MANGANESE DIOXIDE ELECTRODE
VII. EXPERIMENTAL DETERMINATION AND A SIMPLE THEORETICAL DESCRIPTION OF THE ELECTRICAL POTENTIAL OF SOLID SOLUTIONS IN THE RANGE γ-MnO$_2$ TO δ-MnOOH

W. C. MASKELL, J. E. A. SHAW and F. L. TYE

Berec Group Limited, Group Technical Centre, St. Ann's Road, London N15 3TJ (Gt. Britain)

Summary

Measurements made of the potential of oxyhydroxides derived from an electrodeposited γ-MnO$_2$ are presented which when plotted *vs.* degree of reduction show good agreement with curves derived by other workers. Making the assumption that the oxyhydroxide is a thermodynamically ideal mixture of the end members γ-MnO$_2$ and δ-MnOOH results in a theoretical equation for the potential which does not fit the experimental data. However, if in the theoretical analysis the proton and electron introduced during reduction are considered to be independently mobile, *i.e.*, dissociated, in the host lattice, then the resulting theoretical equation for the potential provides a reasonable representation of the experimental data for solid solutions between γ-MnO$_2$ and δ-MnOOH.

Introduction

A number of previous investigations have increased understanding of the factors which determine the electrical potential of oxyhydroxides derived from electrodeposited γ-MnO$_2$. However, as yet no theory has emerged which correlates electrical potential with stoichiometry in a reasonably exact manner.

In this paper new determinations of potential over the range γ-MnO$_2$ to δ-MnOOH are reported and matched with some success against a simple theory.

Experimental

A commercial electrodeposited γ-manganese dioxide of Japanese origin (code R2) was used without pretreatment.

Modified Leclanché cells were constructed, slowly discharged and monitored, as previously described [1]. Electrolyte squeezed from the

discharged mix was analysed as follows. After pH measurement the electro-
lyte was weighed, acidified with concentrated HNO_3, and made up to a
specified volume with water. The Mn^{2+} concentration was determined by
potentiometric titration with $KMnO_4$ solution [2], the latter having been
standardised with 0.1N sodium oxalate solution.

The final r value (in $MnOOH_r$) of the oxyhydroxide after discharge was
calculated from the initial composition of the γ-MnO_2 (prior to discharge),
the quantity of charge passed during discharge, and the final total Mn^{2+} con-
tent of the electrolyte.

The observed e.m.f. values of cells on open-circuit were not entirely due
to changes in the r value of the oxyhydroxide phase, but were also due to
changes in composition of the electrolyte affecting both the zinc and man-
ganese oxyhydroxide potentials. The mixes incorporated excess solid NH_4Cl
to minimise changes in the electrolyte but such changes were not totally
eliminated. In order that suitable corrections could be made to adjust mea-
surements of the cathode potential to a common basis, a cell constructed
as shown in Fig. 1, including a saturated calomel reference electrode (SCE),
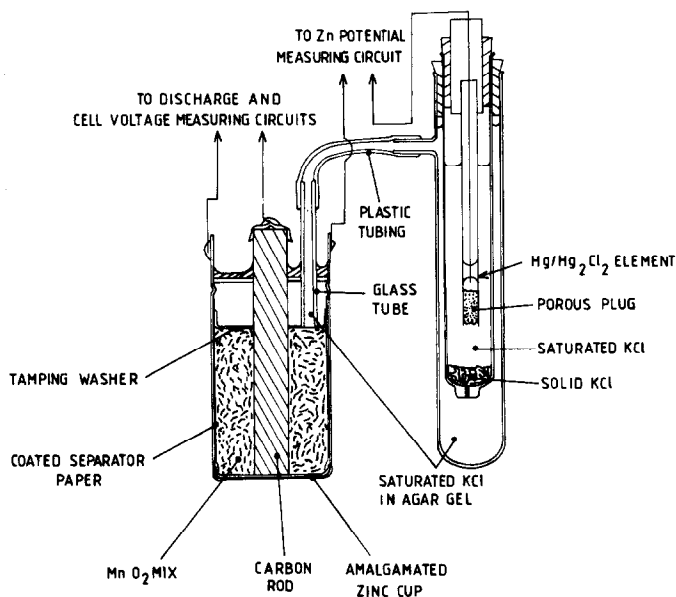was discharged.

Fig. 1. Construction of Leclanché-type cell with reference electrode.

Results

The variation of Zn potential with extent of discharge is shown in Fig.
2. The correction for pH to the manganese oxyhydroxide potential shown is
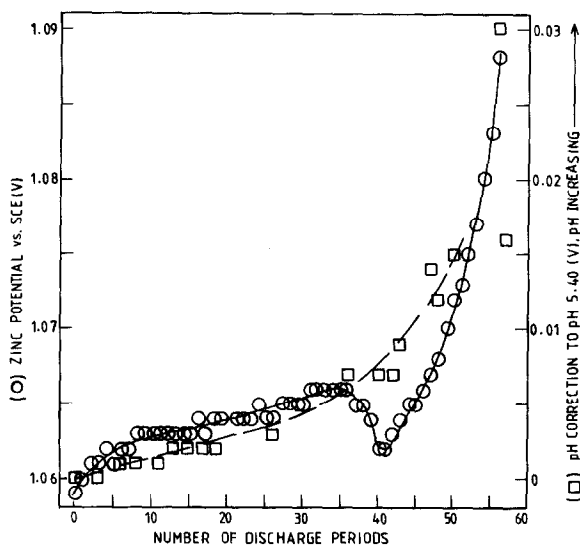
Fig. 2. Corrections to cell e.m.f. for Zn potential (○) and pH changes (□). 10 g MnO_2 in Leclanché mix discharged through 300 ohms, 12 h per day.

0.0592 ΔpH volts [3]. (2.303 RT/F = 0.0592 V at 25 °C, R, T, and F having their usual significance.) ΔpH is the difference between the electrolyte pH and some specified value. It is clear that the adjustments for zinc potential and for pH are similar in magnitude, and as they are applied with opposite sign, each largely cancels the effect of the other. This means that the oxyhydroxide potential at a fixed pH against a reference electrode, and the cell e.m.f., have almost precisely the same dependence upon degree of reduction, differing only by a constant term.

The oxyhydroxide potential *vs.* r (in $MnOOH_r$) is shown in Fig. 3(a). The potential moves to more negative values with increasing degree of reduction, as found by other workers [4 - 8]. This is expected [9] for a single phase process showing homogeneity over the complete range $0 < r < 1$ [1]. The points on Fig. 3(a) form an exceptionally smooth curve considering that the e.m.f. of a different cell was measured for each point. Data from two independent sources are shown in Fig. 3(b) and (c). The results in Fig. 3(b) were obtained by Huber and Bauer [7] who incorporated an electrolytic γ-MnO_2 into standard Leclanché cells. The discharged cells were left on open-circuit for 5 - 6 months before recording the e.m.f. In Fig. 3(b) eight points have been omitted corresponding to cases showing premature decrease in cell voltage: Huber and Bauer suggest that in these cases there may have been formation of a separate phase. The effect was absent when the discharge was conducted through a resistance greater than 100 ohms. The discussion above suggests that the e.m.f. data are probably representative of the oxyhydroxide potential at a fixed pH, differing only by a constant term from values relative to a reference electrode. The data of Neumann and von
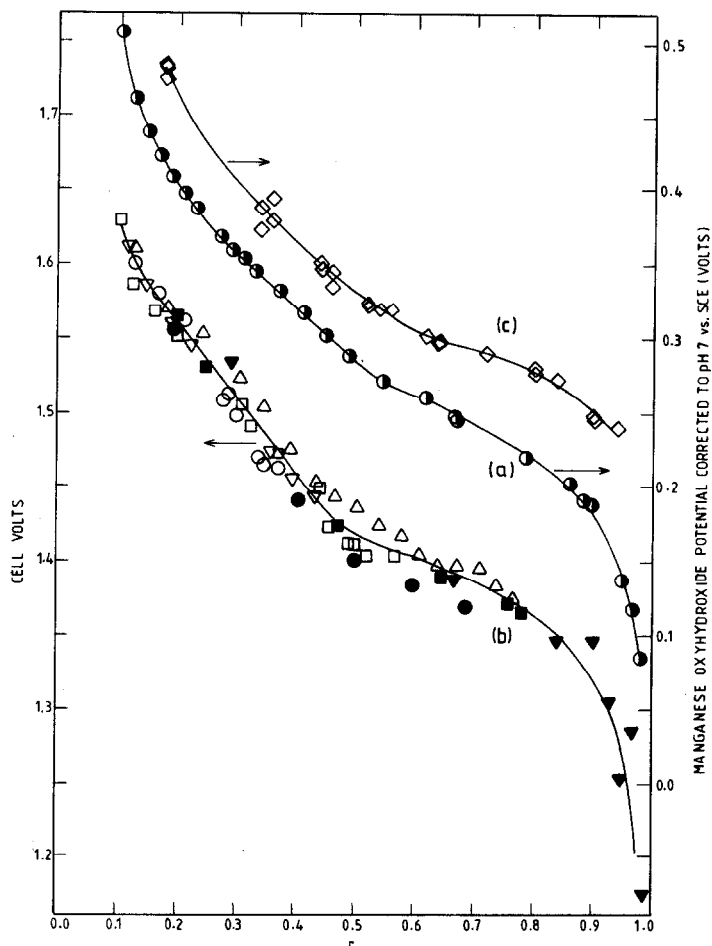
Fig. 3. (a) Variation of the potential of the oxyhydroxide with degree of reduction measured in the present work (◑). (b) Data of Huber and Bauer [7]: Leclanché cell e.m.f. vs. r; symbols (○, □, △, ▽, ●, ■, ▼) as in the original paper. (c) Data of Neumann and von Roda [4]: potential of oxyhydroxide vs. r (◇).

Roda [4] are shown in Fig. 3(c). In this case, the MnO_2 was electrodeposited onto platinum prior to electrochemical reduction.

Clearly, the three sets of data in Fig. 3 show very similar variations of potential with degree of reduction. Thus the data obtained in the present work are in general agreement with previous findings and provide a good basis for testing theoretical equations.

Discussion

The generally accepted electrode reaction is [3, 10, 11]:

$$MnO_2(s, 1-r) + H^+ + e \rightleftharpoons MnOOH(s, r). \tag{1}$$
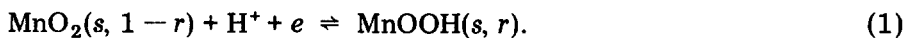
The formalism used in this equation is that suggested by Neumann and von Roda [4], the s indicating the species to be components in a solid solution and $(1 - r)$ and r representing mole fractions of the relevant species. Assuming reversibility, the Nernst equation for reaction (1) may be written as follows:

$$E + 2.303 \frac{RT}{F} \text{ pH} = E^\circ + \frac{RT}{F} \ln a_{MnO_2}/a_{MnOOH} . \tag{2}$$

E and E° are the measured and standard potentials, respectively, and a is the activity of the subscript species.

Equation (2) shows that the potential is related to the activities of MnO_2 and $MnOOH$ in the solid solution. The problem therefore is to find suitable expressions, based upon acceptable models, for these activities in terms of the composition of the mixture.

Previous approaches have been based upon thermodynamic ideality of the solid solution, and it is useful to consider initially the requirements of an ideal solution in order to establish whether ideality is a reasonable assumption for the oxyhydroxides under consideration. In treating this problem Guggenheim [12] considers two kinds of molecules, A and B, sufficiently similar in size and shape that they are interchangeable on the lattice. He defines an interchange energy, w, such that starting with two pure crystals A and B, and then interchanging an interior A molecule with an interior B molecule, the total increase in energy is 2 w. The condition for ideality is that w is zero. This means that the heat of mixing is also zero (no enthalpy change). Guggenheim further indicates that in liquids, in order that the manner of packing may be the same in the pure and mixed phases, the ratio of the molar volumes of A and B should be between 0.5 and 2.

Unit cell volumes of oxyhydroxides derived from γ-MnO_2 [1] are shown in Fig. 4. Clearly, the ratio of molar volumes of the end members fall well within the above specified limits. There should be no volume change when mixing is ideal [13]. Such a condition is indicated by the broken line in Fig. 4. It is apparent that the volume change on mixing in the γ-MnO_2/δ-$MnOOH$ system is not great ($<2\%$). On the basis of the molar volumes of the end members and the small volume change on mixing, ideality seems a reasonable assumption for solid solutions in the range γ-MnO_2 to δ-$MnOOH$. In an ideal mixture the activities of the components are proportional to their mole fractions. Thus, by assuming ideality, and that the components of the mixture are the end members MnO_2 and $MnOOH$, and by defining the activity of the pure end phases as unity, it is possible to write for the oxyhydroxide $MnOOH$,

$$\bar{E} = E^\circ + \frac{RT}{F} \ln \frac{1 - r}{r} \tag{3}$$

where $\bar{E} = E + 2.303 \, RTF^{-1}$ pH, $i.e.$, $\bar{E}$ is the potential corrected for pH. Equation (3) (broken line) is compared with the experimental data in Fig. 5. In this Figure the empirical data have been corrected for inactive Mn(III). It
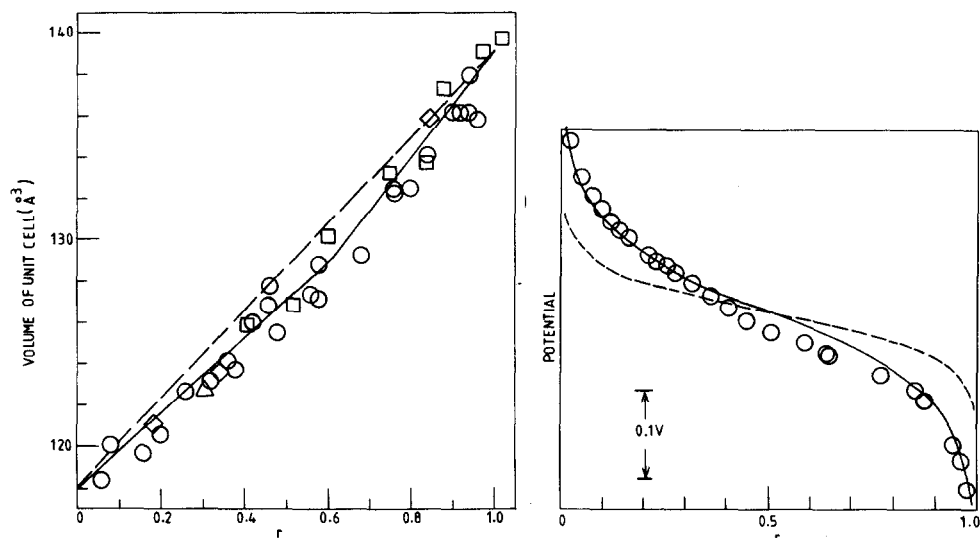
Fig. 4. Variation of the volume of the unit cell with degree of reduction. Reduction mode or agent: ○, electrochemical; □, cinnamyl alcohol; ◇, hydrazine; △, manganous chloride.

Fig. 5. Comparison of theoretical curves with experimental data. − − −, eqn. (3) or (8) with $\psi = 1$; ——, eqn. (7) or (8) with $\psi = 2$; ○, experimental data corrected for inactive Mn(III) equivalent to that in $MnOOH_{0.08}$ (eqn. (5)).

was demonstrated recently [14] using the Gibbs−Duhem relationship that a small amount of Mn(III) (equal to, or a little greater than that in $MnOOH_{0.06}$) was not active in the potential-determining reaction. It is assumed that Mn(III) equivalent to that in $MnOOH_{0.08}$ is inactive. The precise amount chosen as inactive is not critical to the argument presented. The measured value of r (r_{meas}) when corrected for inactive Mn(III) will be written as r_{corr} and defined as taking the value zero when $r_{meas} = 0.08$.

$$r_{meas} = Mn(III)_{total}/(Mn(III)_{total} + Mn(IV)). \qquad (4)$$

It follows that

$$r_{corr} = (1.087 \, r_{meas} - 0.087). \qquad (5)$$

As noted by other workers [8, 15], eqn. (3) does not fit the experimental data. Neumann and von Roda [4] modified the equation by introducing activity coefficients:

$$\bar{E} = E^\circ + \frac{RT}{F} \ln (1 - r)\phi_{MnO_2}/r\phi_{MnOOH}. \qquad (6)$$

ϕ is the activity coefficient of the subscript species. They found, however, that to fit the data, ϕ_{MnO_2} differed from unity by more than five orders of magnitude. This was only partly due to the fact that no correction was made for inactive Mn(III).

There is an alternative approach [8]: the assumption of ideality is retained and the activity of the pure end phases MnO_2 and MnOOH are still defined as unity but the independent components of the ideal mixture are regarded as Mn^{4+}, Mn^{3+}, O^{2-} and OH^-. Thus the activities of MnO_2 and MnOOH may be written in terms of the mole fractions of the above ionic components. De Wolff [16] has explained X-ray spectra by considering γ-MnO_2 to have a ramsdellite structure containing statistically distributed microdomains of pyrolusite. In groutite, the reduced form of ramsdellite, protons are covalently bonded only onto oxygen atoms in a pyramidal coordination with the three nearest manganese atoms [17]. The other half of the oxygen atoms is in a planar coordination with adjacent manganese atoms. Thus, in formulating the mole fraction of O^{2-} it is reasonable to include only those in a pyramidal coordination. This approach leads to the expression

$$\bar{E} = E^\circ + 2\,\frac{RT}{F}\ln\frac{1-r}{r}. \tag{7}$$

A comparison of eqn. (7) with experimental data over the whole range γ-MnO_2 to δ-MnOOH is now shown in Fig. 5. Equation (7) is clearly a much better representation of the data than eqn. (3).

For the components Mn^{4+}, Mn^{3+}, O^{2-} and OH^- to be thermodynamically independent requires only an independence of position and motion of protons and electrons. In an equivalent approach Crandall *et al.* [18] investigating the potential of hydrogen–tungsten bronzes of various degrees of reduction, introduced a spatial correlation coefficient, ψ, which modifies eqn. (3) as follows.

$$\bar{E} = E^\circ + \psi\,\frac{RT}{F}\ln\frac{1-r}{r}. \tag{8}$$

When there is close spatial correlation of the proton and electron, *i.e.*, association, ψ takes the value unity and eqns. (3) and (8) are identical. When there is not close spatial correlation of the proton and electron, *i.e.*, dissociation, ψ takes the value 2 and eqn. (8) becomes equivalent to eqn. (7).

The coefficient ψ has been introduced into equations presented by Barnard *et al.* [19, 20] for the $Ni(OH)_2$/NiOOH system: again a value for ψ of 2 appears to be appropriate.

Conclusion

A theoretical equation applied to the potential of oxyhydroxides derived from γ-MnO_2 shows a reasonable fit with the experimental data. The significant concepts introduced were the following:

(i) ideal mixing was assumed;

(ii) a small amount of Mn(III), present in the oxyhydroxide initially, is inactive towards the potential-determining process;

(iii) the electrons and protons appear to be independently mobile in the homogeneous solid phase, *i.e.*, dissociated.

Acknowledgements

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