ORIGINAL PAPER

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The γ-MnO$_2$ electrode: the electrochemical de-insertion of the (H$^+$, e$^-$) couple from the partly reduced grain

Abstract A considerable understanding of the re-oxidation properties of partly reduced γ-MnO$_2$ is gained through simple phenomenological analysis of the experimental results and exploitation of the advances in the science of carrier injection in semiconductors. It is essentially demonstrated that the de-insertion reaction is still possible if the free or untrapped charges (H$^+$, e$^-$) in the bulk of the host material remain the majority carriers. In contrast, in the existence zone ($r_\mathrm{d} > 0.80$) of δ-MnOOH the trapped particles become the majority (the free ones become minority) carriers and the flux may be stopped or gives rise to further types of reaction (complex formation, oxygen regeneration, etc.). Besides being of interest in themselves, these results are useful in studying the properties of electrode materials or semiconductors in which they occur.

Keywords Manganese dioxide · De-insertion · Semiconductor · Secondary battery

Abbreviations and symbols C: Colman proton concentration · a_i: activity of the species i · f_i: activity coefficient of the species i · $\in_\mathrm{th}$: thermodynamic potential · Φ: flux vector · D: diffusion tensor · $\tilde{D}$: ambipolar diffusion tensor · FDS: free diffusion step · TDS: diffusion with trapping step · ∇C: concentration gradient vector · E_int: internal electric field vector · $V_\mathrm{H}+$: protonic self-velocity vector · $V_\mathrm{e}-$: electronic self-velocity vector · $\tilde{W}$: ambipolar velocity vector · r: MnO$_2$ homogeneous reduction degree · r_d: MnO$_2$ dynamic reduction degree (insertion) · r_d^{-1}: MnO$_2$ dynamic reduction degree (de-insertion) · τ: relative fraction of the untrapped particles · q.a.p.: quasi-amorphous phase · p.r.m.d.: partly reduced γ-MnO$_2$ · t.o.s.: temporarily occupied sites · d.o.s.: definitively occupied sites · ()–: MnO$_6^{8-}$ site · (+): O$_6^{12-}$ site · s_i: area of the reactive sub-surface i · P: pair concentration · $\underline{P}$: unpaired e$^-$ or H$^+$ concentration · C': MnO$_6^{8-}$ or $\overline{\overline{\mathrm{O}}}_6^{12-}$ concentration · p: trapped e$^-$ fraction · $\underline{p}$: untrapped e$^-$ or H$^+$ fraction

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Introduction

Historically, a number of early papers discussed the re-oxidation properties of the γ-MnO$_2$ electrode after partial reduction; subsequently, partly because of the difficulty and partly because of the lack information about the variation of the structural properties, little work was done on this problem. Recently, by reason of increasing need in the field of electrochemical power sources, this has attracted a greater deal of attention. In a blend of theory and experiment, the following article is the sixth part of a series dealing with the physicochemical properties of the important n-semiconductor γ-MnO$_2$ and describes some of the developments in this field during the last few years [1, 2, 3, 4, 5].

The nature of the problem

The most important questions dominating the domain of the γ-MnO$_2$ semiconductor at present are (1) understanding the (H$^+$, e$^-$) de-insertion mechanisms and (2) how to obtain a good cycling of this electrode with the goal to use it as a rechargeable material in secondary batteries. Although the two questions are closely related, it is preferable to treat them separately. Therefore, only the first question will be considered here. Thus the *intent* of this new theoretical study is to provide a thorough exploration of the behaviour of the partly reduced γ-MnO$_2$ when we submit it (by applying an appropriate electric field) to the *first* re-oxidation reaction. It is hoped also that the article will prove useful both to those working in the research or development of

rechargeable batteries systems and to those wishing to study the semiconductor's properties (in fact, the reduction has remained associated with solid state electrochemistry and the science of carrier injection in semiconductors).

The previous transformation

The present work was preceded by a general treatment of the dynamic and thermodynamic phenomena that occur in the course of the reduction reaction of γ-MnO$_2$. In this respect, it is the natural complementary part of this treatment. Therefore, before considering (H$^+$, e$^-$) de-insertion in detail, it is appropriate to review the main previous results in a manner to provide the background required for easier reading and to benefit the reader who is not familiar with this topic [1, 2, 3, 4, 5].

The entire reduction pathway of the γ-MnO$_2$ electrode is governed by two main dynamic steps: the free diffusion step (FDS, $0.08 < r_d < 0.50$) and the diffusion with trapping step (TDS, $0.50 < r_d < 1$), separated by the mid-reduction level ($0.50e^-$/Mn^{4+}) at which the internal electric field (E_{int}) switches over and gives rise to the famous behaviour change of the dioxide. During the former (FDS), the (H$^+$, e$^-$) couples behave approximately like a gas of particles and diffuse without pairing in the host bulk. The principal potential factor for diffusion in a given direction is the difference V_d between the components, along this direction, of the self velocities , V_{H+} and V_{e-}. The value of D_{iid} is a maximum at a low level of insertion and decreases towards zero near $r_d = 0.50$ (where V_{H+} and V_{e-} become equal). The internal electric field (E_{int}) obliges the inserted particles to diffuse with the common diffusion tensor $\tilde{D}$ and ambipolar velocity $\tilde{W}$. The analytical expression of vector E_{int} is:

$$E_{int}(\text{insertion}) = (kT/e)\mathbf{D}_s^{-1}\mathbf{V}_d \tag{1}$$

The reaction equation on the FDS is expressed as follows:

$$(+),\ ()^- + H^+ + e^- \ \xrightarrow{\ I\ } \ (H^+),\ ()e^- \tag{2a}$$
$$a_1 \qquad\qquad\qquad\qquad a_2$$
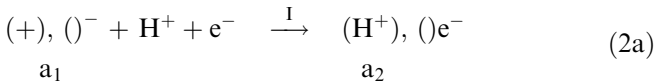
Conversely to the situation in the FDS, the ambipolar diffusion in the second step (TDS) of the insertion is characterized by the value $D_{iid} < 0$ and accompanied by a strong interaction which gives rise to the formation of the pairs [Mn^{4+}, e$^-$] or Mn^{3+}, and [O$_6$, H$^+$] [4]. Stabilized by the Jahn-Teller distortion, the dynamic formation of Mn^{3+} is an irreversible phenomenon and the trapped electron is still definitely localized in the MnO$_6$ octahedron (definitively occupied sites, d.o.s.). Therefore, one can deduce that the pairing interaction progressively destroys the initial structure (FDS)$^\circ$ of the electrode ($r_d < 0.50$) and gives rise to the formation of a quasi-amorphous phase (q.a.p.) in the range $0.50 < r_d < 0.80$, followed by the new phase δ-MnOOH

($0.80 < r_d < 1$). It must be remembered that the existence in the course of the γ-MnO$_2$ entire discharge of the three sub-structures, (FDS)$^\circ$, q.a.p. and δ-MnOOH, has been confirmed by several published works (see [5]). Furthermore, the general problem of insertion on the TDS may be reduced to a problem of comparison between the carrier numbers:

1. q.a.p.: the free particles are majority carriers.
2. q.a.p./δ-MnOOH (transition): equality of the carriers numbers.
3. δ-MnOOH: the free particles are minority carriers.

The general equation for the paired insertion reaction is defined by:

$$(+),\ ()^- + H^+ + e^- \ \xrightarrow{\ I\ } \ (H^+),\ ()e^- \ \xrightarrow{\ II\ } \ (H^+),\ (e^-)$$
$$a_1 \qquad\qquad\qquad\qquad\qquad a_2$$
$$\tag{2b}$$
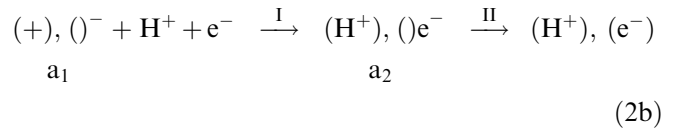
Whereas the equilibrium I is reversible, the equilibrium II is irreversible.

Finally, in order to make progress it was necessary to subdivide the two main steps (FDS and TDS) into five dynamic regimes. The first one of these was called the ideal regime because not only does it correspond to the ideal solid solution but also to the optimum values of the physical quantities implicated in the insertion transformation.

Review of literature experimental results

Observations of various γ-MnO$_2$ re-oxidation curves have been carried out by numerous studies [6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21]. These results have established that the extent and performance of the de-insertion process depend on the reduction depth and experimental conditions. Three regions, delineated through three intervals of r_d, are required to characterize the de-insertion problem on the global insertion pathway, i.e. the partly reduced γ-MnO$_2$ (p.r.m.d.) can re-oxidize: (1) well in the region corresponding to $r_d < 0.50$, especially in the zone $r_d < 0.30$, and the initial capacity of the electrode can be completely recovered by (H$^+$, e$^-$) de-insertion; (2) partly in the region $0.50 < r_d < 0.80$ and an important part of the inserted amount is inhibited ($\sim$20% at the reduction depth $0.8e^-$/Mn^{4+}), i.e. that it remains trapped in the dioxide network and cannot de-insert; (3) very little or none in the region $0.80 < r_d < 1$.

Notice that neither in the above nor in the practical use of the alkaline or Leclanché elements has the reduction level of the positive electrode material reached the theoretical value of $1e^-$/Mn^{4+}. Finally, it is important to point out immediately that these three regions correspond to the three above-mentioned sub-structures, (FDS)$^\circ$, q.a.p. and δ-MnOOH.

Synthesis

The subtlety of the physics underlying (H^+, e^-) de-insertion is revealed if we try to answer the question: what limits the total re-oxidation of the partly reduced ($r_d \gg 0.50$) γ-MnO$_2$? The same question can be paraphrased in another way: what is the impact of the existence of the three sub-structures [(FDS)°, q.a.p. and δ-MnOOH] on the (H^+, e^-) extraction from the host bulk? This is a particularly useful problem to solve because, simple as it is, it nonetheless furnishes a good description of what happens in the structure host during the de-insertion phenomenon. The answer is confined through the next paragraphs to a simple phenomenological analysis. This kind of analysis attempts to describe only the gross, overall features of the current flow. By circumscribing the goal of the analysis in this manner, there is achieved a simplicity of argument which lends a great deal of insight into the underlying physics of the subject studied here [4].

Theory

The complete problem involving drift, diffusion and trapping (recombination is ignored here) has not as yet been attempted.

Basic concepts

The conceptual bases of the insertion dynamic theory, which are quite general, remain valid in the present case, provided that the positive direction of the matter transfer $(-\nabla C)$ is oriented now from the grain center towards the interface s_i [2, 4]. The p.r.m.d. electrode is assumed to:

1. Be immersed in a non-strongly acidic or alkaline medium where the dissolution-precipitation processes are excluded. The behaviour of the dioxide is complicated by their existence. It would, however, be inappropriate to pursue this subject here.
2. Obey the Rueschi formula for the chemical composition [22]. The important case of the chemically or physically modified electrodes is not considered in this study [23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33].
3. Have a well-defined reduction state, i.e. the insertion has been accomplished according to one of the five regimes introduced in [4].
4. Have a well-defined thermodynamic state [5].
5. De-insert by the applying of a convenient "constant electric field" E_{ext} without overcharging or oxygen regeneration [15, 16, 17].

Finally, in the interest of simplicity, throughout this study (as in the entire published series [1, 2, 3, 4, 5]) the discussion and mathematical formulation are confined to generalized and relatively new (in the γ-MnO$_2$ topic)

terminology and symbols (a complete set of notations is presented above).

Boundary condition

When there is no externally applied field the (H^+, e^-) net flux is null.

Various regimes of the de-insertion

It is apparent from the reversibility of reaction I that when the electrode progressively returns (by de-insertion) to its initial state (before insertion) it will be characterized by the same value sets of the physical quantities implicated in the insertion pathway. For this reason, the first main step of the de-insertion reaction and its dynamic regimes well be designated in the following by FDS^{-1} ($0.08 < r_d^{-1} < 0.50$), regime I^{-1} ($0.08 < r_d^{-1} < 0.30$), regime II^{-1} ($0.30 < r_d^{-1} < 0.50$) and regime III^{-1} ($r_d^{-1} \approx 0.50$).

Finally, note that the ratio between two vectors is not well defined from a mathematical point of view, but it will be adopted in the next paragraphs for practical reasons.

De-insertion on the FDS^{-1}

This represents the first step in the complication in the hierarchy of the ambipolar de-insertion problems of the concerned electrode.

A first qualitative approach

Consider the p.r.m.d. at a given equilibrium state (r_d, ε_{th}). When we submit this electrode to the influence of E_{ext} we (by consequence) impose a positive potential difference between the interface and the grain center. While the free electrons are attracted towards the grain surface, their associated protons are repulsed by E_{ext} towards the grain center. A space charge appears and an internal electric field E_{int} builds up which opposes the inductor one (E_{ext}), slows down the electrons' movement, reorients and accelerates the protons towards the interface s_i. During this complex motion the de-inserted particles (H^+, e^-) have the same ambipolar velocity. The p.r.m.d. progressively regains its initial physicochemical state (before the insertion). In fact, whereas the concentration C of the (H^+, e^-) couples and the reduction degree decrease, then conversely the values of the partial diffusivities (D_{iie}^-, D_{iiH}^+) and several other physical quantities or parameters increase and tend to their initial values before the reduction transformation. The electric energy brought by E_{ext} in the host bulk and at the interface is consumed partly to liberate the t.o.s. [5] and partly as kinetic energies of the free particles.

Finally, these results are interesting since they give a qualitative idea of the way in which (H^+, e^-) is extracted from the partly reduced γ-MnO$_2$.

Analytical formulation

The general equations for matter transfer can be written in the following form, which is derived from the dynamic theory of the insertion:

$$\Phi_{H^+} = -[1 - (eC/kT)\mathbf{E}/\nabla C + C\partial \ln f_{H^+}/\partial C]D_{H^+}\nabla C \quad (3)$$

and:

$$\Phi_{e^-} = -[1 - (eC/kT)\mathbf{E}/\nabla C + C\partial \ln f_{e^-}/\partial C]D_{e^-}\nabla C \quad (4)$$

where:

$$\mathbf{E} = \mathbf{E}_{int} + \mathbf{E}_{ext} \quad (5)$$

the global response vector (or field) of the inductor and induced fields which must be, in a way (or strictly), opposed vectors. Taking into account the local neutrality condition:

$$\Phi_{H^+} = \Phi_{e^-} = \Phi \quad (6)$$

we obtain:

$$\mathbf{E} = (kT/e)\mathbf{D}_s^{-1}\mathbf{V}_d \quad (7)$$

$$\tilde{D} = [1 - (eC/kT)E/\nabla C + C\partial \ln f_{H^+}/\partial C]D_{H^+} \quad (8)$$

and:

$$\begin{aligned}\tilde{W} &= -\tilde{D}\nabla C/C \\ &= -[1 - (e/kT)E/\nabla C + \partial \ln f_{H^+}/\partial C]D_{H^+}\nabla C \quad (9)\end{aligned}$$

The relationship of Eq. 7 indicates that $\mathbf{E}$: (1) is (like $\mathbf{D}_s^{-1}\mathbf{V}_d$) a positive vector, i.e. it is oriented towards the interface, and, in a way (like $\mathbf{E}_{int}$), opposed to $\mathbf{E}_{ext}$; that is to say that $\mathbf{E}$ and $\mathbf{E}_{int}$ lie in the positive direction of the matter transfer; (2) has the same formula and role of the Nernst field during the insertion reaction, i.e. it retards the faster carrier (e^-) and enhances the motion of the slower carrier (H^+), until the electrons and protons move together with the same $\tilde{D}$ and $\tilde{W}$.

Summing now Eqs. 3 and 4, we obtain:

$$\begin{aligned}2\Phi + \{D_s + C(D_{H^+}\partial \ln f_{H^+}/\partial C + D_e\partial \ln f_e/\partial C)\}\nabla C \\ = -(eC/kT)D_d\mathbf{E}\end{aligned}$$

or:

$$\phi = CV_s/2 - (eC/2kT)\mathbf{D}_d\mathbf{E} \quad (11)$$

This takes a simpler form if the $\mathbf{E}$ expression as defined by Eq. 7 is inserted:

$$\phi = (C/2)(\mathbf{V}_s - \mathbf{D}_s^{-1}\mathbf{D}_d\mathbf{V}_d) \quad (12)$$

It is important to distinguish between the two cases corresponding respectively to the de-insertion from the

levels (1) $r_d \approx 0.50$, where $\mathbf{D}_{iid} \approx 0$, and (2) $r_d < 0.50$, where $\mathbf{D}_{iid} > 0$ (or $\gg 0$). In the first case (1) the relationship of Eq. 12 reduces to the following form:

$$\phi = C(\mathbf{V}_s/2) \quad (13)$$

Consequently, we obtain:

$$\tilde{D} = -C(V_s/2\nabla C) \quad (14)$$

and:

$$\tilde{W} = V_s/2 \quad (15)$$

In the second case (2), in the light of the relationship of Eq. 5, the previous results (where we have seen that $\mathbf{E}_{int}$ is created by the ambipolar diffusion) and the above boundary condition the Eq. 11 can decompose in the zone of the second level as follows [4, 34]:

$$\phi = -(eC/2kT)\mathbf{D}_d\mathbf{E}_{ext} \quad (16)$$

and:

$$\mathbf{E}_{int}(\text{deinsertion}) = (kT/e)\mathbf{D}_d^{-1}\mathbf{V}_s \quad (17)$$

Discussion

The flux Φ of the matter transfer (lying in a way in the opposed sense of $\mathbf{E}_{ext}$) is proportional to the overall inserted concentration C, difference diffusivity tensor $\mathbf{D}_d$ and the $-\mathbf{E}_{ext}$ vector. On the other hand, it appears from Eq. 16 that $|\Phi| \to 0$ if $C \to 0$.

The internal field $\mathbf{E}_{int}$, as defined by Eq. 17, is now proportional to the velocity sum vector (V_s) and inversely proportional to the difference diffusivity tensor $(\mathbf{D}_d)$. This is the opposite case of the insertion reaction. In fact, during the re-oxidation, a zone of space charge is created, giving rise to $\mathbf{E}_{int}$. The rapidity at which this induced phenomenon takes place is proportional to $\mathbf{D}_d^{-1}$ and the self-velocities, i.e. the higher the $|V_s|$ values the better the response $(\mathbf{E}_{int})$ of the material to the external applied field. On the other hand, Eq. 17 also indicates that, in the course of the (H^+, e^-) de-insertion, the internal electric field will decrease because $\mathbf{D}_{iid}^{-1}$ tends to its maximum value before the insertion takes place at the electrode concerned. To sum up, when the inserted concentration C tends to 0, both Φ and $\mathbf{E}_{int}$ tend to 0. This result confirms that the above analyses are in real harmony.

We have seen above that the two fields $\mathbf{E}_{int}$ and $\mathbf{E}_{ext}$ lie "in a way" or "exactly" in opposed senses; therefore one can "in a first approximation" or "precisely" write $(m > 0)$:

$$\mathbf{E}_{ext} = -m\mathbf{E}_{int} \quad (18)$$

and:

$$\mathbf{E} = (1 - m)\mathbf{E}_{int} \quad (19)$$

However, it was shown above that $\mathbf{E}$ and $\mathbf{E}_{int}$ are positive vectors; therefore, finally:

$$1 - m > 0 \text{ and } 0 < m < 1 \tag{20}$$

It follows from Eqs. 18, 19, 20 that the magnitude of the internal field is higher than that of the external field. This appears at first glance as a striking matter, but we have to remember here that the internal field is in fact induced by the external excitation and ambipolar diffusion.

It seems from the last result that we can obtain a positive impedance or an inductive loop, as was observed in the case of "MnO$_2$-HUO$_2$PO$_4$.4H$_2$O-acetylene black", where a constant 20 mV a.c. voltage was applied between the working and counter electrodes [12].

Combining now the two relationships of Eqs. 16 and 17, and taking Eqs. 18, 19, 20 into account, gives the important relationships:

$$\phi E_{int} = -(C/2)V_s E_{ext} \tag{21}$$

$$\phi = m(CV_s/2) \tag{22}$$

and (see Eqs. 7, 8, 9):

$$\tilde{D} = -mC(V_s/2\nabla C) \tag{23}$$

$$\tilde{W} = m(V_s/2) \tag{24}$$

The ambipolar velocity is now weaker than the mean self-velocity vector ($V_s/2$) (see Eq. 15).

It is matter of interest to directly relate, by using the foregoing equations, the electric fields E_{ext} and E:

$$E = -[(1 - m)/m]E_{ext} \tag{25}$$

or:

$$E = -\mu E_{ext} \tag{26}$$

where:

$$\mu = (1 - m)/m \tag{27}$$

with:

$$0 < \mu < \infty \tag{28}$$

Fixing on the leading terms of Eqs. 26, 27, 28, we see that the factor μ has the following useful properties: (1) it smoothly connects the externally applied field $|E_{ext}|$ and the global response field E, and (2) is a homographic function of m. This important factor well deserves the appellation the "field's correlation factor" or simply the correlation factor.

Consider now Eq. 16, which becomes:

$$\phi = (eC/2\mu kT)D_d E \tag{29}$$

on putting $E = -E_{ext}/\mu$.

It is apparent from the above (Eqs. 26, 27 and 29) that, for a given $|E_{ext}|$, the quantities μ, $|E|$ and $|\Phi|$ vary in the same sense, i.e. when the parameter "m" increases from 0^+ to 1^-, then μ, $|E|$ and $|\Phi|$ decrease in a homographic way from infinity or a maximum value to zero. Therefore, three possibilities are now entertained:

1. $m \to 0^+$:
$\mu \to \infty$, $|E| = |E_{int}| \gg |E_{ext}|$ and $|\Phi| \to |\Phi|_{maximum}$

2. $m = 0.50$:
$\mu = 1$, $|E| = |E_{ext}| = |E_{int}|/2$ and $\Phi = (eC/2kT)D_d E_{ext}$

3. $m \to 1^-$:
$\mu \to 0$, $|E_{int}| \to |E_{ext}|$ and $|E| \to 0$ and $|\Phi| \to 0$

$$\tag{30}$$

Equation 30 represents the set of the three above cases: 1, 2 and 3.

From the dynamic point of view, the last relationships means that under potentiostatic conditions the partly reduced γ-MnO$_2$ electrode must have a "homographic current response". This has been confirmed by experimental data in the literature [35, 36].

Finally, as mentioned above, a considerable understanding of the properties of the de-insertion reaction may be gained through simply taking into account the existence of various dynamic regimes.

Regime I^{-1} or Kordesch regime

This regime corresponds to the ideal regime for insertion [4]. Taking into account the analytical data of the latter, we have:

$$E_{int} = (kT/e)D_d^{-1}V_s = -(kT/e)\nabla C/C \tag{31}$$

$$\tilde{D} = [1 - (eC/kT)(1 - m)E_{int}/\nabla C]D_{H^+} \tag{32}$$

Replacing E_{int} by the expression in Eq. 31, then Eq. 32 becomes:

$$\tilde{D} = (2 - m)D_{H^+} \tag{33}$$

where:

$$1 < 2 - m < 2 \tag{34}$$

Identically:

$$\phi = -(2 - m)D_H + \nabla C \tag{35}$$

and:

$$\tilde{W} = (2 - m)V_{H^+} \tag{36}$$

It is important to notice that the analytical formulation of the Kordesch regime is in real harmony with that we have obtained for the ideal regime during the insertion pathway, especially the existence of the scalar coefficient 2–m (corresponding to the ambipolar diffusion in the presence of the constant external excitation) instead of 2 (corresponding to the ambipolar diffusion without the presence of the external excitation). Nevertheless, the flux and the ambipolar velocity now have weaker magnitude (2–m < 2) and the kinetics is then slower in the re-oxidation pathway than in the reduction one. Finally, it is evident that the difference m between

the two parameters is imposed by the presence of the external excitation.

Regime II^{-1}

The above results, Eqs. 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 and 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, in fact correspond to the (general) regime II^{-1} of the de-insertion.

Regime III^{-1}

The above results, Eqs. 13, 14, 15, in fact correspond to the regime III^{-1} of the de-insertion.

The following section is devoted to describing the re-oxidation processes in the "paired" host bulk of the partly reduced γ-MnO$_2$, based on the results in this paper and in the previous parts of this series.

Reoxidation from a level belonging to the TDS

As already noted above, at a sufficiently high degree of reduction ($r > 0.50$), formation of Mn^{3+} and Jahn-Teller distortion are observed because of the presence of an important (pairing) interaction. It is, of course, implied that the analytical expressions as stated above will be modified because we must take into account the fact that a large part of the inserted particles is now no longer free but trapped. Finally, it is convenient to remember here that we have $r = C/C'$, $p = P/C'$, $\underline{p} = \underline{P}/C'$, $r = p + \underline{p}$ and $\tau = \underline{P}/C = \underline{p}/(p + \underline{p})$ and therefore:

$$\nabla r = \nabla p + \nabla \underline{p} \qquad (37)$$

The thermodynamic point of view

When the electrochemical extraction of the inserted particles proceeds, the equilibrium of Eq. 2b is displaced in the sense to decrease a_2. According to the "equilibrium displacement law", the material electrode must react in the opposite sense, that is, II→I. This implies that some fraction of the trapped particles will be liberated to supply the free particles' flux. Consequently, the value of the p fraction will decrease during this complex phenomenon but (generally) cannot reach its initial value ($p = 0$) at the beginning of the TDS (during the insertion) and we still have $p > 0$ at $r_d^{-1} = 0.50$ [5]. To sum up, it is possible to (partially) extend the de-insertion into the TDS region.

Dynamic equilibrium

Suppose now the following dynamic equilibrium [4, 37]:

$$\underline{P}(C' - P)/P = \varpi \qquad (38)$$

which gives rise to:

$$\underline{P}(C - P) = -(C' - C + \varpi)/2$$
$$+ [(1/4)(C' - C + \varpi)^2 + (\varpi C)]^{1/2} \qquad (39)$$

By applying the ∇ operator on the P quantity we obtain:

$$\nabla \underline{P} = h' \nabla C \qquad (40)$$

where:

$$h' = (1/2)\{1 + [\omega - (C' - C)]/[(C' - C + \omega)^2$$
$$+ 4\omega C]^{1/2}\} > 0 \qquad (41)$$

Similarly, one can write also:

$$P(C - \underline{P}) = -(C' - C + \varpi)/2$$
$$+ [(1/4)(C' - C + \varpi)^2 + (\varpi C)]^{1/2} \qquad (42)$$

and obtain:

$$\nabla \boldsymbol{P} = h'' \nabla \boldsymbol{C} \qquad (43)$$

where:

$$h'' = (1/2)\{1 - [\omega - (C' - C)]/$$
$$[(C' - C + \omega)^2 + 4\omega C]^{1/2}\} > 0 \qquad (44)$$

and:

$$h' + h'' = 1 \qquad (45)$$

The above results mean that during the de-insertion the three vectors ∇C, ∇P and $\Delta \underline{P}$ are oriented in the same negative sense.

From Eqs. 37, 40 and 43 one can write:

$$\nabla \underline{p} = (h'/h'') \nabla p \qquad (46)$$

By means of Eq. 46 we may consider the important following classification:

1. $\nabla \underline{p} < \nabla p$ and $\underline{p} > p$ (because of the fact that the operator ∇ is a negative vector, the sign of the inequality is reversed): the free particles are majority carriers.
2. $\nabla \underline{p} = \nabla p = \nabla r/2$, $p = \underline{p} = r_d^{-1}/2$: equality of the carrier numbers.
3. $\nabla p < \nabla \underline{p}$ and $p > \underline{p}$: the free particles are minority carriers.

The above subdivision of the TDS^{-1} into three dynamic domains corresponds well to the previously defined three sub-structures of q.a.p., phase transition q.a.p./δ-MnOOH and δ-MnOOH, and each one of these can now be characterized by a values set of the parameters r, τ and h'/h'' [5].

At this point we have the basic building blocks with which to construct the de-insertion characteristics for situations in which there are two sets of carriers: the free and the trapped particles.

Analytical formulation

Replace now in the forgoing relations (of the De-insertion on the FDS^{-1} section) the quantities C, ∂C and ∇C respectively by $(C–P)$ or $\underline{P}$, $h'\partial C$ and $h'\nabla C$, they become:

$$\Phi = -\tilde{D}\nabla\underline{P} = -\left[h'/\underline{P}+eE/kT\nabla C+\partial \ln f_{e-}/\partial C\right]\underline{P}D_{e-}\nabla C \tag{47}$$

$$\tilde{D}=\left[h'/\underline{P}+eE/kT\nabla C+\partial \ln f_{e-}/\partial C\right]\underline{P}D_{e-} \tag{48}$$

$$\tilde{W} = -h'\tilde{D}\nabla C/\underline{P}$$
$$= -h'\left[h'/\underline{P}+eE/kT\nabla C+\partial \ln f_{e-}/\partial C\right]D_{e-}\nabla C \tag{49}$$

Equation 7 remains valid in the present case but E is now, like V_d, a negative vector and oriented into the grain; consequently, the role of E, versus the de-inserted particles, is reversed [4]. Using the above relationships one can obtain:

$$\Phi = \underline{p}(C'e/kT)D_{e-}(-E)$$
$$+ C'[1 + (\underline{p}C'/h')\partial\mathrm{In}f_{e-}/\partial C]D_{e-}(-\nabla\underline{p}) \tag{50}$$

and in the particular case of:

$$h'' = h' = 0.50$$

(corresponding to the phase transition q.a.p./δ-MnOOH) we obtain:

$$\Phi = \underline{p}(C'e/kT)D_{e-}(-E)$$
$$+ C'[1 + 2\underline{p}C'\partial\mathrm{In}f_{e-}/\partial C]D_{e-}(-\nabla\underline{p})$$

Finally, it is important to notice here that we can also explain the same physical quantities of the de-insertion reaction in terms of τ [by mean of $p = r\tau$, $p = \tau p$ $(1 - \tau)^{-1}$ and $p = (1-\tau)r$], which plays the $\overline{\mathrm{e}}$ main $\overline{\mathrm{role}}$ in the determination of the thermodynamic electrode potential on the TDS [5].

Discussion

Equation 50 brings in the chief role (during the TDS^{-1}) of the untrapped particles' fraction $\underline{p}$ in the current flux.
In fact, it clearly demonstrates that the higher the value of $\underline{p}$, the higher the magnitude of the de-insertion flux vector. Taking into account Eq. 50, the above classification and the experimental data of the Introduction, one can obtain the important result or the desired scaling answer: in the zone of q.a.p., where the free inserted particles are major carrier, the de-insertion still be significant. Conversely, in the zone of δ-MnOOH, where the free particles become the minor carrier (the trapped particles become the majority), the de-insertion flux is weak or tending towards zero, i.e. it may be stopped or gives rise to further types of reaction (complex formation, oxygen regeneration, etc.).

Summary

A great deal of useful insight into the re-oxidation problem of the partly reduced γ-MnO$_2$ was obtained by the same kind of simple, phenomenological analysis which proved so powerful in previous works, in the study of the thermodynamic and dynamic properties of the insertion reaction. The conceptual framework set up to construct these (dynamic and thermodynamic) theories was largely applied here with emphasis on the underlying physics. The subject matter is covered at several levels, ranging from the purely phenomenological to the purely analytical and divided naturally into two main parts: (1) de-insertion from FDS^{-1} and (2) from TDS^{-1}. The present work shows how much the de-insertion reaction is dependent of the previous physical transformation and explains, in terms of the bad pairing phenomenon, why, if $r_d > 0.50$, we cannot recuperate the total capacity of the p.r.m.d.

The main conclusions emerging from this new study may be summarized as follows:

1. To the ideal regime of insertion ($r_d < 0.30$, $E_{ext} = 0$) and its ambipolar factor 2 correspond an ideal regime of de-insertion ($r_d^{-1} < 0.30$, $E_{ext} \neq 0$) named the Kordesch regime and characterized by the parameter $2–m$ where the parameter m ($0 < m < 1$) is implied by the presence of the externally applied field.
2. It has been found that the (H$^+$, e$^-$) de-insertion is still possible if the free particles are the majority carriers, but conversely it becomes null or very weak or gives rise to further types of reaction (complex formation, oxygen regeneration, etc.) in the opposite case.

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