

ELECTROCHEMICAL BEHAVIOUR OF METALLIC OXIDES*

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Summary

Some of the physico-chemical properties of oxides used as cathodes in batteries or as electrocatalysts are briefly reviewed. Possible relationships between these properties and the electrochemical reactivity of the oxides are considered, and attention is drawn to the important influence of the surface state of electrodes on this reactivity. From consideration of the available information on three metal oxides of technological importance and of spinel type mixed oxides it is apparent that reduction processes take place in the solid state, and that for the metal oxides at least, the presence of OH groups and possibly H₂O molecules is necessary for their activity. For all these materials there appears to be a correlation between electrochemical reactivity and the presence of redox couples in octahedral sites, and it is suggested that further investigation based on this new concept may lead to the development of power sources with increased specific outputs.

Introduction

The choice of metallic oxides as electrodes in galvanic cells for energy conversion is very old. It can be traced back to the pioneer work on electrochemical power sources in the 1850's. The best known metallic oxides, which led later to a large amount of work, are lead dioxides and manganese dioxides. However these two families of compounds are not the only ones to be of great interest nowadays. Other, simple oxides have been used as cathodes: oxides of Ag, Hg, Ni, Cu, for instance. However, recent developments in the field deal with so called "mixed oxides", which are constituted from cations of two or more kinds.

From the electrochemical point of view, one can distinguish two approaches:

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(a) the oxides are used as a positive electrode, that is, as a cathode in a primary or secondary battery.

(b) the oxides are used as electrocatalysts, either in a generator or in an electrosynthesis cell. In this case, it appears that work is not so far advanced. From an historical point of view, it is utilisation as a cathode which has predominated, but during the last twenty years, their use as electrocatalysts has increased in importance, with considerable possible applications in photo-electrochemistry.

We shall try to point out major results concerned with the electrochemical behaviour of certain oxides. Many laboratories are concerned with technological applications, but an attempt to correlate fundamental physico-chemical properties with the technological properties of interest is necessary. From such correlations new research lines should emerge. This is a difficult task, but I would like to propose some thoughts resulting from long experience which, perhaps, permits me to have a global view of the problem. I will put the emphasis, as far as possible, on the properties of those oxides, the electrochemical reactivity of which has been investigated. However, additional knowledge could, in the future, modify these present views. For the oxides with similar properties, I will try to point out the common features which must be understood in order that new oxides, best fitted to the class of processes which occur in electrochemical power sources, may be discovered.

Investigated oxides

The oxides which have had the most investigation to date are manganese and lead "dioxides". I intentionally refer to them as "dioxides" because we know that, for these two metals, their dioxides exist in several crystallographic forms. I will not try to give even a part of the literature on this subject, as I am sure that you all know this field. I will only discuss their physico-chemical properties.

More recently, important, although less extensive, work has been carried out on the oxides of Ag, Hg and especially Ni. These oxides are of considerable interest as electrodes in some kinds of primary or secondary battery.

It appears in the case of nickel oxides that it is primarily Ni^{3+} which is reactive, but it is possible that Ni^{4+} also plays a part in the processes: this cation has been considered, and some authors have envisioned the occurrence of NiO_2 itself.

Besides these simple oxides, we advocated [1, 2] the use of mixed oxides. These are often well known as semiconductors in solid state physics, but very little attention has been paid to them as electrodes in electrochemistry. Some of them have been investigated as catalysts for heterogeneous catalysis. At the same time, 1965, I also suggested the study of semiconducting organic and organometallic compounds. However, in our laboratory, I conducted, with my co-workers Chartier, Ruch, Beley, Nguyen Cong, Koenig and Gautier, studies on some mixed oxides.

Survey of some physico-chemical properties of the oxides of interest for electrochemistry

I have suggested [3 - 5], on the basis of our results with manganese dioxides, that we should look for correlations between electrochemical reactivity and some physico-chemical properties. I am confident that in place of the presently observed correlations, true laws will be found in the future. Let me mention:

(a) *Structural properties*, that is, observations by means of crystallographic methods. The structures of the oxides, more or less distorted, are systematically established. The variations of their crystallographic parameters are correlated with their stoichiometry. Profiles of patterns of X-ray diffraction are of interest, too, as for solid catalysts.

(b) *Magnetic properties* are of great importance, as they are in catalysis (see the work of Selwood). As early as 1948 [6, 7], I tried to correlate the catalytic with the electrocatalytic reactivity, on the basis of observations on MnO_2 , by means of magnetic studies. More recently Labat [8] published some very interesting work concerning NiOOH , and tried to extend his observations to MnO_2 . Very recently, in collaboration with Bernier and Poix (Department of Science of Materials, Strasbourg University), we investigated the magnetic properties of some mixed oxides [9, 10].

(c) *Semiconducting properties*: their study is difficult experimentally because one is dealing with powders instead of monocrystals. We have carried out some research [11 - 13], as have other investigators (Das [14] for the manganese dioxides, and more recently, Preisler [19]). Measurements of the Hall effect to determine the exact nature of the carriers appears to be necessary. The importance of the type of conductivity, either electronic or ionic is obvious, but experimental difficulties explain the lack of results.

(d) *Surface properties*: as for heterogeneous catalysis, surface properties give key information to explain the electrocatalytic behaviour of the oxides. For instance, it is usual to correlate the B.E.T. surface with the electrochemical reactivity. In a number of cases the oxides with a large B.E.T. surface have more or less enhanced reactivities. However, in the case of mixed oxides, the specific B.E.T. surfaces are very low. Therefore the importance of surface area should not be overestimated. For a large number of oxide electrodes or electrocatalysts, the key factor is the organisation of the surface and not its area, as suggested in heterogeneous catalysis by Pretre. Consequently, the physical methods of determination of surface composition, and particularly of the valencies of the surface cations and anions, are of great help. Such observations have contributed, in heterogeneous catalysis, to a better understanding of catalytic mechanisms and similarly for electrochemistry. E.s.c.a. and other related techniques are presently among the methods which are used for this purpose.

This review shows the number of problems that have to be faced and the difficulty in developing rigorous laws relating electrochemical reactivity to physico-chemical properties.

The problem of electrochemical reactivity

We have used the concept of electrochemical "reactivity" without defining it. I think that one must try to give, if not a simple definition, at least a means of characterisation.

For that purpose, one has to consider the idea of fast or slow reactions. In an electrochemical power source, the electrode must be the place where the reactions take place as fast as possible, for, consequently, the overpotential of the reaction (or of the reactions) is low, and the electrode polarisation is small. The rate of an electrochemical reaction is characterised by the so called "Exchange Current", i_0 , which must be as high as possible.

At first, one can consider the classical Butler-Volmer relationship:

$$i = i_0 \left[\exp\left(\frac{\alpha n F}{RT} \eta\right) - \exp\left(-\frac{\beta n F}{RT} \eta\right) \right]$$

α and β being the anodic and cathodic transfer coefficients, n the number of transferred electrons, η the electrode overpotential and i the measured current density through the electrode. A modified form of this equation takes account of the transport of material by diffusion. One has to discuss the true physical meaning of i_0 . In the simple case of a unique electrode in the sense of Lange, i_0 is given by:

$$\begin{aligned} |i_0| &= k_a (\text{Red}) \exp - \frac{\Delta G_a^* - \alpha n F \epsilon_h}{RT} \\ &= k_c (\text{Ox}) \exp - \frac{\Delta G_c^* + \beta n F \epsilon_h}{RT} \end{aligned}$$

ϵ_h being the redox equilibrium potential and ΔG_a^* and ΔG_c^* the chemical Gibbs free energies of activation for the charge transfer process.

If one has a multiple electrode, in the sense of Lange, one has a mixed exchange current, $i_{0,M}$, which is a function of the characteristics of each component reaction [15]. The complete calculation of $i_{0,M}$ is cumbersome without some approximations, but undoubtedly $i_{0,M}$ depends on the Gibbs free energies of activation of each reaction. These free energies themselves depend on the state of the electrode surface, which can be modified by impurities, and also by the position of the Fermi level, though it is admitted that this level stays equal to its value in the bulk.

The Fermi level is related to the nature and number of donor or acceptor levels in the forbidden band. These levels are a function of the impurities, therefore of the doping of the surface. This shows clearly the necessity to characterise the surface of the electrodes, and to look for the physical parameters which can enhance the i_0 of each particular reaction.

From the expressions of i_0 , one sees that the ΔG_a^* and ΔG_c^* and, more precisely, the quantities $\Delta G_a^* - \alpha n F \epsilon_h$ and $\Delta G_c^* + \beta n F \epsilon_h$, have to be lowered as much as possible.

For ΔG_a^* and ΔG_c^* , we must act on the chemical part of the height of the energy barrier at the electrode-electrolyte interface. Of course, one is dependent on the order of magnitude not only of ΔG_a^* and ΔG_c^* , but also of the electrical terms $\alpha n F \epsilon_h$ and $\beta n F \epsilon_h$. These terms are about 1 - 2 eV in magnitude, being determined by the values of α and β (about 0.5) and by the value of the Galvani potential difference, represented by ϵ_h .

The above considerations seem important to me, and ought to be thoroughly examined in order to control the condition of formation of the surfaces of the electrodes. This is a problem which is closely linked to the concept of electrochemically active material, in full analogy with heterogeneous catalysis, as already pointed out.

Data on some electrochemically active metallic oxides

If one tries to summarize our knowledge of the oxides which have been most investigated to date, it appears possible to make a certain number of observations of a general character.

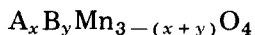
Let us first consider the manganese dioxides, certainly the most widely studied of all the oxides. It is now well established that these active compounds comprise, necessarily, the redox system Mn^{4+}/Mn^{3+} in solid phase. Workers in the field agree nowadays on the presence of both Mn^{4+} and Mn^{3+} ions, as well as of acidic groups, OH, acting as ion exchangers. Such oxides are semiconductors, but there is still some uncertainty as to the type of semiconductivity, n or p. Though they are usually considered to have n-type conductivity, a p-type conductivity cannot be disregarded. During the cathodic reduction of MnO_2 , I showed that, in the case of γ - MnO_2 , which can be formulated $(MnO_2)_{2n-3} (MnOOH)_{4-2n} mH_2O$ [16], there is a dilation of the cell parameters [17], at least during the first step of the reduction. This dilation, now well recognised, *corresponds to a reduction in the solid phase*. Consequently, there must be acceptor levels which, normally, lower the conductivity. This fact agrees well with the experimental observation that γ - MnO_2 is more electroactive relative to cathodic reduction, though it has a lower electrical conductivity than β - MnO_2 , which has little reactivity. The presence of Mn^{3+} ions, linked to the existence of OH groups, creates acceptor levels, and a lowering of the Fermi level results; deep electronic levels are thus created without increasing the total number of electrons which could fill them. It is known that for semiconductors, the excess conductivity is decreased by poisoning of the acceptors. Therefore, as in the general case of semiconductors, the n-type conductivity can be decreased. Ultimately, if the number of acceptors, here the number of OH groups and therefore the Mn^{3+} ions, is large enough, a change from n-type to p-type semiconductivity can be observed.

In this way, it can be explained why both types of semiconductivity have been found with γ - MnO_2 . If the number of acceptor levels due to OH (or Mn^{3+}) is high, all the electrons of the conduction band of γ - MnO_2 are captured; then, the electrons of the valence band are captured also, a p-type conductivity is established, and the electrical conductivity of γ - MnO_2 diminishes.

In the case of PbO_2 , one may perhaps think that things are different. However, one must distinguish α - PbO_2 , orthorhombic, from β - PbO_2 , quadratic. In this case, one can say that PbO_2 is almost a metallic conductor. There is little data on α - PbO_2 , but recent results [18] in our laboratory demonstrated that it is this variety which is electrochemically active. We found that the reactivity could be linked to the total "H₂O" content, but we cannot differentiate OH groups from molecular water. However, in full analogy with γ - MnO_2 , we postulate the existence of Pb^{3+} ions in these lead dioxides, thinking that the total "H₂O" is formed from OH groups. In a solid, this Pb^{3+} ion cannot be ignored, though it is unstable in aqueous solution. We are facing a challenge to prove the existence of such Pb^{3+} ions in the solid phase, a goal which can be reached only through indirect means. On this basis, we propose a formula of the same type as that for γ - MnO_2 : $(\text{PbO}_2)_{2n-3}(\text{PbOOH})_{4-2n}$, with the redox couple $\text{Pb}^{4+}/\text{Pb}^{3+}$ in the solid phase.

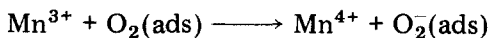
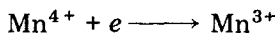
In the case of nickel oxides, one used to consider mainly NiOOH , with Ni^{3+} ions. But the literature has never excluded the existence of NiO_2 . Contrary to the case of γ - MnO_2 and α - PbO_2 , if one postulates the formula: $(\text{NiO}_2)_{2n-3}(\text{NiOOH})_{4-2n}$, the term $2n-3$ is very small ($n \cong 3/2$), and it is the NiO_2 group which exists in a very small quantity. Nevertheless, we find again the hypothesis for the existence in the solid phase of a redox couple $\text{Ni}^{4+}/\text{Ni}^{3+}$.

In the case of mixed oxides of the type:



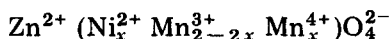
$\text{A} = \text{Ni}, \text{Cu}$, and $\text{B} = \text{Zn}, \text{Al}, \text{Cr}$, $x \geq 0$ and $y \leq 1$, the problem at first appears to be different. However, to explain their good electrochemical reactivity relative to the O_2 reduction, we have been led to consider the redox couples $\text{Mn}^{4+}/\text{Mn}^{3+}$ in the solid phase.

The electrochemical reduction of O_2 could occur through the catalytic mechanism:



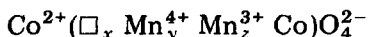
With Bernier and Poix (Department of Materials Science, Strasbourg University) we studied the repartition of the ions through the tetrahedral and octahedral sites, on the basis of the magnetic and crystallographic properties of these oxides.

We have been led to propose, for instance, the formula:



with $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox couples in octahedral sites.

Similarly, the cobaltites can be written:



with the presence of vacancies \square_x beside the redox couple $\text{Mn}^{4+}/\text{Mn}^{3+}$.

Studies by myself, Koenig and Gautier, which are being continued by Koenig, do not lead to any contradiction with the concept of catalytically active $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox couples.

Discussion

The above considerations on $\gamma\text{-MnO}_2$, $\alpha\text{-PbO}_2$, NiOOH and the spinel mixed oxides $\text{A}_x\text{B}_y\text{Mn}_{3-(x+y)}\text{O}_4$ present a common feature: *the presence in octahedral sites of some cations*. Particularly, for $\gamma\text{-MnO}_2$, we know that the Mn^{4+} and Mn^{3+} ions are at the centre of octahedrons of oxygen ions, O_2^- . Those ions are also at the centre of octahedral sites in the spinel oxides.

This fact appears to us to be of sufficient fundamental importance for attention to be drawn to it now because, to our knowledge, *such a correlation between the presence of $\text{Me}^{4+}/\text{Me}^{3+}$ redox couples in octahedral sites and the reactivity of the oxides has never been carried out*.

Another common feature is that both electrocatalytic and electrochemical reduction processes occur in the solid phase. Workers in the field agree on this point, even for NiOOH and PbO_2 .

Finally, at least for $\gamma\text{-MnO}_2$, $\alpha\text{-PbO}_2$ and NiOOH , the existence of OH groups (and perhaps of H_2O molecules) is necessary. These OH groups are responsible for the creation of the redox system $\text{Me}^{4+}/\text{Me}^{3+}$. In the case of the manganese-containing spinels, the $\text{Mn}^{4+}/\text{Mn}^{3+}$ couple appears because of the presence of cations other than Mn, having a multiple valency ($\text{Cu}^{2+}/\text{Cu}^{3+}$, $\text{Co}^{3+}/\text{Co}^{2+}$ couples, for instance). It may be that the redox system $\text{Mn}^{4+}/\text{Mn}^{3+}$ is easier to observe, because of the favourable electronic structure of the Mn atom, due to the $3d^5$ electronic layer.

On the basis of such results and hypothesis, it seems to me that possible suggestions can be formulated for future research on metallic oxides, either simple or mixed, as electrocatalysts or electrodes in electrochemical power sources. The guiding principle is the concept of redox couples in the solid phase. The progress in the direction that I feel authorised to suggest, after a long experience in the field, will be made possible only through the continuous cooperation between specialists in the fields of electrochemistry and of physical-chemistry of the solid state.

I bring these ideas to your attention and for your consideration at a time when I am going to slow down my scientific activity, but will remain, despite these circumstances, as much as possible in close contact with the

specialists who, I hope, will discover the ultimate solutions to the basic problem of making electrochemical power sources with the highest specific gravimetric and volumetric capacity.

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