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ORIGINAL PAPER

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The γ-MnO_2 electrode: from the dynamic transformation to the equilibrium state; the corresponding thermodynamic potential ε

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Abstract The thermodynamic potential ε of the γ- or ε-MnO_2 electrode is studied as a function of the previous dynamic transformation imposed by the (H^+, e^-) couple insertion. To the two main dynamic steps of the total reduction of the dioxide correspond respectively the two following analytical expressions for ε, written at constant pH vs. the standard hydrogen electrode:

$$\varepsilon = \varepsilon'^{\circ} + 2(RT/F)\ln\{(1-r)/r\} - (RT/F)\ln(f_{H^+}f_{e^-})$$

and

$$\varepsilon = \varepsilon'^{\circ} + 2(RT/F)\ln\tau_{st} - (RT/F)\ln(f_{H^+}f_{e^-})_{st}$$

where τ_{st} is the relative fraction of the untrapped particles.

Key words Manganese dioxide · Thermodynamic potential · Electrolytic insertion theory · Semiconductors

List of symbols

C	Colman proton concentration
a_i	Activity of the species i
f_i	Activity coefficient of the species i
ε	Thermodynamic potential
$\boldsymbol{E}_d$	Internal electric field vector
r	MnO_2 homogeneous reduction degree
P	Pair concentration
p	Trapped e^- fraction
$\boldsymbol{p}$	Untrapped e^- or H^+ fraction
$(C-P)$	Unpaired e^- or H^+ concentration
C'	MnO_6 initial concentration
$(\,)-$	MnO_6^{8-} site
$(+)$	O_6^{12-} site
τ	Relative fraction of the untrapped particles
s_i	Area of the reactive sub-surface "i"

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Introduction

The present study is the fifth of a series dealing with a general theory for the important material γ/ε-MnO_2 [1–4]. It presents a new point of view on the thermodynamic potential of this electrode at a given reduction state. The case of a strongly alkaline or acidic medium, which may lead to the dissolution of the dioxide crystalline structure, is excluded [5]. The relevance of the present theory to these important practical conditions will be discussed in a further paper.

The general problem

As it is well known, the γ-MnO_2 semiconductor reduces by the insertion of the (H^+, e^-) couples. The generally adopted equation is:

$$\underset{a_1}{MnO_2} + H^+ + e^- \rightarrow \underset{a_2}{MnOOH} \quad (1)$$

where a_1 and a_2 are activities. In the reversibility domain of this reaction one can apply the Nernst law and obtain an expression for the thermodynamic potential ε (vs. a hydrogen electrode immersed in the same electrolyte):

$$\varepsilon = \varepsilon^{\circ} + (RT/F)\ln(a_1/a_2) - 2.303(RT/F)\mathrm{pH} \quad (2)$$

which becomes at a constant pH:

$$\varepsilon = \varepsilon'^{\circ} + (RT/F)\ln(a_1/a_2) \quad (3)$$

After assuming the total reversibility of Eq. 1 on the overall region of the first-electron reduction of the dioxide, several authors have attempted to express ε in terms of r, the degree of reduction of MnO_2. However, because they used different theories (non-electrolytic

[6–8], electrolytic [9–11], thermodynamic [12, 13] or statistical thermodynamics [12, 14–16]) to define the physical state of the MnO_2/MnOOH mixing, the results are different or conflicting and the problem is still unsolved (for a more general review see [3]).

Finally, after a given dynamic transformation the partly reduced γ-MnO_2 electrode tends to some characteristic equilibrium state which represents, in a way, the thermodynamic image of the transformation. Therefore, before any theoretical development (see below), it is necessary to review the dynamic theory of the (H^+, e^-) insertion in γ-MnO_2 which is based on the strong electrolyte approach and the treatise on carrier injection in semiconductors [1–4, 17, 18].

Summary of the dynamic theory of the (H^+, e^-) insertion in γ-MnO_2

The governing theme of this theory lies in the analogy between semiconductors and aqueous solutions. The MnO_2 material is a solid continuum medium that plays the role of a solvent in which the strong electrolyte (H^+, e^-) can easily dissociate. The dynamic evolution during the total reduction is divided into two main steps, the free diffusion step (FDS) ($0.08 < r < 0.50$) and the diffusion with trapping step (TDS) ($0.50 < r < 1$), separated by the mid-reduction level at which the internal electric field switches over and gives rise to the famous behavior change of the dioxide. During the former (FDS), the inserted species are approximately delocalized and behave like a gas of particles within which the weak "Debye and Hückel" interaction can exist (if $0.38 < r < 0.50$). While the longitudinal component of the internal electric field vector $\boldsymbol{E}_{ld}$ slows down the electron movement and accelerates the protonic one, the transverse component $\boldsymbol{E}_{td}$ repulses the electrons far from the MnO_6^{8-} site octahedra. In the second step, the protons are accelerated (inversely for the electrons) by $\boldsymbol{E}_{ld}$. The transverse component $\boldsymbol{E}_{td}$ attracts the electrons towards the MnO_6^{8-} site octahedra and offers them the necessary energies to jump the existing potential barrier at the octahedron surface, penetrate inside it and reduce the Mn^{4+} ion. In other words, the inserted protons and electrons may be trapped (if $r > 0.50$) within the O_6 and MnO_6^{8-} site octahedra in order to give the pairs [O_6, H^+] and [MnO_6, e^-]. The latter is equivalent to an Mn^{3+} ion.

Finally, it is worth noticing that:

1. Pairing and trapping here explain the same physical phenomenon (designated by strong interaction): the localization of the diffusing particles.
2. The electronic mean diffusivity becomes, if $r > 0.60$, very weak and negligible by comparison to the protonic one.
3. Equation 1 reflects only the continuous dissociation of the (H^+, e^-) couples within the solid solution $MnOOH_r$. It does not take into account the pairing interaction which takes place when $r > 0.50$.

Theory

Dynamic localization of the trapped electrons

Principle

Stabilized by the Jahn-Teller distortion [19–25], the dynamic formation of Mn^{3+} ($r > 0.50$) is an irreversible phenomenon that the driving forces of the continuum medium cannot redissociate or remove. In other words, the trapped electron can no longer diffuse and still be localized in the MnO_6 octahedron, which becomes a definitively occupied site (d.o.s.). The respect of the neutrality principle requires the consideration that the [O_6, H^+] pair is the neighbor of the [MnO_6, e^-] entity, with which it exchanges some attractive forces, and this implies the formation of the [MnO_6, e^-] $\cdots$ [O_6, H^+] dipole. Consequently, some concentration gradient of the [MnO_6, e^-] $\cdots$ [O_6, H^+] dipole will be imposed between the surface and the center of the γ-MnO_2 grain. Thus, one can deduce that the pairing interaction cuts the continuity of the electronic diffusion network and destroys progressively the initial structure (FDS)° of the electrode material by giving rise to the formation of a quasi-amorphous phase (q.a.p.) in the grain region where we have $0.50 < r < 0.80$ [26, 27], or a new phase, if $0.80 < r < 1$, which is called δ-MnOOH by Tye et al. [28]. The protons of this phase are not covalently bound to the oxygen atoms but they are sitting in the center of octahedra in the structure channel [19, 20, 26–28].

The localization of the inserted electrons is confirmed by several published results in which it has been demonstrated that:

1. The solubility of the discharge products is very low in a non-"strongly alkaline or acidic" medium [29–32]. In fact, a good solubility of these discharge products implies some high diffusivity of the trapped electrons in the solid phase, which is not the case here [4].
2. The reoxidation of the γ-MnO_2 electrode, which is completely reversible on the (FDS)° domain, becomes partly or weakly realizable respectively on the (q.a.p.) or δ-MnOOH one. The latter sub-structures cannot return back to (FDS)° [26].

To sum up, by reducing, in the host structure, the number of available sites MnO_6/O_6 and the free charge carriers, the pairing then has a direct influence on the species concentrations, and consequently on the dynamic and thermodynamic electrode potentials.

Comments

The existence of the three successive sub-structures (FDS)°, (q.a.p.) and δ-MnOOH was confirmed also by the three cyclic voltammograms made in the course of the entire discharge of γ-MnO_2 in the (practically) all-solid electrochemical cell:

γ-MnO_2 (35.7 mg) – HUP (300 mg) – acetylene black (4.3 mg)/HUP (300 mg)/Pt, H_2, H_2O

where HUP is the crystallized protonic conductor $HUO_2PO_4 \cdot 4H_2O$. In fact, the voltammograms obtained have the same general form, indicating the uniqueness of the reaction mechanism, but present three distinct slopes for $\Delta I/\Delta\varepsilon$ of 0.150, 0.075, 0.050 A/V, and (if $r > 0.50$) an increasing hysteresis [33–35].

Implied by the trapping/localization action, the decreasing value of $\Delta I/\Delta\varepsilon$ really reflects the decrease of (1) s_i, the area of the reactive sub-surface "i", over which flow the (H^+, e^-) particles [2]; this decrease takes place when s_i becomes partly or totally covered by the (q.a.p.) or/and δ-MnOOH; (2) the numbers of the free charge carriers.

Equilibrium distribution of the untrapped/free particles after a previous dynamic transformation

Case of the TDS

It follows from above that the recovery phenomenon, which takes place after the current is shut off, concerns only the free (H^+, e^-) couples. When the electrode reaches the equilibrium state, the untrapped particles (H^+, e^-) will be homogeneously distributed in the unpaired regions of the γ-MnO_2 grain, and consequently the Nernst field becomes very weak or null. Using this latter result, one can consider that, at the equilibrium state:

1. The pairing phenomenon, characteristic of the TDS, is stopped and the Mn^{4+} ions will no longer be reduced to Mn^{3+} (d.o.s.).
2. The paired sites MnO_6^{9-} and [O_6, H^+] repulse the free inserted particles and cannot be their equilibrium sites.
3. The free inserted electron will be attracted towards a MnO_6^{8-} site octahedron, without the possibility to penetrate inside it ($\boldsymbol{E}_{td} = 0$), giving rise to the formation of the MnO_6^{8-} site...e^- couple.
4. The free inserted proton may occupy the center of a O_6^{12-} octahedron, neighbor to a MnO_6^{8-} site...e^- couple [27, 29].

Therefore, from a statistical point of view, the cluster MnO_6^{8-} site [or ( )–] and O_6^{12-} [or (+)] constitute two independent sub-networks of the available interstitial sites on which the untrapped e^- and H^+ will be sitting at the equilibrium state. That is, the MnO_6^{8-} site...e^- [or ( ) e^-] and [O_6, H^+] [or (H^+)] couples can be considered, at the equilibrium, as the temporarily occupied sites (t.o.s.) in the γ-MnO_2 electrode material. This means that the t.o.s. may be evacuated after the current is turned on and therefore they are fundamentally different from the d.o.s.

Case of the FDS

Here the situation becomes simpler (no pairing effect) and all the inserted particles participate in the recovery process. When a sufficient time has passed, the system reaches the equilibrium state and then the internal electric field is null and the total quantity of the (H^+, e^-) couples is homogeneously distributed on the ( )– and (+) sites. Evidently, the occupation of these latter gives rise to the formation only of the t.o.s. (without d.o.s.) kind: ( )e^- and (H^+).

Concentrations and activities

Finally, it will be assumed in the next sections that initially we have:

$$\text{Concentration of } (+) = \text{concentration of } (\ )- = C' \tag{4}$$

or

$$a_{(+)} = a_{()-} \tag{5}$$

More general reaction equations and equilibrium species activities

Now, on the basis of the previous paragraphs and according to the strong electrolyte theory, we can replace Eq. 1 by one of the two following equations for the FDS or TDS.

Free diffusion step

$$\underset{a_1}{(+),(\ )-} + H^+ + e^- \rightarrow \underset{a_2}{(H^+),(\ )e^-} \tag{6}$$

The continuous dissociation of the inserted couples without any pairing effect implies that, at the equilibrium state, we may consider all the inserted electrons are in the t.o.s. and have a [O_6, H^+] as neighbor. Thus:

$$a_1 = a_{(+)}a_{()-} = (C' - C)^2 \tag{7}$$

$$a_2 = a_{(H^+)}a_{()e^-} = f_{H^+}f_{e^-}C^2 \tag{8}$$

where $a_{H^+} = f_{H^+}C$ and $a_{e^-} = f_{e^-}C$ (C represents here the concentration of the t.o.s. in the electrode material).

Diffusion with trapping step

$$\underset{a_1}{(+),(\ )-} + H^+ + e^- \xrightarrow{\text{I}} \underset{a_2}{(H^+),(\ )e^-} \xrightarrow{\text{II}} (H^+),(e^-) \tag{9}$$

where the equilibrium II is irreversible (see above) and a_1 is still defined by Eq. 7.

Some concentration P of the inserted particles is in the d.o.s. which is not to be considered when we count the number of the formed t.o.s. within the host structure [4]. Therefore Eq. 8 becomes:

$$a_2 = a_{(H^+)}a_{()e^-} = f_{H^+}f_{e^-}(C - P)^2 \tag{10}$$

where C represents here the sum of the total concentration of the "t.o.s. and d.o.s." in the electrode material.

As a matter of great interest, equilibrium II seems, by free particle trapping, to displace equilibrium I in the sense of the increasing insertion rate. According to the law of equilibrium displacement, the host material must react in the opposite sense of this modification, that is in the deinsertion one. This fact is verified in all the literature data, where we know well that the insertion is less rapid in the TDS region than in the FDS one. From the thermodynamic potential point of view, this opposition must appear in a faster decrease (relative to the general evolution of ε in the FDS region) of ε versus the reduction degree in the TDS region. That is to say that a supplementary drift η (V) of the potential ε is to be taken into account in the TDS region; see below.

The γ-MnO_2 reduction degree

Numerous published studies concerning the γ-MnO_2 material have dealt with the reduction degree r. Calculated from the total debited quantity of electricity, r is in fact a mean or a "homogeneous state" quantity. However, the potential of the γ-MnO_2 electrode has to be calculated as a function of the interfacial quantity "r_s" which (1) is the effective reduction degree of the grain reactive sub-surfaces [2]; (2) has always a dynamic value r_{sd} higher than r; (3) takes after the current cut-off an equilibrium value r_{st} ("t" means thermodynamic) which may be higher or equal to r, depending on the presence or absence of the pairing phenomenon. Therefore, one has to distinguish between the following three dynamic cases coupled with their corresponding thermodynamic ones:

$$\begin{aligned}
&1.\ r_{sd} < 0.50,\ \text{FDS or no pairing } r_{st} = r \\
&2.\ 0.50 \le r_{sd} \le 0.80,\ \text{TDS, pairing } r_{st} > r \\
&3.\ 0.80 \le r_{sd} \le 1,\ \text{TDS, globalpairing} \\
&\quad \text{and formation of } \delta\text{-MnOOH } r_{st} \ge r
\end{aligned} \tag{11}$$

In the three cases we have $r_{sd} > r_{st}$. Equation 11 represents the set of the three above cases: 1, 2 and 3.

Equilibrium potential on FDS, $r_{sd} < 0.50$

Using Eqs. 3 and 6–8 one can obtain the thermodynamic potential expression of the solid solution:

$$\varepsilon = \varepsilon'^{\circ} + 2(RT/F)\ln\{(C' - C)/C\} - (RT/F)\ln(f_{H^+}f_{e^-}) \tag{12}$$

or, after division by C':

$$\varepsilon = \varepsilon'^{\circ} + 2(RT/F)\ln\{(1 - r)/r\} - (RT/F)\ln(f_{H^+}f_{e^-}) \tag{13}$$

With the relationships 12 and 13 and 6–8 we can easily justify the origin of the existence of factor 2 in the expression for ε and identify numerically the weak (Debye and Hückel) interaction part [3].

By referring to a pure solvent, f_{H^+} and f_{e^-} must be equal to or less than unity. Consequently the weak coulombic interaction is then:

$$-(RT/F)\ln(f_{H^+}f_{e^-}) \ge 0 \tag{14}$$

According to Eqs. 13 and 14 one can deduce that, at the equilibrium state, the Debye and Hückel interaction contributes positively to the thermodynamic potential of the electrode. This result may appear in a first impression as a striking matter, but on the basis of the above developed theory we can easily interpret it. In fact, the repulsion between the inserted protons and between the inserted electrons must be considered, at equilibrium, as a working factor in the sense of the deinsertion and consequently for the returning back of the electrode potential to its initial higher value. Finally, we should keep in mind here that the same interaction has, inversely, a negative role (or value) during the dynamic steps [4].

Equilibrium potential on the TDS, $r_{sd} > 0.50$

Principle

It should first be noticed that, because of the irreversibility of equilibrium II of Eq. 9, it is implied that the Nernst law can no more be applied [36]. This reflects the difficulty that is normally encountered in trying to obtain the analytical form of ε in the total range of the reduction reaction. This fundamental problem can be reduced by assuming that on the TDS the equilibrium state corresponds to the two previous dynamic transformations: (1) the continuous dissociation of the strong electrolyte (H^+, e^-), which is reversible, and (2) the irreversible pairing interaction. That is to say that the potential ε can simply be expressed in terms of r_{st} (see above) and defined (or approached) by the relationship 13 modified by taking into consideration the perturbation introduced by the pairing phenomenon. We have seen above that the latter yields a supplementary potential drop η which has to be analytically stated.

Analytical expression for η

If the insertion process is represented, as in Eq. 13, by the physical quantity $(RT/F)\ln a_1/a_2$, it is clear that the deinsertion can be described by the expression $-(RT/F)\ln a_1/a_2$ or $(RT/F)\ln a_2/a_1$, where a_1 and a_2 are defined by Eqs. 7 and 10. That is to say that the supplementary decrease η, due to the trapping effect (see above), could be asserted or defined by

$$\eta = -2(RT/F)\ln\{(1 - r_{st})/(r_{st} - p_s)\} \tag{15}$$

Combined with the experimental curve obtained by Tye et al. [11], the relationship 15 allowed the author to

determine a reasonable set of values of the fraction p on the TDS region [3]. This approximative determination represents, in fact, an important verification of the validity of our concepts.

Analytical expression for ε

As stated above, the thermodynamic potential of the electrode on the TDS may be defined or approximated by

$$\varepsilon = \varepsilon'^{\circ} + 2(RT/F)\ln\{(1 - r_{st})/r_{st}\} - (RT/F)\ln(f_{H^+}f_{e^-})_{st} + \eta \quad (16)$$

which reduces (using Eq. 15) to the simpler form

$$\varepsilon = \varepsilon'^{\circ} + 2(RT/F)\ln\{(r_{st} - p_s)/r_{st}\} - (RT/F)\ln(f_{H^+}f_{e^-})_{st} \quad (17)$$

or

$$\varepsilon = \varepsilon'^{\circ} + 2(RT/F)\ln\{(\boldsymbol{p}_{st}/(p_s + \boldsymbol{p}_{st})\} - (RT/F)\ln(f_{H^+}f_{e^-})_{st} \quad (18)$$

Now, by putting

$$\tau_{st} = (r_{st} - p_s)/r_{st} \quad (19)$$

or

$$\tau_{st} = \boldsymbol{p}_{st}/(p_s + \boldsymbol{p}_{st}) \quad (20)$$

we finally obtain

$$\varepsilon = \varepsilon'^{\circ} + 2(RT/F)\ln\tau_{st} - (RT/F)\ln(f_{H^+}f_{e^-})_{st} \quad (21)$$

From Eq. 21 one can deduce that the fraction τ_{st} is the governing factor in the determination, on the TDS, of the potential electrode ε.

Boundary conditions

The dynamic region $0.50 < r_{sd} < 1$ corresponds to the thermodynamic one $1 > \tau_{st} > 0$, where $\tau_{st} = 1$ if $r_{sd} = 0.50$, and $\tau_s = 0$ if $r_{sd} = 1$ and $p_s = 1$. (22)

Consequences

Clearly, Eqs. 20 and 22 indicate the existence, in the $0.50 < r_{sd} < 1$ region, of the following three steps:

1. $p_s < \boldsymbol{p}_{st}$; free particles are the majority carriers; thus $p_s + \boldsymbol{p}_{st} < 2\boldsymbol{p}_{st}$ and then $0.50 < \tau_{st} < 1$.
2. $p_s \approx \boldsymbol{p}_{st}$; equality of the carriers numbers; thus $\tau_{st} \approx 0.50$. (23)
3. $p_s > \boldsymbol{p}_{st}$; the free particles are the minority carriers; thus $p_s + \boldsymbol{p}_{st} > 2\boldsymbol{p}_{st}$ and then $0 < \tau_{st} < 0.50$.

Equation 23 represents the set of the three above cases: 1, 2 and 3.

Discussion

It is very tempting to correspond the three cases of Eq. 23 respectively to those which are stated in the section on Dynamic localization of the trapped electrons (see above) (q.a.p.), phase transition (q.a.p.)/δ-MnOOH and δ-MnOOH. That is to say that the step $p_s \approx \boldsymbol{p}_{st}$ may be realised at or just before the transition between the two sub-structures (q.a.p.) and δ-MnOOH. This point of view seems to be confirmed by the inelastic neutron scattering (INS) experimental data, where Fillaux et al. [27] have observed an abrupt change of the INS spectrum (or lattice modes) in the region preceding the phase transition. This result appears to be quite valid, because if the upper limit of the (FDS)° was defined by the equality between the numbers of the t.o.s. and free sites in the host structure, it should be logical then to define the upper limit of the second region (q.a.p.) by the equality between the numbers of the trapped and untrapped particles. Finally, this result consolidates the proposed theory and demonstrates that its different parts are in real harmony.

Whereas the ratio $(1 - r)/r$ is defined in Eq. 13 by referring to C', that is to the (absolute) framework of the host structure, the fraction τ_{st} may be (relatively) related in Eq. 20 to the concentration C of the all inserted particles within the (absolute) structure. This means that $(1 - r)/r$ and τ_{st} are respectively absolute and relative fractions. That is to say, τ_{st} is, in a way, the relative fraction of the untrapped particles. Therefore, while the relationship of Eq. 13 reflects well the continuous dissolution of the strong electrolyte into the continuum medium of the solvent, Eq. 21 indicates that ε becomes simply a logarithmic function of the relative fraction of the untrapped (or free) particles. Nevertheless, we should keep in mind the fact that the limiting and irreversible reaction of pairing is always supported by the reversible one represented by Eq. 6.

Finally, this relative aspect of the pairing/insertion seems to be the source from which arise, in the literature, some interpretation like the behavior change and the existence of a second solid solution appearing in the dioxide when $r_{sd} > 0.50$.

Conclusion

The physicochemical concepts of the dynamic theory of the partly reduced γ-MnO_2 are extended and completed with the aim of defining the thermodynamic state of this electrode. The equilibrium is regarded as the consequence of the previous dynamic transformation which may be reversible (no pairing) if $r_{sd} < 0.50$, or irreversible

(pairing) corresponding to $r_{sd} > 0.50$. Thus, as a function of the reversibility factor, two analytical expressions have been proposed for the thermodynamic potential of the γ-MnO_2 electrode. These expressions are (1) both based on the continuous dissociation of the (H^+, e^-) couples and their random distribution, at equilibrium, on the available sites in the host structure, (2) originally differing by the existence or not of η, the supplementary potential drop due to the trapping process, and by the use of r or r_{st} terms.

Finally, one great advantage of the adopted approach in this study is that it is based on very simple physicochemical ideas, and this enables the solution of a number of important problems concerning the general theory of manganese dioxide. In the next paper it will be time to treat the important question of the reoxidation of the partly reduced γ-MnO_2.

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