MECHANISM OF CATHODIC MnO_2 REDUCTION IN NEUTRAL SOLUTIONS

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How MnO_2 is cathodically reduced, whether in the solid phase or through the solution, has been discussed intensively (in the modern formulation) for more than 20 years, but still causes an animated discussion. Coleman [1], Lukovtsev [2], Vosburgh [3], and others have supported one mechanism, and Cahoon [4] and Drotschmann [5] have supported another, the latter very persistently. Brenet [6] has taken a middle position, considering that many reactions flow concurrently.

In the solid phase, the problem is formulated as

$$MnO_2 + H^+ + e \rightarrow MnOOH, \quad (1)$$

and it is assumed that the product forms as a solid solution in the initial manganese dioxide.

The second mechanism corresponds to the over-all equation

$$MnO_2 + 4H^+ + 2e \rightarrow Mn^{2+} + 2H_2O \quad (2)$$

and to the possible interaction of manganese ions in the electrolytic solution with the solid phase.

For acidic solutions (pH < 3), there is no doubt that Eq. (2) is applicable, even on the part of those who support the first mechanism. For neutral and alkaline solutions, the following have been offered as support of Eq. (1) and the first mechanism: a) during the cathodic reduction of MnO_2 electrodes in the form of compressed pellets or sinter cakes in dry cells, there is a rather clearly expressed concentration polarization in the solid phase, and in the alkaline region, it is also found with electrolytically deposited MnO_2 electrodes; b) x-ray analysis shows that solid solutions of MnOOH in MnO_2 form under these conditions; and c) the yield of the cathodic process for both alkaline and neutral electrolytes in Leclanché cells never exceeds 100% of that calculated from Eq. (1).

Other evidence, e.g., the descending nature of the potential curve and the amount of charge passed, is of a more indirect nature.

On the other hand, it is difficult to explain on the basis of the solid-phase mechanism certain facts emphasized by adherents of the second mechanism: a) during cathodic MnO_2 reduction in electrolytes with $3 \leq pH \leq 6$, noticeable amounts of Mn^{2+} ions appear in the solution; b) under certain conditions, the value of $dE/d(pH)$ is ~ -110 mV per (pH unit) for the MnO_2 electrode in the interval $3 \leq pH \leq 7.5$; and c) with thin electrodes produced by electrodeposition of MnO_2 on Pt, the cathodic-process yield in an excess of electrolyte with pH values up to six is 200% of that calculated by Eq. (1) and 100% of that calculated by Eq. (2). The E(t) curve in this case has a small slope and there is no evidence of a division into two steps.

It was shown in recent studies by this author and Dam'e [7] that the same cathodic-process yield could be obtained with compressed MnO_2 electrodes in excess electrolyte with pH from three to five, and perhaps higher, if small current densities are used for the polarization. Moreover, it was shown in these studies that under these same conditions with a limited amount of electrolyte, one could produce a horizontal rather than descending E(t) curve when manganese dioxide with high proton-exchange properties is used for the electrodes. This behavior is independent of the features of the manganese dioxide lattice: the process occurs by the formation of a new phase (heterolytic) rather than in solid solutions. The two groups of evidence above can be reconciled and explained under the assumption that the mechanism for cathodic MnO_2 reduction in a neutral electrolyte depends on the magnitude and nature of the change of the solution pH near the electrode during the process.

As was mentioned above, there is general agreement about the mechanism for cathodic MnO_2 reduction in acidic solutions (at a pH not greater than three): it is described by Eq. (2). It may be that the process can go by

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Eq. (2) at higher pH also, but that its rate is sharply reduced. In this connection, the fraction of the process going by the mechanism described by Eq. (1), whose rate depends little on the pH and is governed by proton diffusion in the solid phase, increases significantly. The limiting bulk-electrolyte pH value for this change is close to six, but may depend slightly on the current density and solution agitation because of concentration polarization.

If thin electrodes are polarized in an excess of an agitated electrolyte with a constant pH, process (2) would prevail up to a pH of about six. At higher pH, the process would go basically by Eq. (2), in accordance with the remarks above. We note that the sharp reduction in the rate of process (2) at pH 6 may be due to a decrease in both the hydrogen-ion concentration and the possible Mn^{2+} concentration in the solution [8], which could also reduce the exchange current of process (2).

If thick compressed electrodes are cathodically reduced in a neutral electrolyte (with initial pH less than six) at current densities which are not too small, process (2) is rapidly attenuated in electrode pores because of intense alkalization of the electrolyte, and further reduction occurs by the solid-phase mechanism. Only at small current densities and in the presence of a proton source, when a sufficiently low pH is maintained in the electrode pores (not greater than five or six), does the process occur by Eq. (2) in the case of thick electrodes. If such a process occurs in a limited amount of electrolyte, conditions are usually favorable for the occurrence of secondary processes, e.g., heterolytic formation.

A similar point of view about the pH dependence of the mechanism of MnO_2 reduction in neutral solutions was taken in a study by Era, Takehara, and Yoshizawa [9], who based their arguments on slightly different ideas and facts. Their treatment did not, however, place enough emphasis on the role of concentration polarization due to possible changes in electrolyte pH during the cathodic process.

In particular, this effect could be easily explained by a large polarization of the MnO_2 electrode in neutral solutions, in comparison with alkaline solutions, but the authors of [9] used a considerably more complicated and debatable explanation.

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