Electrochemical Impedance Spectroscopy Study into the Effect of Titanium Dioxide Added to the Alkaline Manganese Dioxide Cathode

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A combination of step potential electrochemical spectroscopy (SPECS) and electrochemical impedance spectroscopy (EIS) has been used to examine the effect of anatase titanium dioxide added to the alkaline manganese dioxide electrode. The inclusion of titanium dioxide was found to improve performance by lowering the resistance to charge transfer at the MnO₂/electrolyte/graphite interface. Furthermore, a consideration of mass transport processes within the electrode indicates that titanium ions may become incorporated into the γ -MnO₂ lattice upon cycling, impacting H⁺/e⁻ mass transport.
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Energy storage in consumer electronics.—Modern society is increasingly saturated by the presence of portable electronic devices, and it is these which form the backbone of a massive consumer electronics industry. The growth of this industry has been enabled by, and is dependent on, the development of high energy and power density energy storage devices. Batteries are the leader in this domain because of their portability, reliability and excellent performance under a wide variety of conditions. Indeed for small-scale devices, batteries are the power source of choice, resulting in global battery sales exceeding \$10 billion per year. By far the most popular battery system (in terms of cell numbers) in use is the alkaline Zn/MnO₂ system. Its dominance in terms of market share arises from its low cost and strong performance in a wide variety of applications. However, this system suffers from the limitation that it is generally regarded as a primary system. Disposal of the large volume of spent cells entails a significant, and undesirable, contribution to worldwide landfill. To address this, it is desirable to make the system rechargeable. In this manner it is possible to improve energy efficiency (and material utilization) while maintaining the strong performance characteristics of the system.

The alkaline manganese dioxide electrode.—The excellent performance of the alkaline Zn/MnO₂ system is due in part to the manganese dioxide cathode. This cathodic material can exist in a variety of structural forms;¹ however, the structure preferred for use in alkaline media is γ -MnO₂, which is best regarded as a microscopic intergrowth between the pyrolusite and ramsdellite forms of manganese dioxide, as shown in Fig. 1.^{2–4} Additional structural features include cation vacancies, lower valent manganese ions (particularly Mn³⁺), structural water (present as protons to accommodate absent of lower valent manganese species^{5–7}), and possibly microtwinning,⁸ although there is still debate as to its presence.⁹ Chemically, the structure can therefore be defined as

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

The basis for the currently accepted discharge mechanism of manganese dioxide in an alkaline environment was proposed originally by Kozawa et al.,^{10–14} and further refined by others.^{15–20} 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. The discharge mechanism can therefore be summarised by

It is important to note that the position of individual ionic species (Mn⁴⁺, Mn³⁺, O²⁻, OH⁻) within the lattice is not fixed, with proton and electron movement tending towards a homogeneous distribution of inserted species.¹⁸ Additional complexity in the single electron discharge behaviour arises as a result of the presence of Mn⁴⁺ ions in different structural domains which gives rise to the appearance of a number of individual processes during discharge.⁸ The sequence of domain reduction has been the subject of intensive research, and is currently believed to consist of defect regions and surface sites at high voltages, followed by ramsdellite domains, and finally pyrolusite domains at the lowest voltages.⁸ Work is currently ongoing in this area with the aim of furthering knowledge into both the underlying mechanistic model, and the complex interplay between material properties and electrochemical performance.

Rechargeability.—A number of attempts have been made, with some commercial success, to make the alkaline manganese dioxide cathode rechargeable. These efforts have involved the use of different manganese dioxide phases (γ -MnO₂ and birnessite),^{18–20} controlling depth of discharge (DOD),^{21–25} and the inclusion of foreign cations (such as Bi³⁺, Pb²⁺, Ti⁴⁺ and Ba²⁺).^{26–30} The use of γ -MnO₂ is of particular interest given that the insertion/extraction of protons during discharge/charge is to a certain degree reversible if the DOD is controlled (<0.5 e⁻/Mn).²⁵ Indeed commercially viable cells have been developed based of this idea of limited DOD, in this case achieved by controlling the amount of Zn in the anode.^{21–24} However, if discharge is allowed to proceed beyond 0.5 e⁻/Mn the system is no longer reversible and a steady decline in capacity occurs with cycling. It is this steady decline in capacity which limits the service life of these cells and represents the major drawback of this system.

Previous studies have shown that the inclusion of foreign cations (such as Bi³⁺, Ba²⁺ and Ti⁴⁺) in the form of oxides are capable of suppressing this secondary capacity fade, along with improving overall discharge performance.^{26–30} Mechanistically, in the case of bismuth or barium, these effects have been linked to interactions which occur in the soluble state.^{26,27} Specifically, the interaction between soluble negatively charged [Mn(OH)₆]^{3–/4–} species and positively charged [Bi₆(OH)₁₂]⁶⁺ clusters has been proposed to underlie these effects by preventing the formation of electrochemically inactive

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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 .

phases (such as hausmannite and birnessite). In the case of titanium (IV), its beneficial effects upon cyclability have also been reported in the literature.^{28–30} Its use has been investigated both in the form of chemically modified electrolytic manganese dioxide (EMD) (Ref. 28) and as a chemical additive into the manganese dioxide cathode.^{29,30} In both cases the inclusion of the Ti^{4+} cation improved cathodic performance, although the mechanism underlying its role requires further investigation.

This work.—In this work the effect of the inclusion of anatase titanium dioxide into the γ - MnO_2 cathode will be investigated in terms of its impact and role in improving rechargeable performance. Electrochemical cycling will be used to compare the performance of a standard γ - MnO_2 electrode to that of an electrode doped with titanium dioxide. Subsequently, an in-depth characterisation of electrochemical behaviour upon cycling will be carried out using the combination of step potential electrochemical spectroscopy (SPECS) and electrochemical impedance spectroscopy (EIS).

Experimental

Materials.—The electrolytic manganese dioxide (EMD) used in this work was produced 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- $105\text{ }\mu\text{m}$ powder (mean particle size of $\sim 45\text{ }\mu\text{m}$), neutralised 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 -crystal structure (X-ray diffraction using $\text{Cu K}\alpha$ radiation),⁸ had an x in MnO_x value of 1.95,³¹ a cation vacancy content of 0.07 (Refs. 5–7) and a BET surface area (N_2 adsorption at 77 K) of $37.2\text{ m}^2/\text{g}$.³² The anatase titanium dioxide used was a commercial material sourced from Sigma Aldrich ($>98\%$).

Electrode preparation.—The EMD working electrode used in the electrochemical cell was prepared by mixing together the manganese dioxide sample (0.2 g), Timcal SFG 6 graphite (2.0 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 (0.2 g) mixed with Timcal SFG 6 graphite (2.0 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.

Figure 2. Schematic of assembled electrochemical cell.

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 min. A perforated Perspex separator disc was then placed onto the electrode and a stainless steel counter electrode sleeve slid into place. The chamber was then filled with ~ 10 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 three securing bolts that were each tightened to a torque of 75 cNm to ensure a uniform pressure. Finally, a Hg/HgO reference electrode was inserted into the cell, which was then allowed to equilibrate for 60 min prior to cycling. A schematic of the cell can be found in Fig. 2.

Electrochemical protocol.—The electrochemical performance of both types of electrode 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 V . 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.

A more detailed analysis of the cycle stability was conducted using a combination of step potential electrochemical spectroscopy (SPECS) and electrochemical impedance spectroscopy (EIS), carried out using the combination of a Solartron 1254 Frequency Response Analyser and a Solartron 1287 Electrochemical Interface controlled by ZPlot software. Initially, the voltage was stepped from the OCV to 0.1 V and the cell allowed to equilibrate for 60 min. After this an impedance spectrum on the electrode was measured using the frequency range 20 kHz–0.1 Hz with a 10 mV excitation signal. The voltage was then stepped in the anodic direction 25 mV, the electrode again allowed to equilibrate for 60 min, and a further impedance spectrum recorded. This sequence was repeated to the upper limit (0.3 V), down to the lower limit (-0.3 V), and then back up and down, giving a total of two full cycles. The resultant impedance spectra were then interpreted using an appropriate equivalent circuit (to be described later), which was fitted to the data using complex non-linear least squares (CNLS) regression, as used in the ZView software package.

Results and Discussion

Voltammetric cycling.—Voltammetric curves for the standard EMD electrode and the 10% TiO_2 electrode (Ti-EMD) are shown in Figs. 3a and 3b, respectively. During initial charging both electrodes

Figure 3. Cyclic voltammograms recorded for the (a) EMD and (b) 10% TiO₂ electrodes.

behaved similarly, although an increase in the open circuit voltage (from 0.091 to 0.099 V) was noted for the TiO₂ containing electrode. Upon primary discharge the 10% TiO₂ electrode exhibited a high energy process at 0.080 V (not observed for EMD) which may arise from changes to the EMD surface due to the presence of adsorbed TiO₂. As discharge continued, variation in the position of the dominant reduction process was observed (shifted from -0.158 to -0.147 V in the presence of TiO₂), along with a significant increase in the primary discharge capacity (219 mA.h/g vs. 192 mA.h/g, respectively). Despite these differences during primary discharge, the 10% TiO₂ electrode tended towards the behaviour of the EMD electrode upon cycling. This was evident in the voltammetric behaviour as early as the second cycle (see Fig. 3) and further cycling only reinforced this tendency.

In terms of common features, a high energy process (0.094 V) was noted to emerge during the second discharge (in both cases) and remained throughout further cycling. In this case its emergence replaced the previous high energy process noted for the 10% TiO₂, and likely results from the mechanical breakdown of EMD particles during cycling, and hence the increased number of higher energy surface sites. Comparing secondary discharge behaviour, the

dominant reduction process was reduced in capacity, broader and shifted to a lower voltage (-0.188 V). This was further reflected in a noticeable drop in overall capacity in both cases (Fig. 4). With further cycling, a continued broadening of this process, and steady decrease in overall discharge capacities was observed. Also of note is that the dominant reduction process was observed to resolve into at least two underlying processes with cycling, with these processes likely reflecting reduction occurring within different structural domains (i.e., ramsdellite and pyrolusite domains), as described earlier. The voltammetric behaviour observed here indicates that the inclusion of titanium dioxide into the electrode alters both the surface (at least during primary discharge) and bulk properties (shifting the dominant reduction process) of the EMD, resulting in improved electrode performance. To investigate this further in-depth characterisation, employing a combination of SPECS and EIS, was carried out.

EIS characterization.—Identical electrodes as were used to evaluate voltammetric performance were subjected to the combination of SPECS and EIS electrochemical methods, as described in the Experimental. The use of this combination of techniques enables a wealth of information to be gathered on the underlying processes which occur during electrochemical cycling.³³ Sample EIS spectra recorded at -0.20 V (during discharge) for both electrodes are shown in Fig. 5. Briefly, the spectra show a semi-circular arc at high frequencies which tails off to much higher impedance values at lower frequencies. Comparing the EMD and 10% TiO₂ electrodes, it is clear that the electrode behaviour has been modified substantially by the inclusion of TiO₂. Furthermore, the behaviour upon secondary discharge is noted to be similar to that of primary discharge. This observation is consistent with a quasi-reversible system, such as the one examined, and was noted for both electrodes.

Modelling of EIS data.—To quantitatively understand the observed EIS behaviour, an equivalent circuit approach based on a physical understanding of underlying electrochemical processes was developed. This was achieved by taking into account the various paths charge traverses through each electrode, considering both charge build up at the interface and the act of charge transfer. To begin, the movement of charge to the electrode surface needs to be considered. Primarily this occurs by charge transport through bulk electrolyte (R_e), in combination with a solid state contribution due to charge transport within the porous electrode (R_m). Overall, this process can be readily represented by a series resistance (R_s). As this is the only path available for charge transport it will be in series with all the other equivalent circuit elements.

Once the ionic charge in the electrolyte reaches the EMD surface, one of two options become available. Firstly, charge transfer can take place, such that during the cathodic portion of the applied ac signal the homogenous reduction of γ -MnO₂ occurs. The details of this process have been described earlier, but it is important to

Figure 4. Discharge capacities as a function of cycle number for examined electrodes.

Figure 5. Sample electrochemical impedance spectra taken at -0.2V during 1st and 2nd discharge cycles for the EMD and 10% TiO_2 electrodes.

note that for meaningful data to be obtained charge transfer needs to be reversible over the voltage window imposed by the ac signal. In the case of EMD based electrodes this assumption is reasonable,³⁴ and allows the charge transfer process to be represented by a resistance (R_{ct}).

The alternative process, modelled in parallel with R_{ct} , is for ionic charge in the electrolyte to remain at the interface and contribute to the establishment of a double-layer capacitance. In the case of EMD, with its combination of variable surface composition, roughness and porosity, the formation of numerous intersecting double layers is anticipated. As a result, different regions of the EMD surface will have different intrinsic capacitances, resulting in a distribution rather than a single capacitance value. To account for this non-ideal capacitance, a constant phase element (Z_{CPE}) is often employed^{34–36}; i.e.

$$Z_{CPE} = \sigma \omega^{-m} \left\{ \cos\left(\frac{m\pi}{2}\right) - j \sin\left(\frac{m\pi}{2}\right) \right\} \quad [3]$$

where σ is the CPE prefactor ($\Omega \text{ s}^{-m}$), m the exponent, and ω the angular frequency (rad/s). Once protons and electrons have been inserted into the $\gamma\text{-MnO}_2$ structure, a diffusional aspect to their behaviour must also be considered, with this becoming most evident at low frequencies. Specifically, during the impedance measurement a frequency is reached where the kinetics of mass transport are the limiting factor in the impedance response. As a means of accounting for this, a second constant phase element (CPE2) will be employed in series with R_{ct} , giving rise to the equivalent circuit shown in Fig. 6. The development of this equivalent circuit model accounts for a single semicircular arc and a low-frequency diffusion tail; readily fitted to the recorded data (Fig. 6). This, combined with a series resistance (R_s), composed of electrolyte (R_e) and solid state (R_m) contributions, is best regarded as a modified Randles circuit.³⁷

Figure 6. Equivalent circuit model employed in EIS analysis.

Figure 7. Variation in the charge transfer resistance (R_{ct}).

To obtain the optimized values for the equivalent circuit components compared to experimental data a complex non-linear least squares (CNLS) regression technique was employed. This method was proposed initially by Boukamp,^{38,39} and involves simultaneously fitting the real and imaginary components of the impedance, predicted from the equivalent circuit, using the expression

$$S = \sum_i w_i [\{Z'_i - Z'_i(\omega)\}^2 + \{Z''_i - Z''_i(\omega)\}^2] \quad [4]$$

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

$$w_i = \frac{1}{|Z_i^*|^2} \quad [5]$$

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

Parameter variation.—Having recorded EIS spectra for the first two full-cycles of both electrodes and modelled the response using an appropriate equivalent circuit model, we can now examine how each of the equivalent circuit parameters changes with cycling. Firstly, due to the presence of a large excess of conductive graphite in both electrodes, the series resistance (R_s) essentially reflects variability in electrode construction. For both electrodes R_s was found to be relatively stable across the entire voltage range, with values of 0.61 ± 0.04 and $0.65 \pm 0.04 \Omega$ obtained for the EMD and 10% TiO_2 electrodes, respectively. The similarity in obtained R_s values indicates that electrode construction is reproducible, and as such any observed variation in equivalent circuit components can be confidently assigned to intrinsic differences between the electrodes, rather than reflecting variability in electrode construction.

The modelled charge transfer resistance (R_{ct}) is shown in Fig. 7, and shows a dramatic reduction ($\sim 75\%$) in the presence of titanium

dioxide. In both cases the electrodes contain an abundance of electroactive species (in this case protons from the electrolyte and electrons from the graphite) in close proximity with EMD particles. Under these circumstances, the path which protons and electrons must traverse for reduction to occur is relatively short, and, in the case of electrons, highly conductive. As such, R_{ct} is best considered as representing the energy barrier that must be overcome at the MnO_2 /electrolyte/graphite interface for reduction to occur. The observed drop in R_{ct} indicates that the TiO_2 interacts favourably at this junction, resulting in a facilitation of the charge transfer process. In terms of electrochemical behaviour (see Fig. 3) this explains the shift in the dominant reduction process to higher voltages upon inclusion of TiO_2 , with a lower energy barrier shifting the process by increasing its kinetic facility.

The next circuit component to be considered is that of CPE1, in this case representing the build up of charge at the electrode-electrolyte interface in the form of a double-layer capacitance. As introduced previously, the nature of the MnO_2 particle surface (with its combination of variable surface composition, roughness and porosity) requires the use of a constant phase element. However, modelling using a constant phase element yields two parameters (σ and m) which must first be combined to yield a single value representative of the double layer capacitance (C_{dl}) at that voltage. This can be achieved using Ref. 40

$$C_{dl} = \frac{1}{\sigma} (\omega_{max})^{m-1} \quad [6]$$

where σ is the CPE pre-factor, m the exponent and ω_{max} the frequency corresponding to the maximum imaginary impedance in the semi-circular arc.

Treating the parameters in this manner yields values for the double layer capacitance, shown for the discharge half-cycles of both electrodes in Fig. 8. In the context of this electrode-electrolyte system, in which the surface of the EMD will be saturated with K^+ ions from the 9 M KOH electrolyte,⁴¹ the double layer capacitance refers to the accumulation of electrolyte ions, electrostatically attracted to the EMD surface, but not bound as surface ions. In the case of the EMD electrode the capacitance was observed to decrease initially, and then build up as discharge progressed. This behaviour can be explained by considering both intrinsic changes to the EMD

surface (i.e., specific capacitance, $\mu F/cm^2$), along with changes in surface area during discharge. Initially, as the voltage is swept in the cathodic direction, the double layer capacitance slowly decreases as reduction occurs and the BET surface area decreases.⁴¹ Here it is appropriate to mention that the BET surface area and the electrochemically active surface area of the EMD may not be the same value, and not undergo similar changes with discharge. However, in the absence of a better measurement, this is the best indication available of how the surface area will change with depth of discharge. As discharge proceeds towards 0 V bulk reduction processes begin and a steady build up of charge occurs due to kinetic limitations associated with charge transfer. During the second discharge half-cycle the capacitance values were all shifted to slightly higher values, indicating that the nature of the electrode surface had been intrinsically altered by the redox process. Furthermore, upon reaching 0.15 V the capacitance increased sharply, peaked, and then followed the behaviour of primary discharge. Interestingly, this behaviour correlates with the emergence of the high energy processes observed during electrochemical discharge, and indicates that bulk mechanical breakdown during cycling results in an EMD surface which allows a greater build up of charge.

For the TiO_2 -modified electrode the behaviour is initially similar to the standard EMD material (Fig. 8). Both electrodes begin with a similar capacitance, which decreases as the voltage is swept in the cathodic direction. However, upon reaching 0.15 V the behaviour varies for the TiO_2 -modified electrode, with the capacitance peaking, and then levelling out as discharge continued. The emergence of this peak in capacitance during primary discharge correlates with its electrochemical behaviour, previously assigned to surface interactions. As discharge continued, the plateau in capacity indicates that less charge is building up at the electrode surface. This can be explained by considering the previously observed R_{ct} values. With lower values obtained for the charge transfer resistance we expect less charge to build up at the surface, with charge transfer occurring more readily, and this correlation between R_{ct} and C_{dl} provides strong evidence that surface TiO_2 acts to facilitate charge transfer into the bulk EMD structure. During the second discharge half cycle the capacitance values are shifted in a similar fashion to that observed for the standard EMD electrode. Having considered both the charge transfer and charge build up as they occur as a function of cycling, a focus will now be made of the nature of mass transport processes within the electrodes.

Mass transport processes.—The diffusional processes occurring within the electrode also need to be considered in terms of the nature of the impedance response under diffusion limited conditions and the modelled CPE2 parameter values. During the impedance experiment a frequency is reached at which point the impedance response becomes mass transport limited. As the experiment continues, and the frequency continues to decrease, this gives rise to a steadily increasing impedance response or diffusional tail (as shown in Fig. 5). This diffusional tail reflects limitations in the diffusion of protons within the bulk γ - MnO_2 structure, and under the assumption of semi-infinite diffusion is related to the modelled impedance response according to the following equation (Ref. 40)

$$A\sqrt{D} = \frac{RT}{\sigma F^2 \sqrt{2} [H^+]} \quad [7]$$

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

As the electrochemically active surface area is not known with certainty,⁴² and likely changes during cycling,⁴¹ mass transport within the electrode is best considered in terms of $A\sqrt{D}$ values. In order to calculate these values it is first necessary to determine the effective solid-state proton concentration ($[H^+]$) at each step during

Figure 8. Comparison of the calculated double layer capacitance values during discharge for the EMD and 10% TiO_2 electrodes.

Table 1. Unit cell volume change with reduction (Ref. 41).

x in MnO _x	r in MnOOH _r	Unit cell volume (nm ³)	[H ⁺] ($\times 10^3$ mol/m ³)
1.97	0.06	0.121	0.33
1.87	0.26	0.124	1.39
1.79	0.42	0.128	2.18
1.76	0.48	0.128	2.49
1.63	0.74	0.130	3.79
1.58	0.84	0.134	4.17

cycling. To determine these values it is necessary to know both the degree of reduction (readily determined from the amount of charge passed) and the unit cell volume at each voltage step. The changes which occur in the unit cell volume during reduction of γ -MnO₂ have been previously reported by Malloy and Donne,⁴¹ and by making use of these values [H⁺] was determined for certain x in MnO_x values (as shown in Table I), and the following relationship established

$$[H^+] = -23501x^2 - 15888x + 125760 \quad [8]$$

In this manner $A\sqrt{D}$ values were determined at each voltage step and are shown in Fig. 9. In terms of electrode behaviour, it was generally observed that $A\sqrt{D}$ values increased during the charging half-cycles, and decreased during the discharge half-cycles. This implies that oxidation of the material results in improved proton diffusion, whereas reduction (by swelling the structure and making the hop distance between adjacent sites too large for effective conductivity^{43,44}) results in poorer proton diffusion. During the first discharge half-cycle a steady decrease in $A\sqrt{D}$ values occurs until about -0.075 V; after which the values drop off dramatically. This initial steady decrease is best assigned to losses in electrochemically active surface area upon reduction (as previously reported in terms of losses in BET surface area⁴²), while the dramatic drop off is a reflection of the voltage range appropriate to the dominant reduction process. In line with this, we observe a correlation between the

Figure 9. Comparison of calculated $A\sqrt{D}$ values for the EMD and 10% TiO₂ electrodes.

voltammetric data (in terms of the position of the dominant reduction process; see Fig. 3) and the sharp decreases in $A\sqrt{D}$.

A similar pattern occurs during the second discharge half-cycle, except that in this case $A\sqrt{D}$ values are steady within the initial region (0.3 to -0.05 V), and the drop occurs earlier (and less severely) than in the initial discharge. Interestingly, the behaviour of the two electrodes is comparable for the first charge-discharge cycle (indicative of consistent electrode construction), but further cycling results in $A\sqrt{D}$ values which are consistently lower in the presence of titanium dioxide. Furthermore, it is noted that the drastic drop in $A\sqrt{D}$ values upon reduction occurs earlier in the case of the 10% TiO₂ electrode. While the slight shift which occurs during the first discharge half-cycle can be explained in terms of surface titanium (as outlined in the previous section), the clear variation in values with further cycling implies incorporation of titanium into the γ -MnO₂ lattice. At this point we propose that during reduction the titanium adsorbed at the EMD particle surface enters the lattice in place of soluble Mn(III) ions.⁶ In this manner we get a progressive inclusion of Ti⁴⁺ ions which disrupts the underlying lattice structure, resulting in an altered hop distance between cations, inhibiting the mass transport of H⁺/e⁻ pairs.

Summary and Conclusions

In this work we have combined the electrochemical techniques of step potential electrochemical spectroscopy (SPECS) and electrochemical impedance spectroscopy (EIS) to characterize the quasi-equilibrium electrochemical behaviour of an alkaline manganese dioxide electrode modified by the inclusion of titanium dioxide. Electrochemical cycling revealed that the presence of titanium dioxide alters both the nature of the γ -MnO₂ surface (by inducing reduction of near surface cations) and improves the kinetics associated with single electron reduction to δ -MnOOH (by shifting the position of the reduction processes). Modelling of the EIS data allowed characterisation of the charge transfer, charge build-up and mass transport processes occurring within both a standard EMD electrode, and one modified by inclusion of titanium dioxide. The key findings were:

- (i) The inclusion of titanium dioxide resulted in a drop in the charge transfer resistance (R_{ct}) by approximately 75% across the entire voltage range examined. This occurred consistently during both cycles examined and indicates that the favourable interaction of TiO₂ at the MnO₂/electrolyte/graphite interface facilitates charge transfer processes.
- (ii) By lowering the resistance to charge transfer (and allowing electron/proton pairs to more easily enter/leave the MnO₂ structure) the presence of TiO₂ alters the nature of charge build up at the MnO₂ surface. Specifically, at lower voltages the double layer capacitance remains stable in the presence of TiO₂ rather than steadily increasing (as with the standard electrode).
- (iii) As cycling progresses it appears that titanium ions (present at the MnO₂/electrolyte/graphite interface) become incorporated into the γ -MnO₂ lattice. The effect of titanium inclusion is an alteration in mass transport processes with the electrode, resulting in lowered proton diffusion due to distortion of the underlying lattice structure.
- (iv) Overall the inclusion of TiO₂ has been shown in our work and the literature to improve the cyclability of the alkaline manganese dioxide cathode.²⁸⁻³⁰ The results presented here therefore indicate that it is the reduction in charge transfer resistance is the dominant factor underlying performance improvements, rather than the solid state inhibition of proton diffusion which would be expected to negatively impact on performance.

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