Comparison of pH 6 potentials, alkaline potentials and initial open circuit voltages of electrolytic MnO$_2$

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Abstract

The alkaline battery industry typically reports three electrolytic MnO$_2$ (EMD) potentials: alkaline potentials, pH 6 potentials, and initial open circuit voltages (IOCV). These measurements differ with the electrolyte, the reference electrode, and the cathode composition. Despite such physical differences, theoretical relationships exist between the electrolytic potentials that are verifiable by experiment. The calculated difference (alkaline potential − pH 6 potential) is 0.785 V, which compares favourably with the experimental value of 0.795 ± 0.003 V. Another difference (alkaline potential − IOCV) depends on carbon-induced EMD reduction, which varies with EMD type and graphite:EMD ratio. After determining the carbon effect experimentally and graphically estimating [ZnO$_2^{2-}$], (alkaline potential − IOCV) was calculated as −0.045 V. This is roughly 60 mV from the experimental value of +0.017 V. Our analysis shows that when the differences in electrolyte and cathode compositions, and reference electrodes, are accounted for, the three EMD potentials are equivalent.

List of symbols

$E\{r/o\}$	electrode potential for redox couple r/o (reductant/oxidant) with respect to the standard hydrogen electrode
$E^0\{r/o\}$	standard electrode potential for redox couple r/o; electrode potential at (chosen) standard state
f_x	mole fraction of x
F	faradaic constant (96 487 C mol^{-1})
m_x	molality of species x
M_x	molarity of species x
$(pH)_z$	pH in test z
R	gas constant (8.309 J K^{-1} mol^{-1})
T	absolute temperature (K)
γ_x	activity coefficient of species x

Symbols

(z)	activity of species z
$[z]$	concentration of species z

1. Introduction

The most important performance features of EMD in Zn–MnO$_2$ cells are the discharge capacity and IOCV. Numerous studies relate discharge performance at various rates to EMD physicochemical properties and deposition parameters [1–4]. Although less frequently cited than the capacity, battery manufacturers typically include alkaline potential in their specifications. Published results [1, 5–7] establish that EMD IOCV correlates with discharge capacity over a wide range of discharge rates and battery cutoff potentials, including Leclanché (ZnCl$_2$/NH$_4$Cl) and alkaline (KOH) electrolytes. Recent patents from different laboratories teach EMD equilibrium potentials are indicators of high-rate performance in alkaline cells [8, 9]. High-rate discharge capacities and energies of AA batteries and laboratory alkaline cells are greatest for EMDs that yield the

highest IOCV in 9 M KOH [8]. Manganese dioxide with low potassium impurities and a pH 6 (Leclanché-type) potential exceeding 0.860 V yields unexpected high-rate discharge improvements in alkaline cells [9]. The above studies employed several EMD cathode formulations, varying the percentage and sometimes the type of carbon, and this factor requires definition.

We compared theoretical and experimental EMD potentials measured by three common procedures from the battery community: pH 6 (Leclanché) potentials [9]; alkaline potentials, that is, initial open circuit voltages [8]; and an alternative alkaline potential employed by EMD suppliers and specified by battery manufacturers. EMD thermodynamic models and literature data were the bases for calculation of theoretical potentials. Measuring the potentials of various EMDs by the three cited methods and calculating the theoretical potential differences allow a comparison of these differences that validates the experimental work.

2. Experimental tests and procedures

2.1. Potential determination

2.1.1. pH 6 potential [9]
A cathode mixture of EMD and battery grade graphite (Union Carbide, Cleveland, OH; EMD/C = 3/1) was ground to −200 mesh and pressed onto cloth. Cathode construction involved rolling the impregnated cloth face-in onto a carbon (rod) current collector and attaching it firmly with elastic bands. We measured (test) electrode potentials against a calomel reference electrode (Hg_2Cl_2/Hg in saturated KCl solution) in a $ZnCl_2$–NH_4Cl electrolyte at pH 6.0, after equilibrating the system for 18–24 h. We further normalized this experimental potential to an internal EMD standard monitored daily, and referenced it to the standard hydrogen electrode (SHE) at the test temperature through conversion tables or graphs.

2.1.2. IOCV [10]
A 9.0 M KOH electrolyte was prepared from AR–KOH pellets (<0.5% K_2CO_3) dissolved in deionized water. Specific gravity was monitored as a function of temperature, and the concentration adjusted as required. A sealed container minimized CO_2 absorption.

EMD was blended with Timcal KS-44 graphite and 9 M KOH to make an electrode paste with the proportions EMD:graphite:base = 22:65:13 (by weight). This cathode mixture was aged overnight. Electrodes were prepared by pressing 4.6 g of the mix into a plastic cell with a steel bottom (current collector). After placing a separator on the cathode paste, we filled the cell with the KOH electrolyte and placed a Zn wire anode in the middle. Roughly 3.5 h equilibration at 22 °C insured a stable IOCV measurement.

The anode reacts with the strong base during equilibration, forming zincate ions (ZnO_2^{2-}), which remain in solution adjacent to the Zn; thus, the reference couple is Zn/ZnO_2^{2-}. Quality protocols dictated referencing and normalizing results to an internal EMD standard tested with each batch of EMD. Thus, the relative and absolute IOCVs are closely related.

2.1.3. Alkaline potential
This test is similar to the IOCV protocol, with two significant differences: (i) the electrolyte contains a fixed concentration of ZnO_2^{2-} and (ii) the cathode incorporates a different EMD–carbon composite. In this procedure, the EMD/graphite–Zn potential difference is measured at 20 °C using a ~5.3 M KOH/ZnO electrolyte (659 g KOH and 40.0 g ZnO in 2.000 L solution). Cell construction proceeds by laying a separator on a Zn strip, wetting both with electrolyte, spreading EMD–KOH slurry on the separator, and pressing the slurry against the separator with a graphite disc current collector. Electrochemical measurements were at 20 °C.

2.2. EMD sampling

Three types of EMD manufactured by Kerr-McGee Chemical LLC are the basis for this study: AB grade, a standard alkaline battery cathode material; HD grade, for rapid-discharge cells [8]; and HSA grade, for primary lithium batteries. Differences in surface area and electrochemical capacity, as listed in Table 1, characterize these three EMD varieties. (Briefly, capacity is measured with an IOCV test cathode discharging at 20 mA g^{-1}-EMD to a cutoff voltage of 1.0 V vs Zn. See [10] for a complete test description.) A Quantachrome Autosorb 6 measured surface areas after out-gassing the samples in vacuum at 150 °C for 7 h.

Nine samples were examined in the tests/EMD grades of pH 6/HD and IOCV/HSA, and two samples were employed for the tests Alkaline/HSA and pH 6/HSA. All other tests included more than 50 EMD samples. Standard process controls insured prompt measurement of potentials from AB and HD samples manufactured in 2000 or 2001. The HSA samples were from lots produced in the 1990s, but their alkaline and pH 6 potential measurements are contemporary. The IOCVs of the HSA samples were determined within a few months of EMD manufacture. We consider comparison with the more recent measurements of AB and HD EMD samples valid due to the use of two internal standards with every set of experimental samples. These standards yielded the same relative value of IOCV both in the 1990s and in 2000/01, varying only within the 10 mV ($\pm 3\sigma$) control range.

Table 1. Capacity and surface area of EMD grades

EMD grade	Capacity /mAh g^{-1}	Surface area /m^2 g^{-1}
HD	257	23 ± 2
AB	252	31 ± 3
HSA	244	46 ± 4
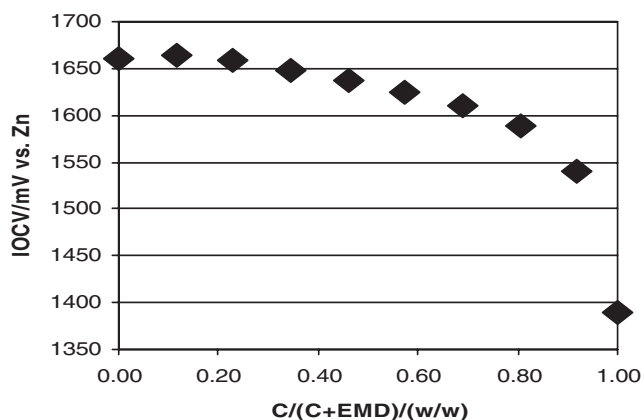
Fig. 1. AB EMD IOCV variation with cathode graphite content.

Table 2. Equilibrium potentials for different test methods and EMD grades

EMD grade	pH 6 potential /V vs SHE	IOCV /V vs Zn	Alkaline potential /V vs Zn
HD	0.875	1.633	1.669
AB	0.839	1.620	1.637
HSA	0.805	1.600	1.597

Table 3. Differences between various potentials and EMDs

Type of EMD	Alkaline − pH 6 /V	IOCV − pH 6 /V	Alkaline − IOCV /V
HD	0.794	0.758	0.036
AB	0.798	0.781	0.017
HSA	0.792	0.795	−0.003

Equivalent samples of each EMD type were drawn from lots manufactured under identical conditions, within production parameters. The small variation in BET surface areas reflects batch-to-batch consistency (Table 1). Also, the measured potentials for the various samples from each EMD grade were identical within the precision of the methods. The standard deviations for all determinations were <5 mV except for the pH 6 potential of HSA EMD, which was 20 mV. This larger value reflects both the greater imprecision of the pH 6 method and the small test population.

2.3. *Effect of cathodic carbon loading*

Each potential measurement described above utilizes positive electrodes with different graphite:EMD ratios, specifically 1:3 for the pH 6 test, 3:1 for the IOCV procedure, and 0 for the alkaline test. Results of IOCV tests quantified the dilution effect, wherein graphite lowers EMD potential (Figure 1). The ratio of graphite:EMD was varied between 0 and ∞, while the 9 M KOH solution remained fixed at 13 wt % of the electrode. Positive electrodes contained 4.60 g of cathode mix (EMD–graphite–KOH solution), and evaluations were in triplicate.

3. Experimental results

3.1. *Equilibrium potentials*

Table 2 presents the mean potentials for all test/EMD types, and Table 3 summarizes the differences between these means. These seemingly disparate data were examined and proved equivalent.

Potentials within each type of test increase in parallel with EMD electrochemical capacity, in the order HSA < AB < HD. This order is statistically significant, based on the standard deviations of all the potential measurements. This same grade order gives rise to a slight increase in (alkaline – IOCV) potential, and a slight corresponding decrease in (IOCV – pH 6) potential.

The dissimilarities in potential are dependent on the test, not the EMD grade. For pH 6 and alkaline potentials, the differences (HD-AB) and (AB-HSA) are 30–40 mV, and somewhat less (10–20 mV) for IOCVs (Table 2). From Table 3, the variations in potential differences are nearly independent of sample type. This is especially true for the (alkaline – pH 6) potentials, but more diverse for relationships involving IOCV. The difference between alkaline potential and IOCV is logically small, since both tests utilize a Zn reference electrode and similar electrolytes. This discrepancy is real, however, and is a function (at least in part) of the graphite loading in the EMD–carbon cathode mix, as detailed below.

3.2. *Effect of cathodic graphite on IOCV*

Figure 1 depicts the IOCV of AB grade EMD as it varies with the weight fraction of graphite in the dry cathode mix (KOH content is constant and omitted for clarity). The maximum IOCV is 1.665 V with 11.5% graphite/EMD, equal within experimental error to the 1.660 V measured with no graphite. From its zenith, IOCV decreases at ~1 mV per percent, to 70% graphite loading, where the IOCV decline accelerates to a final value of 1.390 V (100% graphite vs Zn). EMD reduction by carbon surface functional groups at the cathode graphite–electrolyte interface lowers the IOCV. Since the alkaline test uses no cathodic graphite and the pH 6 test employs only 25% carbon, the calculated error introduced by ignoring this carbon effect is ⩽5 mV and considered negligible. For a dry cathode mix that contains 75% graphite [8, 10], as done in this work, the estimated potential from Figure 1 is 1.60 V.

We assigned the true IOCV of EMD to the maximum measured potential; graphite in the standard test [10] lowers the IOCV by 60 mV, as interpolated from Figure 1. In turn, this 1.60 V potential is a mixed potential, determined by EMD reduction and graphite oxidation. The potential differences (IOCV – pH 6) and (alkaline – IOCV) listed in Table 3 reflect kinetic

variations in the rate of EMD reduction by the graphite. The effects of battery-mix equilibration time and carbon type (graphite vs acetylene black, for example) on the lowering of IOCV would be useful results but are outside the scope of this study.

4. Derivation of electrode potentials

4.1. *EMD potential*

Andersen [11] reviewed numerous studies of EMD and other MnO_2 equilibrium potentials at all states of discharge in battery electrolytes. These electrolytes (i.e., KOH in alkaline cells and NH_4Cl–$ZnCl_2$ mixtures in Zn–C cells contain no Mn^{2+} ions. The studies show that the potential-determining redox couple is Mn(IV)/Mn(III) in the cathode, and the potential is governed by the ratio of Mn^{4+} to Mn^{3+}. Thus, the potential-determining mechanism is

$$MnO_2 + e^- + H_2O = MnOOH + OH^- \qquad (1)$$

MnOOH is the product of shallow or slow discharge, forming as a molecular mixture with MnO_2, since the proton–electron pair are very mobile. Many researchers have focused on the MnOOH structure, MnOOH–MnO_2 mixtures, and the as-produced EMD [11–13]. The approximate equilibrium potential for Reaction 1 is

$$\begin{aligned} E\{EMD\}_z &= E\{MnOOH/MnO_2\}_z \\ &= E^\circ\{MnOOH/MnO_2\} \\ &\quad + (ART/F)\ln(f_{MnO_2}/f_{MnOOH}) \\ &\quad - (2.3\,RT/F)\log(OH^-)_z \end{aligned} \qquad (2)$$

where the constant A is rounded to 2 [14]. Although the expanded form of Equation 2 is very involved [11], this simplistic version is sufficient, since the A term is the same for the three EMD grades in this work. Chemical and battery manufacturers assay the Mn content and the total oxidizing power of EMD during reduction to Mn^{2+} to determine the ratio $(f_{MnO_2})/f_{MnOOH})$. These analyses reveal ~7% Mn^{3+} content in as-produced EMD [15, 16].

$E^\circ\{MnOOH/MnO_2\}$ in Equation 2 is the principal factor that differentiates EMD grades. $E^\circ\{MnOOH/MnO_2\}$ is directly related to the standard free energy of EMD, and thereby is indicative of the structural differences that result from dissimilar EMD production conditions.

4.2. *Zn potential*

Both the alkaline potential and the IOCV utilize the Zn/ZnO_2^{2-} couple as the reference electrode, for which the equilibrium equation is

$$Zn + 4\,OH^- = ZnO_2^{2-} + 2\,H_2O + 2\,e^- \qquad (3)$$
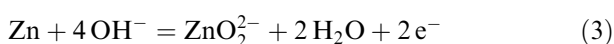
The Zn electrode potential, therefore, is

$$\begin{aligned} E\{Zn/ZnO_2^{2-}\}_z &= E^\circ\{Zn/ZnO_2^{2-}\} \\ &\quad + (2.3\,RT/2F)\log(ZnO_2^{2-})_z \\ &\quad - (2 \times 2.3\,RT/F)\log(OH^-)_z \end{aligned} \qquad (4)$$

4.3. *EMD potentials*

Determining EMD potentials at pH 6 requires a saturated calomel reference electrode, which in turn necessitates converting the measured potentials to the SHE scale. Equations 5–7 are the data sources for Table 2.

$$\text{pH 6 Potential} = E\{MnO_2/MnOOH\}_{pH\,6} \qquad (5)$$

$$\begin{aligned} \text{Alkaline potential} \\ = E\{MnOOH/MnO_2\}_{alk} - E\{Zn/ZnO_2^{2-}\}_{alk} \end{aligned} \qquad (6)$$

and

$$\begin{aligned} IOCV &= E\{MnOOH/MnO_2\}_{IOCV} \\ &\quad - E\{Zn/ZnO_2^{2-}\}_{IOCV} \end{aligned} \qquad (7)$$

4.4. *Measured EMD potentials*

The measured potential for each test is the difference between the potentials of EMD and a reference electrode, that is, saturated calomel or Zn. Calculating theoretical potential differences requires referencing the E° values in Equations 2 and 4 to the SHE half-cell. Therefore, $E^\circ\{r/o\}$ and $E\{r/o\}$ will signify those respective potentials relative to the SHE, and allows a standardized formulation and analysis of experimental potentials and potential differences.

5. Results and discussion

Information from Figure 1, coupled with measured EMD potentials, supports our contention that the three potential differences are equivalent within the experimental variations of cathode mix, electrolyte and reference electrode.

5.1. *(Alkaline potential − pH 6 potential)*

From Equations 2, 4, 5 and 6, the desired potential difference is

$$\begin{aligned} &(\text{Alkaline potential} - \text{pH 6 potential}) \\ &= (2.3\,RT/F)\log(OH^-)_{alk} - E^\circ\{Zn/ZnO_2^{2-}\} \\ &\quad - (2.3\,RT/2F)\log(ZnO_2^{2-})_{alk} \\ &\quad + (2.3\,RT/F)\log(OH^-)_{pH\,6} \end{aligned} \qquad (8)$$

The $E°\{MnOOH/MnO_2\}$ terms from Equation 2 cancel: therefore, Equation 8 is independent of EMD type. As the test temperature was $\sim$20 °C, $(2.3RT/F) = 0.0581$ V. Also, $(OH^-)_{pH\,6} = 10^{-8}$. Thus, the unknowns in Equation 8 are $E°\{Zn/ZnO_2^{2-}\}$, $(ZnO_2^{2-})_{alk}$, and $(OH^-)_{alk}$.

5.1.1. $E°\{Zn/ZnO_2^{2-}\}$

We derived $E°\{Zn/ZnO_2^{2-}\}$ from the Pourbaix equilibrium potential [17]. After rearranging the Pourbaix expression into the same form as Equation 4, and substituting pH for OH^- activity, (OH^-), the relationship is

$$E\{Zn/ZnO_2^{2-}\}_z = 0.441 + (2.3\,RT/2F)\log(ZnO_2^{2-})_z$$
$$- (2 \times 2.3\,RT/F)pH \qquad (9)$$

$E°\{Zn/ZnO_2^{2-}\}$ is now readily calculated as -1.1848 V.

5.1.2. OH^- activity, $(OH^-)_{alk}$

To calculate (OH^-), we must first determine the activity coefficient, γ_{OH}, of the electrolyte solutions, a function of KOH molality, m_{KOH} [18]. Calculation of m_{KOH} requires the KOH_{aq} density, measured at $\sim$20 °C as 1.2416 g mL^{-1}. Acid titrating the electrolyte proved the effective hydroxide concentration was 5.28 M. (This included any K_2CO_3 impurity in the solution.) In strong base, ZnO forms ZnO_2^{2-} [19], and we assumed that acid titration converts ZnO_2^{2-} back to ZnO. Correspondingly, charge balance indicates the solution comprised 4.79 M KOH + 0.246 M K_2ZnO_2.

We verified our assumption of the electrolyte definition by determining the electrolyte density, which for 4.79 M KOH is 1.2066 g mL^{-1} [20]. Adding 0.246 M K_2ZnO_2 to this solution increases the calculated density to 1.2459 g mL^{-1}, which compares favourably with the measured value above. The molal electrolyte concentration in the alkaline potential procedure is now calculable from the molar quantities.

$$4.79\,M(KOH) + 0.246\,M(K_2ZnO_2)$$
$$= 5.15\,m(KOH) + 0.265\,m(K_2ZnO_2) \qquad (10)$$

From [20], the mean activity coefficient, $\gamma_\pm$, of 5.15 m KOH is 1.93, and since KOH is a strong base, γ_{OH^-} is also 1.93. Therefore, OH^- activity in the alkaline electrolyte is

$$(OH^-)_{alk} = (m_{OH^-})_{alk}(\gamma_{OH^-})_{alk} = 9.94 \qquad (11)$$

5.1.3. ZnO_2^{2-} activity, $(ZnO_2^{2-})_{alk}$

Isaacson et al. [21] measured the potential difference between Zn/ZnO_2^{2-} and Hg/HgO electrodes in KOH–K_2ZnO_2 solutions as a function of composition and temperature. Their results fit the following equation:

$$E\{Zn/ZnO_2^{2-}\} - E\{Hg/HgO\}$$
$$= A_0 + A_1\log(m_{KOH}) + A_2\log(m_{K_2ZnO_2}) \qquad (12)$$

At 20 °C, the constants are $A_0 = -1316$ mV, $A_1 = -45.0$ mV and $A_2 = 27.25$ mV; it follows that $E\{Zn/ZnO_2^{2-}\} - E\{Hg/HgO\} = -1.3637$ V. Substituting Equations 4 and 10 for $E\{Zn/ZnO_2^{2-}\}$, and incorporating the Pourbaix expression $0.114 - (2.3\,RT/F)\log(OH^-)_{alk}]$ for $E\{Hg/HgO\}$ [17], the activity of ZnO_2^{2-} is calculated as 0.592. Therefore, $\gamma_{ZnO_2^{2-}} = 0.592/0.246 = 2.234$.

5.1.4. Calculated versus theoretical

Substituting the results from Sections 5.1.1.–5.1.3. into Equation 8 gives

$$\text{Alkaline potential} - \text{pH 6 potential}$$
$$= 0.0580 + 1.1848 + 0.0066 - 0.4648$$
$$= 0.785\,V\,(\text{theoretical}) \qquad (13)$$

Comparing this theoretical difference with the experimental values in Table 3 shows excellent agreement (0.785 V vs 0.795 $\pm$ 0.003 V, respectively), especially in light of approximations used in the theoretical analysis. In particular, the activity coefficient of the zincate ion should be smaller than that for OH^-, and lowering (ZnO_2^{2-}) by a factor of 2–3 would increase the calculated difference $\sim$10 mV. The experimental value for (alkaline potential – pH 6 potential) is independent of the EMD grade, as predicted, and the variations between grades are well within the error limits for these measurements.

5.2. (Alkaline potential – IOCV)

Substituting Equations 2 and 4 into Equations 6 and 7 yields the relation

$$\text{Alkaline potential} - \text{IOCV}$$
$$= (ART/F)\log[f_{MnO_2}/f_{MnOOH}]_{alk}$$
$$+ (2.3\,RT/F)\log(OH^-)_{alk}$$
$$- (2.3\,RT/2F)\log(ZnO_2^{2-})_{alk}$$
$$- (ART/F)\log[f_{MnO_2}/f_{MnOOH}]_{IOCV}$$
$$- (2.3\,RT/F)\log(OH^-)_{IOCV}$$
$$+ (2.3\,RT/2F)\log(ZnO_2^{2-})_{IOCV} \qquad (14a)$$

Neglecting the 0.7% temperature difference between the alkaline potential and IOCV procedures simplifies Equation 14(a) to 14(b).

$$\text{Alkaline potential} - \text{IOCV}$$
$$= (ART/F)\log\{[f_{MnO_2}/f_{MnOOH}]_{alk}$$
$$/[f_{MnO_2}/f_{MnOOH}]_{IOCV}\}$$
$$+ (2.3\,RT/F)\log\{(OH^-)_{alk}/(OH^-)_{IOCV}\}$$
$$- (2.3\,RT/2F)\log\{(ZnO_2^{2-})_{alk}/(ZnO_2^{2-})_{IOCV}\}$$
$$\qquad (14b)$$

Four items are undefined in Equation 14(b): the activities of hydroxyl and zincate ions during the IOCV procedure, and the cathodic mole fraction ratios in both tests. As before, we start by determining the electrolyte composition.

5.2.1. IOCV electrolyte

The electrolyte begins as Zn-free 9.0 M KOH. During the equilibration period, the zinc corrodes, consuming OH^- to produce ZnO and ZnO_2^{2-}. Zinc species concentrate at the anode surface, diffusing very slowly into the (unstirred) bulk solution, and are inaccessible for chemical analysis. The potential governing $[ZnO_2^{2-}]$, however, is established only in that small electrolyte volume nearest the Zn surface (the outer Helmholz plane).

We derived relevant information using an Hg/HgO reference electrode and a Zn anode. The half-cell equilibrium for the reference electrode is

$$Hg + 2\,OH^- = HgO + H_2O + 2\,e^- \qquad (15)$$
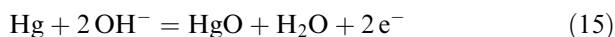
We measured the potential difference, $(E_{Zn} - E_{Hg/HgO})$, directly from a 22 °C test cell that incorporated Zn wire and Hg/HgO electrodes with 9.0 M KOH electrolyte. This difference stabilized after about 1 h at -1.45 V. Stirring the solution caused a rapid shift to about -1.47 V. When agitation ceased, the potential again drifted to its equilibrium value. This IOCV test indicates that Zn corrosion at the anode surface under these conditions has a steady state potential of -1.45 V.

Burkhardt [10] corroborated these results by measuring the discharge of various IBA EMD standards, in a form akin to the IOCV cathode. His study showed discharge plots at two different rates for three standards vs an Hg/HgO reference electrode, with 10 mV error limits. The curves reveal an initial EMD potential, that is, potential before current passes, of 0.15 V for the various trials. The IOCVs for these EMD samples averaged 1.58 V, indicating the potential difference $(E_{Zn} - E_{Hg/HgO})$ is in the range -1.41 to -1.45 V. The average EMD potentials vs Hg/HgO compared to the mean IOCVs vs Zn for a given EMD were consistent for all three standards. Allowing for an extended equilibration period, we assigned a mean value of -1.43 V for $(E_{Zn} - E_{Hg/HgO})$.

Isaacson et al. [21] determined that for $(E_{Zn} - E_{Hg/HgO}) = -1.43$ V, $[KOH] = 10.50\,m$, and 25 °C, $[ZnO_2^{2-}] = 0.0045\,m$. (9.0 M KOH has a density of 1.3625 g cm^{-3} at 22.2 °C, thus $[KOH] = 10.50\,m$) Considering all the results, including visible anode corrosion, we estimate that Zn oxidizes under cell conditions to yield $0.0045\,m$ ZnO_2^{2-}, leaving $[KOH]$ at 9 M or $10.5\,m$.

The activity coefficient of 10.5 m KOH is 7.84 [20]. Multiplying this by the IOCV electrolyte concentration yields the OH^- activity, 82.3. The cell was maintained at 22 °C: neglecting the minor temperature error incurred between tests, the second term in Equation 14(b) is

$$(2.3\,RT/F) \log\{(OH^-)_{alk}/(OH^-)_{IOCV}\}$$
$$= (0.0581) \log\{[9.94]/[82.3]\}$$
$$= -0.053\,V \qquad (16)$$

The activity coefficient of ZnO_2^{2-} is not explicitly known. Results show, however, that this property is independent of $[ZnO_2^{2-}]$ (i.e., $dE_{Zn}/d(\log m_{ZnO_2^{2-}})$ is a constant) [21]). In other words, the ratio of ZnO_2^{2-} molalities in the two tests is equivalent to the ratio of activities. When $m_{ZnO_2^{2-}} = 0.0045$ and the temperature is 22 °C, the third term of Equation 14(b) is

$$-(2.3\,RT/2F) \log\{(ZnO_2^{2-})_{alk}/(ZnO_2^{2-})_{IOCV}$$
$$= -(0.0292) \log(0.265/0.0045)$$
$$= -0.052\,V \qquad (17)$$

Excluding ZnO from the alkaline potential test lowered the potential by roughly 50 mV, thus establishing an excellent corroboration.

Equation 17 is sensitive to $[ZnO_2^{2-}]$, which varies greatly in the Zn ionic layer. At the high end of the $(E_{Zn} - E_{Hg/HgO})$ range, -1.41 V, $[ZnO_2^{2-}]$ is interpolated as $0.031\,m$ [21]. This in turn causes Expression 17 to increase to -0.027 V. Alternately, if the potential difference is -1.45 V, corresponding to $[ZnO_2^{2-}] = 0.0001\,m$, Equation 17 drops to -0.100 V. Such a low concentration is unrealistic, and we discount this probability in favour of a higher $(E_{Zn} - E_{Hg/HgO})$.

The second and third terms in Equation 14(b) (cf. Equations 16 and 17) contribute -0.105 V to the difference (alkaline potential – IOCV). Since the measured difference is $\geqslant 0.0$ V (Table 3), the first term in Equation 14(b) must be dominant, and this is the EMD expression. The ratios of Mn^{4+} to Mn^{3+} (f_{MnO_2} and f_{MnOOH}) define this term in the two tests. These fractions appear in Equation 14(b) as $[f_{MnO_2})/f_{MnOOH}]_{alk}/[f_{MnO_2})/f_{MnOOH}]_{IOCV}$; it follows that the EMD is either more oxidized in the alkaline-potential test or more reduced in the IOCV procedure.

The determining factor in (alkaline potential – IOCV) lies in the carbon content of the cathode mix. In the alkaline potential protocol, that electrode contains no graphite. The IOCV test, however, has a cathode mix of EMD:graphite = 1:3, and the excess carbon reduces some potential-determining Mn^{4+} before the discharge starts. This initial potential lowers the IOCV of AB EMD by 60 mV (interpolated from Figure 1), the value of the first term in Equation 14(b).

This quantifies Equation 14(b) and yields the difference in measured potentials.

$$Alkaline\ potential - IOCV = -0.053 - 0.052 + 0.060$$
$$= -0.045\,V \qquad (18)$$

While agreement with the experimental value of +0.017 V is only fair, if Zn corrosion is somewhat higher than our estimate, the second term in Equation 18 would decrease up to 50%, and the expression would equal −0.020 V. These theoretical values are sufficiently close to rationalize the differences between the alkaline potentials and the IOCVs in Table 3. The graphite-induced reduction term (third term in Equation 18) increases with EMD activity, explaining the trend in (alkaline potential − IOCV) in Table 3, that is, HSA < AB < HD. Other factors that would mitigate the above disparity include CO_2 absorption by the electrolyte and more extensive carbon-induced Mn^{4+} reduction.

6. Conclusions

We measured the potential of electrolytic manganese dioxide by three different methods common to the battery industry, and, although the EMD potentials vary with the method, the results are equivalent within the precision of the tests. We verified this equivalence through thermodynamic calculations. Test procedures included a Leclanché-type cell (pH 6, calomel electrode) and two Zn/MnO_2 chemistries with KOH electrolyte. Key factors in these potential values are differences in electrolyte compositions and pH, reference electrodes, and carbon/EMD ratios in the cathode.

Acknowledgements

References

1. T.N. Andersen, *Prog. Batt. Battery Mat.* **11** (1992) 105.
2. E. Preisler and G. Mietens, *DECHEMA Monogr.* **109** (1987) 123.
3. R. Williams, R. Fredlein, G. Lawrance, D. Swinkels and C. Ward, *Prog. Batt. Battery Mat.* **13** (1994) 102.
4. M. Mauthoor, '*The Effect of Operating Parameters on the Properties of Electrolytic Manganese Dioxide*', PhD thesis, University of the Witwatersrand, Johannesburg, South Africa (1995).
5. A. Kozawa and R.A. Powers, *Electrochem. Technol.* **5** (1967) 535.
6. A. Kozawa, *Manganese Dioxide*, in 'Batteries', Vol. 1 (Marcel Dekker, New York, 1974), p. 483.
7. R.P. Williams, A.R. Gee, G.A. Lawrance and D.A.J. Swinkels, *Prog. Batt. Battery Mat.* **15** (1996) 48; D.A.J. Swinkels and R.P. Williams, *Prog. Batt. Battery Mat.* **15** (1996) 1.
8. T.N. Andersen, S.F. Burkhardt, W.F. Howard, Jr., R.F. Wohletz, V. Kazerooni, M.R. Moumenzadeh and A.W. Unsell, *US Patent. 6 214 198*, 10 March 2001.
9. D. Kilby and P.J. Slezak, *PCT Internat. Pub. WO 01/11703*, 15 Feb 2001.
10. S.F. Burkhardt, *in* D. Glover, B. Schumm, Jr. and A. Kozawa (Eds), 'Handbook of Manganese Dioxides, Battery Grade' (International Battery Materials Association, Cleveland, OH (1989), p. 217.
11. T.N. Andersen, *in* R.E. White, B.E. Conway and J.O'M. Bockris (Eds), 'Modern Aspects of Electrochemistry', Vol. 30 (Plenum, New York, 1996), p. 313.
12. Y. Chabre and J. Pannetier, *Prog. Solid State Chem.* **23** (1995) 1.
13. W.C. Maskell, J.E.A. Shaw and F.L. Tye, *Electrochim. Acta* **26** (1981) 1403.
14. F.L. Tye, *Electrochim. Acta* **21** (1976) 415.
15. P. Ruetschi, *J. Electrochem. Soc.* **131** (1984) 2737.
16. D.A.J. Swinkels and K.J. Doolan, *Prog. Batt. Battery Mat.* **10** (1991) 176.
17. M. Pourbaix, 'Atlas of Electrochemical Equilibria in Aqueous Solutions' (Pergamon, New York, 1966).
18. H.S. Harned and B.B. Owen, 'The Physical Chemistry of Electrolytic Solutions, 3rd edn' (Reinhold, New York, 1958), p. 730.
19. T.P. Dirkse, *J. Electrochem. Soc.* **101** (1954) 328.
20. 'Handbook of Chemistry and Physics, 59th edn' (CRC, Boca Raton, FL, 1978–79), p. D-291.
21. M.J. Isaacson, F.R. McLarnon and E.J. Cairns, *J. Electrochem. Soc.* **137** (1990) 2361.