reliability and excellent performance characteristics. Within this domain the alkaline Zn/MnO₂ system is prominent due to its low cost and strong performance in a wide variety of applications. While still widely regarded as a primary system, significant progress has been made in the development of rechargeable manganese dioxide (RAMTM) cells.^{1–3} The commercialisation of such cells remains hampered by both consumer perception of the primary nature of the system, and the limitations imposed by poor cathodic rechargeability.

Structure and discharge mechanism of γ-MnO₂.— The preferred cathode material for use in both primary and secondary alkaline Zn/MnO₂ cells is that of electrolytic manganese dioxide (EMD). 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.^{4,5} A schematic of the random intergrowth nature of γ-MnO₂ is shown in Figure 1. Its structure has been considered in depth by Chabre and Pannetier,⁶ 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 anion that compensate for the charge deficiency incurred by Mn³⁺ ions and cation vacancies.^{7–9} Chemically, the structure can therefore be defined as

where *x* and *y* represent the mole fractions of cation vacancies (□) and Mn³⁺, respectively.

The basis for the currently accepted discharge mechanism of manganese dioxide in an alkaline environment was proposed originally by Kozawa et al.^{10,11} For the single electron reduction to δ-MnOOH, the proposed model is a homogeneous process based essentially on concerted proton and electron insertion into the host γ-MnO₂ structure. The inserted electron originates from the external circuit, passing through the conductive pathway in the electrode to be inserted in 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. As such, the discharge mechanism can be written as

In terms of rechargeable performance, manganese dioxide is known to suffer from a steady decline in capacity with cycling.^{1–3} This loss of capacity arises from both fundamental limitations in the active material (γ-MnO₂),¹² and the solubilisation (and subsequent side reactions) of reduced Mn(III) species formed upon discharge.¹³ These effects can be minimized by controlling the depth of discharge, and it is this approach which is employed in commercially available RAMTM cells. However, by limiting the depth of discharge in this manner the power available from the system is also restricted and thus further work is required in this area.

The use of Titanium(IV) as an electrode additive.— One avenue for improving the performance of the system is through the use of electrode additives. This can be achieved by either physically mixing the MnO₂ with the electrode additive prior to inclusion, or by chemically modifying the material so that the additive is incorporated in the bulk MnO₂ structure. The use of additives based on the Ti⁴⁺ ion has received particular attention in the literature due to early work carried out by Kordes and Gsellman.¹⁴ These authors were able to produce titanium-doped EMD which showed a significant improvement in rechargeable performance when compared to a reference MnO₂ material (International Common Sample (ICS) No.2). Later work carried out by Binder et al.^{15–17} expanded on this and confirmed that titanium doping resulted in superior charge retention and rechargeability when compared to undoped MnO₂. The use of Ti(IV) species in physically modified electrodes has also received attention in the literature,^{18–20} with its presence shown to improve rechargeability in the one-electron region. Raghuveer and Manthiram^{18,19} reported that these improvements in performance could be related to the suppression of inactive manganese oxide phases like birnessite (δ-MnO₂) and hausmannite (Mn₃O₄) formed during cycling.

This work.— Recently, we have also reported on the beneficial effects of TiO₂ inclusion on electrode performance.²⁰ On the basis of electrochemical studies, we were able to show that the inclusion of TiO₂ improves electrode performance via favorable interactions with the MnO₂ surface which facilitate the charge transfer process. Furthermore, a study of diffusion processes carried out therein revealed that TiO₂ contained in the electrode may be incorporated into the bulk MnO₂ structure with cycling, ultimately inhibiting mass transport characteristics. In this work we will investigate the role of TiO₂

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Figure 1. Basic building blocks of the γ - MnO_2 structure in which (a) pyrolusite (β - MnO_2) and (b) ramsdellite have been microscopically intergrown to produce (c) γ - MnO_2 .

in improving cathode performance through the use of electrode imaging, porosity changes, and changes in the chemical composition of constituent γ - MnO_2 particles. This latter feature is of particular importance, and will be examined in detail through the use of time-of-flight secondary ion mass spectrometry (ToF-SIMS). Finally, the implications of these findings in terms of the role which TiO_2 plays in electrode performance will be considered.

Experimental

Materials.— The electrolytic manganese dioxide (EMD) used in this work was provided by Delta EMD Australia, Pty Limited. It was prepared by the electrolysis of a hot ($\sim 98^\circ\text{C}$), acidic (H_2SO_4) solution of MnSO_4 (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 sub $105\ \mu\text{m}$ powder (mean particle size of $\sim 45\ \mu\text{m}$), 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 sample possessed a γ - MnO_2 crystal structure (Figure 2),⁶ had an x in MnO_x value of 1.97,²¹ a cation vacancy content of 0.07^{7–9} and a BET surface area (N_2 adsorption at 77 K) of $30.0\ \text{m}^2/\text{g}$.²² Peak broadening evident in the X-ray diffraction pattern in Figure 2 is indicative of small crystallites within the structure. Based on high resolution TEM imaging reported in the literature,²³ these crystallites agglomerate to form the much larger macroscopic particles. The anatase titanium dioxide employed as an electrode additive was a commercial material sourced from Sigma Aldrich ($>98\%$).

Electrode preparation and electrochemical protocol.— The EMD working electrode used in the electrochemical cell was prepared by mixing together the manganese dioxide sample (0.200 g), Timcal SFG 6 graphite (2.000 g) and 9 M KOH ($\sim 0.3\ \text{g}$) using a mortar and pestle. For the working electrode containing titanium dioxide, EMD and TiO_2 were first mixed in a 1:10 ratio, and then a sub-sample (0.200 g) mixed with Timcal SFG 6 graphite (2.000 g) and 9 M KOH ($\sim 0.3\ \text{g}$). After being thoroughly mixed, the blackmix was stored in an airtight container for 24 h to allow equilibration to occur.

Cell assembly involved placing 0.200 g of the blackmix into a Teflon-lined Au-coated C-size battery can. After the addition of two separator papers, the electrode was compacted under 1 t for ~ 2 minutes. 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 $\sim 10\ \text{mL}$ of 9 M KOH electrolyte, sealed with Parafilm-M (SPI Supplies) and mounted between a Perspex cover and base-plate. The cell was held in place with

Figure 2. XRD pattern of the EMD used in this work showing the γ - MnO_2 structure, with the corresponding Miller indexes indexed using an orthorhombic unit cell.

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.

The electrochemical performance of both electrodes was determined using a cycling regime consisting of charging the electrode (0.05 mV/s) from the open circuit voltage ($\sim 0.1\ \text{V}$) to the upper limit of 0.3 V, holding the potential here for 1.5 h, and then discharging to $-0.3\ \text{V}$ (0.05 mV/s). The cell was subsequently cycled between these limits at 0.05 mV/s for a total of ten cycles with the data recorded using a Princeton Applied Research VMP 16-channel potentiostat. After cycling the active material was removed from the electrochemical cell, washed to remove entrained electrolyte, and dried at 70°C for 1 h.

As reported in our previous work,²⁰ a more detailed analysis of cycle stability was conducted using a combination of step potential electrochemical spectroscopy (SPECS) and electrochemical impedance spectroscopy (EIS). Briefly, this technique 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 $-0.3\ \text{V}$, and then back up and down, giving a total of two full cycles. At each step the electrode was allowed to equilibrate for 60 min, and an impedance spectrum measured using the frequency range 20 kHz to 0.1 Hz with a 10 mV (AC) excitation signal. The resultant impedance spectra were then interpreted using a modified Randles circuit,²⁴ which was fitted to the data using complex non-linear least squares (CNLS) regression, as used in the ZView software package.

Material characterization.— The structure of each sample was confirmed by X-ray diffraction using a Phillips 1710 diffractometer equipped with a $\text{Cu K}\alpha$ radiation source ($\lambda = 1.5418\ \text{\AA}$) operated at 40 kV and 30 mA. The scan range was from 10° to $80^\circ\ 2\theta$, with a step size of $0.05^\circ 2\theta$ and a count time of 2.5 s.

Morphology was examined by gas adsorption using a Micromeritics ASAP 2020 Surface Area and Porosity Analyser. A representative 0.10 g sample of the manganese dioxide material was degassed under vacuum at 110°C for 2 h prior to analysis. An adsorption isotherm was then determined over the partial pressure (P/P_0) range of 10^{-7} –1 using N_2 gas as the adsorbate at 77 K. The specific surface

area was extracted from the gas adsorption data using the linearized BET isotherm in the range $0.05 < P/P_0 < 0.3$, while the pore size distribution was determined using a Density Functional Theory-based approach (Micromeritics DFTPlus V2.00).

To further investigate the morphology of particles present in both cycled and uncycled blackmixes a Philips XL30 scanning electron microscope (SEM) was employed. Mounted samples were examined using an accelerating voltage of 15 kV, a working distance of 10 mm, and either a secondary electron (SE) or back scattered electron (BSE) detector. SEM imaging was also combined with energy dispersive X-ray spectroscopy (EDX) to give a qualitative analysis of the elemental composition of examined particles.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) experiments were performed using a Physical Electronics Inc. PHI TRIFT V nanoTOF instrument (Physical Electronics Inc., Chanhassen, MN, USA) equipped with a pulsed liquid metal ^{79}Au primary ion gun (LMIG), operating at 30 kV energy. Dual charge neutralization was provided by an electron flood gun and 10 eV Ar^+ ions. Experiments were performed under a vacuum of 5×10^{-6} Pa or better. "Bunched" Au^1 instrumental settings were used to optimize mass resolution for spectra, while "unbunched" Au^1 beam settings were used to optimize spatial resolution for collection of images. SIMS depth profiles were performed in a phased manner, with a Au^1 pulsed beam for the analysis phase and DC beam for the sputter phase. A 10 μm analysis raster within a 50 μm sputter raster on a 'flat' surface of a particle was typically used. Depth profiles were collected from a number of particles per sample to ensure a representative data set. Sample spectra, images and depth profiles were processed and interrogated using WincadenceN software (Physical Electronics Inc., Chanhassen, MN, USA).

Results and Discussion

Electrode imaging and morphology.— To assess the particle morphology of the electrode blackmixes, the use of SEM/EDX was initially employed. In the case of the blackmix, $\sim 45 \mu\text{m}$ particles of EMD were observed interspersed through the underlying graphite matrix. The use of the BSE detector allowed the MnO_2 particles (white) to be clearly distinguished from the graphite (gray), and thus further examined. EDX spectra recorded for the MnO_2 particles confirmed the presence of manganese, along with potassium (emanating from the electrolyte), and low levels of sulfur (present in the EMD). In the case of the TiO_2 containing blackmix, distinct MnO_2 and TiO_2 particles were observed, as shown in Figure 3. Alongside these particles were others which were predominately MnO_2 with small amounts of TiO_2 . The composition of these particles was confirmed by EDX, with the MnO_2 and TiO_2 particles both showing up the presence of

potassium from the electrolyte, and the mixed particles showing predominately manganese with small amounts of titanium and potassium. At this early stage, the finding that some MnO_2 particles contained small amounts of TiO_2 hints that this species may be mobile in the blackmix, resulting in an association with the MnO_2 surface.

After electrochemically cycling (detailed below), a sub-sample of each blackmix was also examined via SEM/EDX. In terms of particle morphology, very little change was evident upon cycling, with $\sim 45 \mu\text{m}$ MnO_2 particles observed in both cases. Surprisingly, in the case of the TiO_2 containing blackmix, the presence of titanium (as either isolated particles or in association with the MnO_2) could no longer be established by EDX. The absence of titanium therein suggests that during cycling titanium dioxide present at the particle surface may become incorporated into the bulk MnO_2 structure.

To investigate the effect of any surface association between TiO_2 and MnO_2 , two equilibrated samples were prepared. These consisted of 1 g of EMD, or 1 g of a 1:10 mixture of TiO_2 and EMD, suspended in 20 mL of 9 M KOH. Samples were shaken over the course of 48 h, filtered, washed to remove entrained electrolyte, and then dried at 70°C in air for 1 h. Adsorption isotherms were then determined over the partial pressure (P/P_0) range of 10^{-7} – 1 using N_2 gas as the adsorbate at 77 K. A plot of the cumulative pore volume as a function of pore width is shown in Figure 4. Comparing the standard EMD to that which had been suspended in 37% KOH, we observe a distinct decrease in meso-porosity. This loss results in a decrease in the BET surface area from $30.0 \text{ m}^2/\text{g}$ to $24.7 \text{ m}^2/\text{g}$, and arises from the adsorption, and potentially precipitation, of KOH from the electrolyte. The blocking of the pores in this manner can be readily compared to the previous surface titration studies of $\gamma\text{-MnO}_2$.^{25–28} Adsorption of K^+ ions can thus be predicted to initially occur via ion exchange with acidic hydroxyl groups on the MnO_2 surface. The K^+ bound in this way would then remain after washing, providing an explanation for the loss in meso-porosity in this sample. Moving to the equilibrated sample containing titanium dioxide, a large drop in both micro-porosity and meso-porosity was observed. This finding confirms that Ti^{4+} is mobile in the electrolyte, and what is surprising is that it indicates that Ti^{4+} is able to penetrate deep into the porous MnO_2 structure. As with K^+ , adsorption of Ti^{4+} can be predicted to occur via ion exchange with acidic hydroxyl groups on the MnO_2 surface; however, in this case the highly charged Ti^{4+} ion is more likely to hydrolyse and precipitate upon washing. The net effect is that the precipitated TiO_2 blocks off these pores, and this gives rise to the low BET surface area ($17.1 \text{ m}^2/\text{g}$) measured for this sample.

Electrochemical behavior of TiO_2 modified electrodes.— As previously reported,²⁰ the inclusion of TiO_2 in the MnO_2 cathode results

Figure 3. SEM images of (a) manganese dioxide and (b) titanium dioxide particles in the initial blackmix, imaged at 2500X using the BSE detector.

Figure 4. Cumulative pore volume as function of pore width for (a) EMD, (b) EMD equilibrated in 37% KOH, and (c) 10% TiO₂/ 90% EMD mixture equilibrated in 37% KOH.

in improved electrode performance. The discharge capacities determined for cycling between 0.3 V and -0.3 V (V vs. Hg/HgO) are presented in Table I, and show improved performance at each cycle. This is particularly evident at the first cycle, where the capacity is significantly higher (219 vs. 192 mA.h/g), and reflects the enhanced reduction of near surface cations, along with improvements in the kinetics associated with reduction. In light of the electrode imaging and morphology studies, we can now be confident that TiO₂ is indeed mobile in the electrolyte, and associates with the γ -MnO₂ surface upon electrode equilibration. While the effects of this association are predominately observed during the first discharge cycle (shifting the peak position of the reduction process, and improving the reduction of near surface cations), improvements in discharge capacity were observed at each subsequent cycle. A comparison of the first two charge-discharge cycles is shown in Figure 5. As a result of the improvement in capacity, the cumulative (10 cycle) discharge capacity for the TiO₂-modified electrode was 1644 mA.h/g, ~7% higher than the standard EMD electrode (1537 mA.h/g).

Table I. Discharge capacities for the EMD and 10% TiO₂ electrodes.

Cycle no.	Discharge Capacity (mA. h/g)	
	EMD	10% TiO ₂
1	192	219
2	162	177
3	158	169
4	157	164
5	152	160
6	150	157
7	147	154
8	144	151
9	141	150
10	135	144

Figure 5. Cycling behavior of the EMD and 10% TiO₂ electrodes.

To investigate the role of titanium dioxide in further detail, the combination of step potential electrochemical spectroscopy (SPECS) and electrochemical impedance spectroscopy (EIS) was also previously employed.²⁰ Modeling of the EIS data using an appropriate equivalent circuit²⁴ allowed characterisation of the charge transfer resistance (R_{ct}), charge buildup and mass transport processes occurring at each potential step during cycling. The first key finding of this work was that the modeled charge transfer resistance decreased substantially upon addition of titanium dioxide. As shown in Figure 6, the charge transfer resistance was not only lowered across the entire voltage range examined, but also remained relatively stable during cycling. If we consider

Figure 6. Variation in the charge transfer resistance as a function of cycling. Half-cycles are denoted C1 and C2 for charging, and D1 and D2 for discharging.

the two discharge half-cycles (D1 and D2) for the EMD electrode, we observe a buildup and then decrease in R_{ct} which correlates with the potential of the dominant reduction peak (see Figure 5). This behavior can be explained in terms of the energy barrier (to reduction) at the EMD surface. As the potential decreases we approach the region where bulk reduction occurs, and R_{ct} first increases, and then decreases once the applied potential is sufficiently negative to overcome this energy barrier. In this region, where R_{ct} is comparatively low, electron/proton pairs can more easily enter/leave the MnO_2 structure. The behavior of the 10% TiO_2 electrode is surprising in that R_{ct} remains lowered and relatively stable across the entire potential range. The observed drop in R_{ct} provides strong evidence for a favorable interaction of TiO_2 at the MnO_2 /electrolyte/graphite interface which allows electron/proton pairs to more easily enter/leave the MnO_2 structure, and in turn results in improved electrode performance.

The second key comes from a consideration of the mass transport processes occurring within both electrodes. By combining the impedance response under mass transport limited conditions (i.e., low frequencies) with the effective solid-state proton concentration we were able to determine $A\sqrt{D}$ values for both electrodes at each potential step.²⁰ The change in $A\sqrt{D}$ values as a function of applied potential and time is shown in Figure 7. As is clear from this figure, $A\sqrt{D}$ values increased during the charging half-cycles (C1 and C2), and decreased during the discharge half-cycles (D1 and D2). The behavior is typical of MnO_2 , with the swelling associated with reduction making the hop distance between adjacent sites too large for effective conductivity,^{29,30} and conversely, the contraction associated with oxidation improving conductivity (and hence proton diffusion). At first glance it is clear that the $A\sqrt{D}$ values are highest at the end of the first charge half-cycle (C1), but are lowered at the equivalent position at the end of the second charge half-cycle (C2). This inhibition of proton diffusion upon cycling is indicative of a change in the underlying material, such as a loss of underlying structural integrity,³¹ and is consistent with the cycling behavior of MnO_2 .³²

Comparing the two electrodes we see a strong correlation between the voltammetric behavior (in terms of the position of the dominant reduction process; see Figure 5) and the sharp decrease in $A\sqrt{D}$. Both electrodes are remarkably similar in behavior for the first charge-

discharge cycle, providing a strong indication that later variation in the 10% TiO_2 electrode arises from a change in the active MnO_2 material. During the latter stages of the first discharge half-cycle (D1) we observe a subtle change in the $A\sqrt{D}$ values for the 10% TiO_2 electrode. Subsequent charging (C2) reveals inhibition of proton diffusion, and this carries through to the second discharge. Given the solubility of Mn(III) in alkaline environments,³³ and the prolonged time at which the electrode is held at high levels of discharge, Mn^{3+} solubilisation would be expected to occur. In this manner, Ti(IV) associated with the EMD surface may exchange with soluble Mn(III) species and thus become incorporated in the bulk EMD structure. From a size perspective, the ionic radius of Ti^{4+} (60.5 pm) is quite similar to that of both Mn^{4+} (53.0 pm) and Mn^{3+} (64.5 pm), such that its inclusions would incur no additional structural strain.³⁴ Furthermore, the octahedral metal environment in the manganese dioxide structure also matches the preferred geometry of the Ti^{4+} ions.³⁴ Subsequent behavior is consistent with a progressive inclusion of Ti^{4+} ions, which act to disrupt the underlying lattice structure, resulting in the lowered $A\sqrt{D}$ values observed for this electrode. This secondary effect would be anticipated to reduce electrode performance; however, it appears that the significant lowering of R_{ct} by surface Ti^{4+} is sufficient to result in overall improved performance. While these effects were noted in our previous work,²⁰ we are now in a position to examine these further through the use of time-of-flight secondary ion mass spectrometry (ToF-SIMS).

ToF-SIMS analysis of the EMD surface.— To characterize the surface association of Ti(IV) species, along with the intercalation of Ti^{4+} ions into the $\gamma\text{-MnO}_2$ structure, the use of ToF-SIMS has been employed. Briefly, ToF-SIMS is a surface sensitive analytical technique used to image and record organic and inorganic mass spectral data of solid materials. It involves the analysis of ionized particles that are emitted when the surface is bombarded with an energetic primary ion beam. Emitted particles are accelerated to a constant kinetic energy before entry into the time-of-flight chamber, where mass separation is achieved according to mass-to-charge ratio. It is a highly surface sensitive technique, as only the secondary ions generated from the outer 10–20 Å region have enough energy to escape the surface for detection and analysis. In this manner qualitative surface chemistry analysis can be carried out and comparisons made between samples. Depth profiling can also be carried out by using the analysis beam in a phased profile with a sputter beam, and it was this approach which was employed to gather information of the incorporation of titanium; i.e., the longer the sputter duration the deeper the analysis.

Focusing on the EMD surface, a series of ToF-SIMS images were recorded for the EMD blackmix, 10% TiO_2 blackmix and cycled 10% TiO_2 blackmix. Shown in Figures 8a–8f are the total ion and Ti^+ ion ToF-SIMS images recorded for each sample prior to depth profiling. For the initial EMD blackmix (Figure 8a), an EMD particle ~40 μm in diameter is shown and is consistent with the SEM images presented in Figure 3. As a baseline comparison the Ti^+ ion image for this particle is also presented (Figure 8b), and as expected shows the absence of Ti(IV) in the blackmix. Moving to the uncycled sample containing TiO_2 , we observe a Ti^+ ion response consistent with an EMD particle covered with surface Ti(IV) (Figure 8d). This observation is consistent with both the electrode imaging/morphology studies, and the electrochemical behavior of the electrode prepared from this blackmix. With cycling a similar response is observed (Figure 8f); however, in this case the Ti(IV) species are more dispersed, consistent with its inclusion into both the porous and bulk EMD structure. Also of interest are the dark shaded regions present on the EMD particle shown in Figure 8e. These regions reflect graphite which has become associated with the surface during electrode construction and/or cycling. Interestingly, the corresponding Ti^+ ion image (Figure 8f) shows an absence of Ti(IV) in these regions. This indicates that Ti(IV) preferentially binds to the EMD surface, rather than the abundant graphite in the blackmix.

Figure 7. Comparison of calculated $A\sqrt{D}$ values for the EMD and 10% TiO_2 electrodes. Half-cycles are denoted C1 and C2 for charging, and D1 and D2 for discharging.

Figure 8. SIMS total ion and Ti^+ ion responses prior to depth profiling for the (a)-(b) EMD, (c)-(d) 10% TiO_2 , and (e)-(f) cycled TiO_2 blackmixes. N.B. scale bar = 10 μm .

Figure 9. ToF-SIMS depth profile data. ■ Normalized Mn^+ response, ◆ uncycled K^+ response, ◇ cycled K^+ response, ▲ uncycled Ti^+ response and △ cycled Ti^+ response.

As described earlier, depth profiles were obtained on a number of particles in each sample and the Mn^+ , Ti^+ and K^+ responses recorded as a function of sputter time. As a result of ion-ion interactions in the gaseous state and preferential sputtering resulting from particle topology, count numbers cannot be directly related to solid state concentrations and hence it was necessary to normalize the response. For

each depth profile recorded this was first carried out by normalizing the response relative to the total number of counts. To compare the response obtained for an uncycled versus cycled particle these values were then normalized to the average Mn^+ response and it is these values which are presented in Figure 9. In this manner we can compare the relative response for a single ion (either Ti^+ or K^+) to the baseline Mn^+ response which should be essentially constant irrespective of the sample. For the Ti^+ ion the depth profile obtained prior to cycling is consistent with the build up of Ti(IV) at the particle surface. After peaking early, the response drops off steadily as we move into the bulk structure. In contrast, the Ti^+ depth profile recorded after cycling is much larger in magnitude and first increases, then decreases, as we move into the bulk structure. The response obtained here is consistent with the incorporation of Ti(IV) into the bulk structure upon cycling, and thus provides clear evidence for the occurrence of this second process. Also shown in Figure 9 is the response for the K^+ ion, and in this case it is worth noting that the level of K^+ (coming from the electrolyte) also increases, with these results consistent with the K^+ ion insertion/surface film formation previously proposed by Minakshi et al.^{35,36} While not the focus of this work, this aspect of $\gamma\text{-MnO}_2$ chemistry in alkaline electrolytes is important given that the formation of this surface film of K^+ was reported to retard the usual electron/proton mechanism with further cycling.³⁶ This leads to the possibility that the Ti(IV) species present at the surface is inhibiting the formation of this K^+ containing surface film, and in this manner enabling the MnO_2 to retain its ability to intercalate protons and electrons in a facile manner.

Having considered the ToF-SIMS results we can conclude that during cycling TiO_2 contained in the blackmix (i) moves through the electrolyte, (ii) enters the microporous structure of EMD, and (iii) subsequently becomes incorporated into its bulk structure by replacing soluble Mn^{3+} ions. This latter notion is further reinforced by the ToF-SIMS images recorded after depth profiling (see Figure 10), in which Ti(IV) is both more prominent, and more dispersed, throughout the bulk structure of the cycled particle. For the uncycled particle the image is consistent with the presence of Ti(IV) throughout the porous EMD structure, whereas the

Figure 10. SIMS total ion and Ti^+ ion responses post depth profiling for the (a)-(b) 10% TiO_2 , and (c)-(d) cycled TiO_2 blackmixes. N.B. scale bar = 10 μm .

appearance of the cycled particle reflects the effect of the Ti^{4+} incorporation process.

Conclusions

In this work we have investigated the role of TiO_2 in improving cathode performance though the use of electrode imaging, porosity changes, electrochemical characterisation and changes in the chemical composition of constituent $\gamma\text{-MnO}_2$ particles. The use of SEM/EDX imaging provided evidence that TiO_2 is mobile in the electrolyte, with the solubilisation of TiO_2 allowing its movement to the $\gamma\text{-MnO}_2$ surface. A study of the porosity changes occurring upon equilibration of a mixture of TiO_2 and $\gamma\text{-MnO}_2$ showed that Ti(IV) not only moves to the $\gamma\text{-MnO}_2$ surface but also makes its way into the micro-porous structure of the material. Electrochemical cycling revealed that the presence of titanium dioxide results in improved electrode performance, both during primary discharge and in subsequent cycles. A detailed characterisation of the electrochemical behavior, carried out using the combination of SPECS and EIS, showed that the charge transfer resistance (R_{ct}) drops considerably ($\sim 75\%$) upon inclusion of TiO_2 . With TiO_2 shown to be present through the porous structure of the material, this demonstrates that the interaction of Ti(IV) at the MnO_2 surface enables electron/proton pairs to more easily enter/leave the MnO_2 structure. Additionally, this study revealed a change in bulk mass transport processes consistent with a progressive incorporation of Ti(IV) (in place of soluble Mn(III)) during cycling. While this latter effect inhibits proton diffusion in the $\gamma\text{-MnO}_2$ structure, the beneficial effects arising from Ti(IV) at the surface result in an overall improvement in performance. By employing time-of-flight secondary ion mass spectrometry (ToF-SIMS) we were able to conclusively observe both of these effects (i.e., the movement of Ti(IV) ions to the electrode surface, and their subsequent incorporation in the bulk $\gamma\text{-MnO}_2$ structure upon cycling) and thus understand the role which TiO_2 plays in improving electrode performance.

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