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On the manganese dioxide electrode. V. The evidence indicating the presence of two solid solutions in the range MnO_2–$MnO_{1.5}$ with γ-MnO_2 as one end member

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An examination of the literature has revealed that several of the properties of oxyhydroxides derived from γ-MnO_2 show a sharp change around the midpoint at $MnO_{1.75}$. These include the lattice parameters, the activation energy for semiconduction, the magnetic susceptibility, the thermal behaviour and the electrical potential. Intermediate compounds have been observed by X-ray diffraction in the closely related systems ramsdellite/groutite and VO_2/VOOH. It is suggested that for the γ-MnO_2/δ-MnOOH system two solid solutions exist, one between MnO_2 and $MnO_{1.75}$ (e.g. Mn_2O_4H) and another between Mn_2O_4H and MnOOH. Ways in which the two solid solutions may arise involving different proton–electron filling mechanisms above and below the midpoint are discussed.

1. Introduction

The voltage of a Leclanché cell decreases on discharge. The voltage recovers when the discharge ceases although it does not reattain the value for the undischarged cell. This effect is principally associated with the manganese dioxide cathode. In 1882 Divers [1] suggested that the overpotential was the result of blocking by the accumulation of reduction products on the surface. According to Keller [2], Schreiber realised that the effect was due to solid solution formation between MnO_2 and the reduction product.

The generally accepted discharge reaction is [3–5]

$$MnO_2 + H^+ + e \rightleftharpoons MnOOH. \qquad (1)$$

When the MnO_2 cathode is discharged the reduction product MnOOH is formed on the surface of the oxide particles. The formation of a solid solution between MnO_2 and MnOOH requires that they can interdiffuse and form a stable non-stoichiometric phase. Several workers [3, 6, 7] have pointed out that this could occur simply by the movement of protons and electrons from the surface into the bulk of the solid phase. Scott [8] assumed semi-infinite diffusion and satisfactorily fitted discharge and recovery potential–time curves in $NH_4OH + NH_4Cl$ at pH 7.

In neutral solutions little of the reduction product can be removed via the solution. Therefore a high diffusion coefficient for protons and electrons in the solid phase is essential for a manganese dioxide cathode to operate at reasonable current densities. If the diffusion coefficient is low, the reduction product accumulates on the surface during discharge and the potential of the cathode moves to negative values resulting in early cell failure.

Clearly the formation of solid solutions is central to the operation of the γ-MnO_2 electrode used in batteries. The literature relating to observations of the variation in properties of these solid solutions will therefore be reviewed with a view to gaining a better understanding of the processes involved when protons and electrons enter the γ-MnO_2 structure.

2. Variation of properties of γ-MnO_2 with degree of reduction

2.1. *X-ray diffraction studies*

The crystalline structure of γ-MnO_2 has been

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shown by de Wolff [9] to be closely related to that of the rare mineral ramsdellite. Bystrom [10] showed the latter to have an orthorhombic structure consisting of close-packed oxygen layers containing double strings of manganese atoms running in the direction of the *c*-axis. The common mineral pyrolusite, on the other hand, has the rutile structure with single strings of manganese atoms running in the *c*-direction. De Wolff [9] noted the similarity between the X-ray spectra of γ-MnO_2 and ramsdellite and showed that the patterns were consistent with γ-MnO_2 having the ramsdellite structure with randomly distributed microdomains of pyrolusite.

Brenet [11] observed that when γ-MnO_2 was electrochemically reduced, the latter dilated progressively with increasing degree of reduction. This was the result of the incorporation of protons and electrons into the γ-MnO_2 lattice. Feitknecht *et al.* [12] confirmed this result using an electrolytic γ-MnO_2 which was slowly reduced by dropwise addition of hydrazine sulphate to a suspension of the oxide in NH_3/NH_4Cl solution. It was shown that the volume of the unit cell increased approximately linearly with x (in MnO_x) and that the process occurred in a single phase.

Laurent and Morignat [13] reduced an electrolytic γ-MnO_2 by discharging in Leclanché cells. They calculated the *a*, *b* and *c* parameters of the orthorhombic unit cell and noted a discontinuity in the slope of the first two parameters when plotted against x (in MnO_x). This effect was also observed [14] for γ-MnO_2 suspended in xylene and slowly reduced using cinnamyl alcohol.

Maskell *et al.* [15] recently confirmed the above results using an electrolytic γ-MnO_2. The lattice parameters and the volume of the unit cell are shown in Fig. 1. Discontinuities in the slopes of the *a*, *b* and *c* parameters are clearly evident at about $MnO_{1.75}$. The X-ray studies showed that the reduction of γ-MnO_2 proceeds via a single phase. The end member at $MnO_{1.5}$ was named [15] δ-MnOOH to distinguish it from groutite (α-MnOOH). δ-MnOOH appears to be an intergrowth structure of groutite with randomly distributed microdomains of manganite (γ-MnOOH) [16].

2.2. *Electrical conductivity and magnetic measurements*

Gabano *et al.* [17] reduced γ-MnO_2 using cinnamyl alcohol and then pressed pellets of the resulting oxyhydroxide. The electrical conductance of these pellets was measured by a d.c. method in the temperature range 25–80° C. From these results an activation energy for semiconduction was determined as shown in Fig. 2. As with the unit cell parameters a sharp change in slope was apparent at about $MnO_{1.75}$.

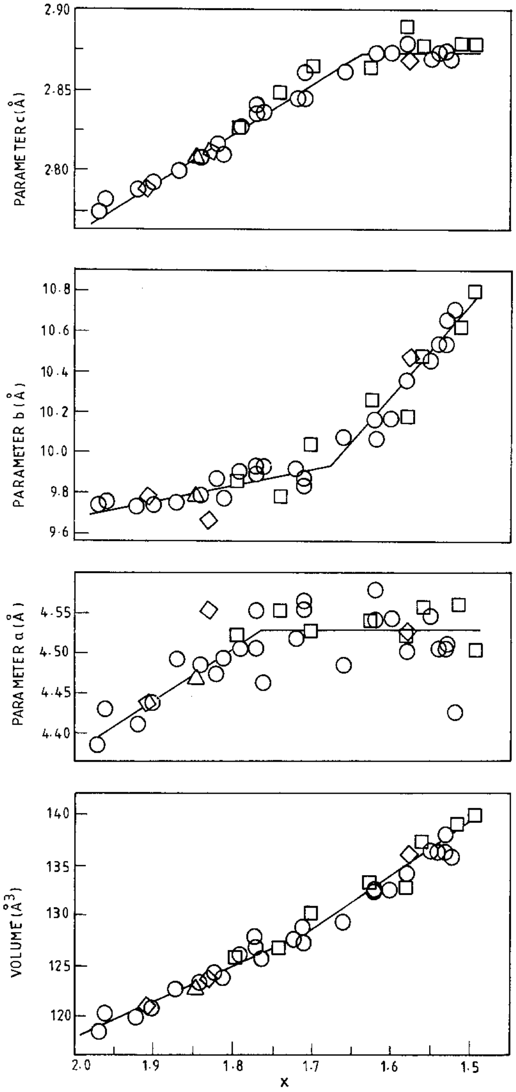

Fig. 1. Variation of parameters of the unit cell with degree of reduction x. Reduction mode or agent: ○, electrochemical; □, cinnamyl alcohol; ◇, hydrazine; △, manganous chloride.

The magnetic properties of an electrolytic γ-MnO_2 reduced using hydrazine hydrate were investigated by Lee *et al.* [18]. The magnetic moment increased with degree of reduction as

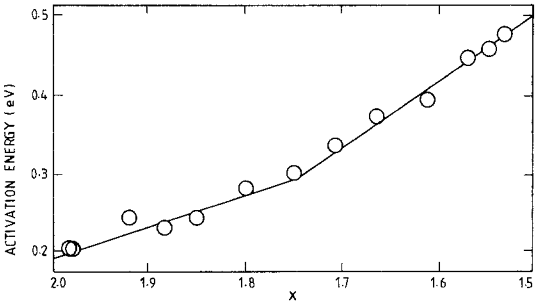

Fig. 2. Activation energy for semiconduction for pressed pellets versus degree of reduction x.

expected for a change from Mn(IV) to Mn(III). At the midpoint, however, the magnetic moment was anomalously high as shown in Fig. 3.

2.3. *Thermogravimetric analysis*

Lee *et al.* [18] also analysed the reduced electrolytic γ-MnO_2 samples thermogravimetrically. The results under 10 Torr of oxygen are shown in Figs. 4 and 5. The former figure relates to samples in the range MnO_2–$MnO_{1.75}$ and the important feature, as far as the present discussion is concerned, is that there was very little dependence of the type II feature upon x. Type II weight loss was attributed to irreversibly bound water comprising water held in the bulk of the oxide (type IIa) and water produced by condensation of hydroxyl groups (type IIb). The invariance of the type II feature with x (Fig. 4) has been taken [19] to indicate the occurrence of the reaction

$$4MnOOH + O_2 \rightleftharpoons 4MnO_2 + 2H_2O. \qquad (2)$$

The net weight loss in this reaction would be small.

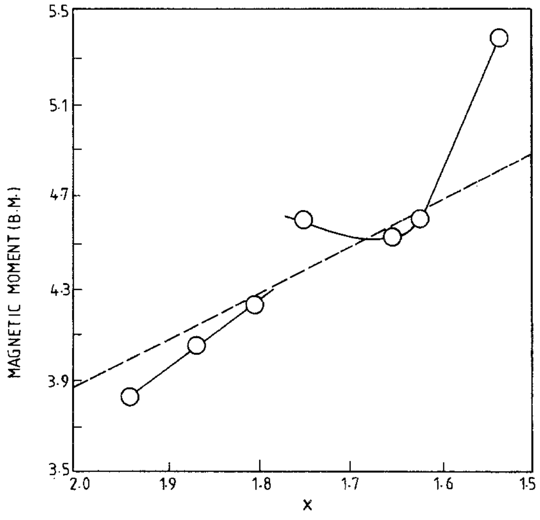

Fig. 3. Magnetic moment as a function of sample composition for partially reduced γ-MnO_2.

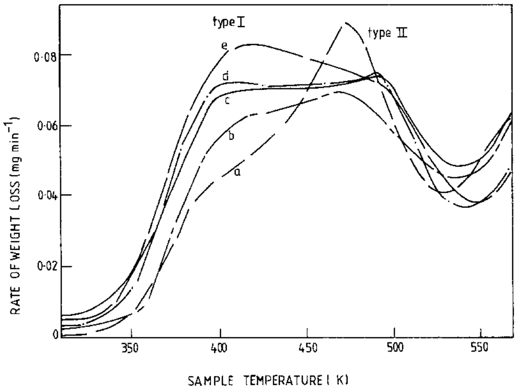

Fig. 4. Temperature programmed desorption of partially reduced γ-MnO_2 in a static oxygen environment (10 Torr). Values of x: (a) 1.946; (b) 1.931; (c) 1.909; (d) 1.870; (e) 1.825.

The thermal behaviour of samples in the range $MnO_{1.75}$–$MnO_{1.5}$ is shown in Fig. 5. Here the type II feature was markedly dependent upon x. This suggests [18] that the decomposition route ($1.75 > x > 1.5$) involved an intermediate which was less susceptible to oxidation (e.g. Mn_2O_3–corundum). Thus

$$2MnOOH \rightarrow Mn_2O_3(\text{corundum}) + H_2O. \qquad (3)$$

Clearly the oxyhydroxides produced in the ranges MnO_2–$MnO_{1.75}$ and $MnO_{1.75}$–$MnO_{1.5}$ decompose thermally via different routes.

2.4. *Potential measurements*

Bode and Schmier [20] showed that the potential of an electrolytic γ-MnO_2 decreased continuously with increasing degree of reduction and this effect has been confirmed by many other workers [5, 21–24]. It has been interpreted [25] as indicating that the oxide is reduced in a homogeneous phase.

In a recent investigation Maskell *et al.* [26] electrochemically reduced an electrolytic γ-MnO_2 very slowly in modified Leclanché cells and observed the equilibrium open-circuit potentials. The cathode mixes contained an excess of non-MnO_2 components, particularly NH_4Cl so that

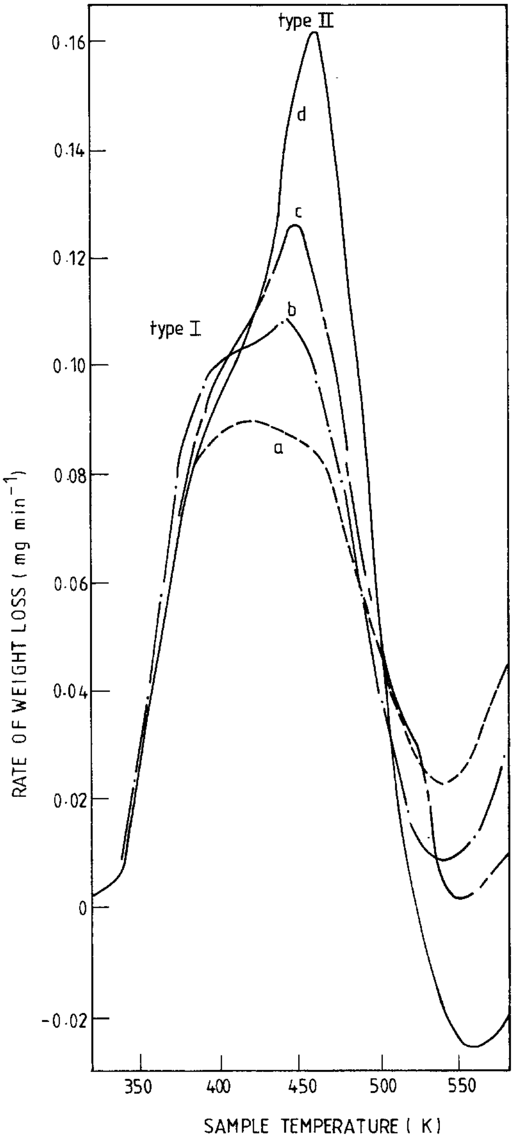

Fig. 5. As Fig. 4. Values of x: (a) 1.73; (b) 1.65; (c) 1.62; (d) 1.54.

electrolyte composition changed little throughout discharge. The results are shown in Fig. 6. The significant feature of this data is the sharp change in slope around the midpoint ($x = 1.75$, log $Mn^{3+}/Mn^{4+} = 0$).

3. Discussion

It has been shown that many of the properties of manganese oxyhydroxides derived from γ-MnO_2 show a sharp change around the midpoint $MnO_{1.75}$. These include the lattice parameters, the activation energy for semiconduction, the magnetic susceptibility, the thermal behaviour and the electrical potential. Thus it is tempting to consider the existence of an intermediate at $MnO_{1.75}$ (e.g. Mn_2O_4H) which is the endmember of two solid solutions, one between MnO_2 and $MnO_{1.75}$ and the other between $MnO_{1.75}$ and $MnO_{1.5}$ (MnOOH).

Groutite (α-MnOOH) is the reduced form of ramsdellite. Klingsberg and Roy [27] investigated this oxyhydroxide/oxide system and showed the end members to be interconvertible by low temperature oxidation or reduction. X-ray diffraction revealed an intermediate compound in the reduction of ramsdellite which was given the name groutellite.

A closely related system is that of $VOOH/VO_2$. VOOH like α-MnOOH has the diaspore (AlOOH) structure and occurs naturally as the mineral montroseite. Evans and Mrose [28] examined mineralogical samples of the system $VOOH/VO_2$ and were able to index three distinct structures, namely, monstroseite (VOOH), paramontroseite (VO_2) and another tentatively ascribed V_2O_4H. They proposed that the oxidation of VOOH occurs geologically at temperatures below 50° C by a diffusion of protons to the surface and reaction with oxygen according to the reaction

$$2VOOH + \tfrac{1}{2}O_2 \rightarrow 2VO_2 + H_2O. \qquad (4)$$

It was suggested that the process may pass through an intermediate stage involving V_2O_4H. The synthesis of VOOH was achieved more recently by Muller and Joubert [29]. This oxyhydroxide was heated in air for several days at 80° C to prepare the metastable VO_2 via Reaction 4. Most importantly Muller and Joubert [29] also observed the formation of an intermediate which they suggested was probably identical to that indexed by Evans and Mrose [28] and tentatively ascribed the formula V_2O_4H.

The evidence for the formation of an intermediate in the systems ramsdellite/groutite and paramontroseite/montroseite makes the present proposal of an intermediate for the system γ-MnO_2/δ-MnOOH a reasonable one. In fact Atlung [30] found it useful to postulate the intermediate Mn_2O_4H in order to obtain a reasonable fit between a theoretical curve and practical data of potential versus x for γ-MnO_2.

The results in Fig. 1 suggest that the filling

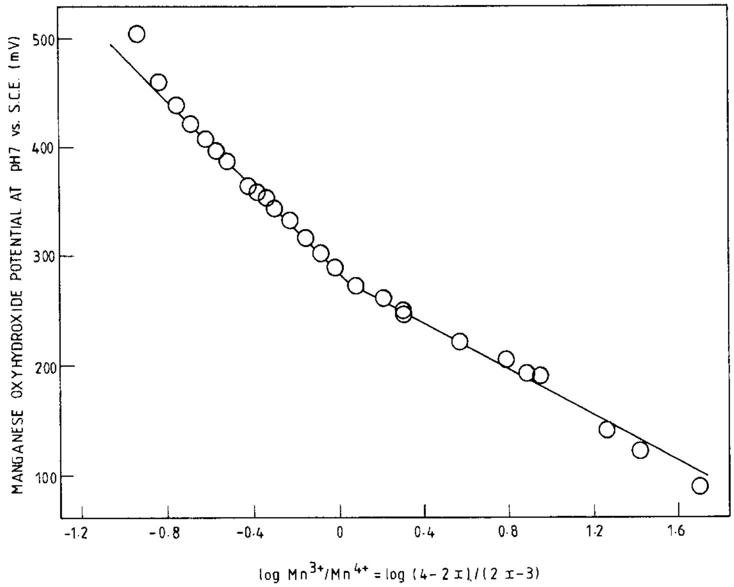

Fig. 6. The potential of partially reduced γ-MnO_2 versus degree of reduction.

of the MnO_2 lattice by protons and electrons proceeds differently in the ranges above and below $MnO_{1.75}$. Two possible explanations for this have been proposed by Maskell *et al.* [15]. One concerns proton filling and the other electron filling.

The proton filling mechanism may be understood by reference to Fig. 7. The ramsdellite [10] and groutite [31, 32] structures in the 0 0 1 plane are shown in Fig. 7a and b respectively. Oxygen atoms occupy two distinct positions having either planar or pyramidal co-ordination with respect to the manganese atoms. These are designated 0(1) and 0(2), respectively, as shown in Fig. 7a. It was suggested [15] that this allowed two types of location for proton bonding (a) type A or interpyramidal, where a proton is bonded to an oxygen in the 0(2) co-ordination and hydrogen-bonded to another also in the 0(2) co-ordination as shown in Fig. 7c, and (b) type B or pyramidal/planar, where a proton is covalently bonded to an oxygen in the 0(2) co-ordination and hydrogen-bonded to another in the 0(1) co-ordination as shown in Fig. 7b. An oxide ion could not be involved simultaneously in more than one bond and there are only sufficient locations for type A bonds for this mode of filling to occur exclusively in the region MnO_2 to Mn_2O_4H. Addition of each further proton for $x > 0.5$ must result in the location of at least two protons in type B positions i.e. there must be a switching of existing protons from type A to type B. At the composition MnOOH only type B positions may be occupied.

The second possibility suggested was that an electron entering the structure ($2.0 > x > 1.75$) is shared by two adjacent Mn^{4+} ions. The electron does not therefore reduce a single Mn^{4+} ion but is delocalized over two such units. In the second half of reduction ($1.75 > x > 1.5$) an electron entering the matrix is associated with a single Mn^{4+} ion and displaces an electron in resonance between this ion and an adjacent Mn^{4+} onto the latter.

Consideration will now be given to the anticipated variation of the lattice parameters if proton or electron filling were to proceed according to the models proposed. Lattice expansion is expected on reducing MnO_2 to MnOOH due to the difference in size of the Mn^{3+} and Mn^{4+} ions.

Oxygen atoms at 0(2) positions, between which it has been suggested a proton may bond in the first half of discharge (Fig. 7c), lie at depths $0.25c$ and $0.75c$. Hence proton bonding between two oxygens of this type would tend to restrict expansion in the *a*- and *c*-directions. On the other hand, two oxygen atoms at positions 0(1) and 0(2), between which a proton would bond in the second half of discharge (Fig. 7b), would both lie in the *a–b* plane. The hydrogen bond would be expected to cause some twisting of the structure but would result in very little restriction of the *a* parameter and have negligible influence on *c*. It appears that

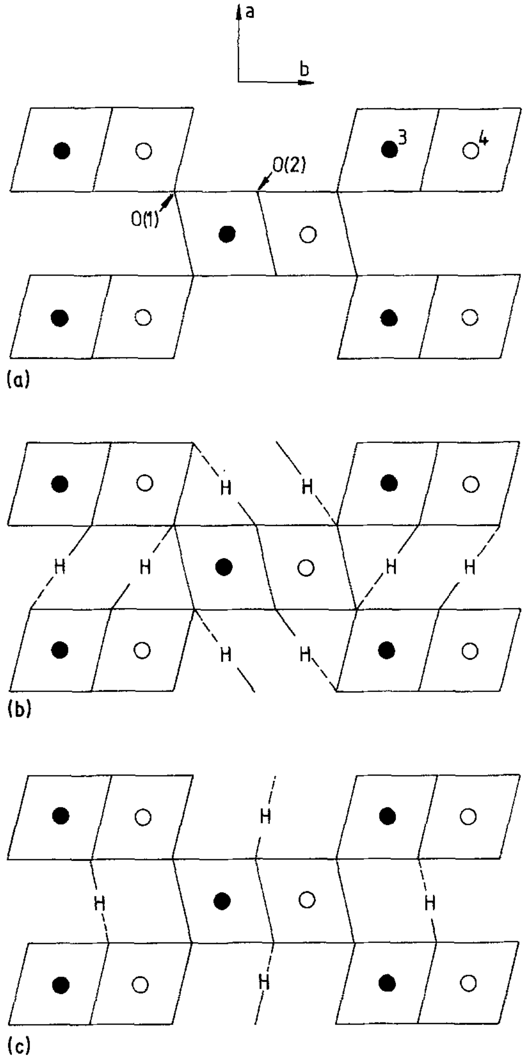

Fig. 7. Representation in the 0 0 1 plane of ramsdellite and related oxyhydroxides. Mn atoms are represented by filled and open circles at depths 0.75*c* and 0.25*c*, respectively. Oxygen atoms are at the corners of the octahedra. (a) Ramsdellite; (b) groutite; (c) suggested structure of the compound $MnO_{1.75}$ midway between ramsdellite and groutite. The *c*-direction is normal to the plane depicted.

proton filling according to the proposed model would have the reverse effect on the *a* and *c* parameters with reduction to that observed (Fig. 1).

Delocalization of an electron between two adjacent Mn^{4+} ions (shown as 3 and 4 in Fig. 7a) should tend to restrict expansion in the *b*- and *c*-directions compared with residence of the electron on a single Mn^{4+} ion. This is because the probability of an electron being between the two Mn^{4+} ions is greater for a delocalized than for a localized electron. An electron between the two quadrivalent ions both shields the positive charges from each other so reducing the repulsion and attracts each in the direction of the other (unlike charges, Mn^{4+} and e^-). Thus the model involving electron filling qualitatively predicts the observed variation of the *b* parameter but not that of the *c*. However, the variation of the latter may be a consequence of Jahn–Teller distortion as described below. The model involving electron filling therefore appears to be the more successful of the two in explaining the variation of the lattice parameters observed.

The Jahn–Teller distortion was calculated [15] using the data in Fig. 1. The result is shown in Fig. 8 where a''/a' is the ratio of two edges of an octahedron [14, 33]. It is found [33] that in structures containing Mn^{4+}, Al^{3+}, V^{3+}, Fe^{3+} and Ga^{3+} the ratio a''/a' is approximately 0.96 while those containing Mn^{3+} exhibit a ratio of about 1.05. Thus the result in Fig. 8 suggests that Mn^{3+} ions are not being formed until the second half of discharge and supports the electron filling mechanism proposed above.

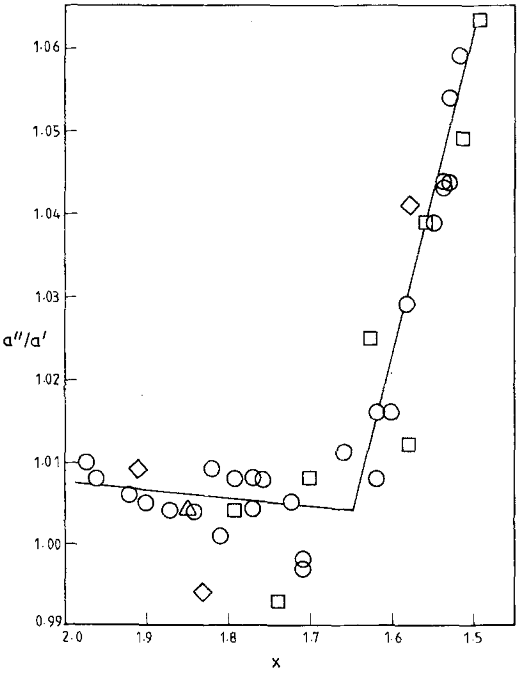

Fig. 8. Jahn–Teller distortion versus the degree of reduction *x*. Symbols as in Fig. 1.

4. Conclusion

There is substantial evidence in the γ-MnO_2/δ-MnOOH system for the existence of two solid solutions, one between MnO_2 and $MnO_{1.75}$ (e.g. Mn_2O_4H) and another between Mn_2O_4H and MnOOH. The two solid solutions may arise because of different proton–electron filling mechanisms above and below the midpoint.

One possibility is the existence of two proton locations, type A between pyramidal oxygens and type B between pyramidal and planar oxygens. Protons may be preferentially located in type A positions in the composition range MnO_2 to Mn_2O_4H but in the range Mn_2O_4H to MnOOH there must be a switch to type B positions so that at the composition MnOOH only type B locations are occupied as found for groutite (α-MnOOH).

Another possibility is that between MnO_2 and Mn_2O_4H added electrons are delocalized between two manganese ions so that Mn^{3+} ions as such are not present. Between Mn_2O_4H and MnOOH delocalization of an electron between two manganese ions can only occur to a restricted degree and some Mn^{3+} ions must be present. At the composition MnOOH all the manganese is present as Mn^{3+} ions.

The evidence, from variations of lattice parameters and Jahn–Teller distortion is in favour of the model involving electron filling. Both possibilities could, of course, occur together.

As a final comment, it is tempting to speculate for the range MnO_2 to Mn_2O_4H that the delocalization of an electron between two manganese ions and effectively the delocalization of a proton between two equivalent 0(2) sites would offset the coulombic penalty of spatial independence of added proton–electron pairs. The assumption of spatial independence of proton and electron, or dissociation as it has been called is necessary to understand quantitatively, the potential and equilibrium data obtained with γ-MnO_2 at compositions near to MnO_2 [34].

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