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Redox switching and oxygen evolution at oxidized metal and metal oxide electrodes : Iron in base[1]

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Supplementary Material

Appendix A

From a thermodynamic viewpoint, oxide electrodes are frequently regarded as metal/insoluble salt electrodes in which the activity of the metal ion is modified by interaction with the ligands, which in this case are the OH^- ions. The use of oxide electrodes such as Hg/HgO to measure pH is a well established electroanalytical technique. Any metal/metal oxide system is suitable for such an application provided its oxide and hydroxide (in this area the two are usually assumed to be in equilibrium according to the reaction $MO_{n/2} + n\ H_2O \leftrightarrows M(OH)_n$) are fairly insoluble and the metal itself is not attacked by the solution whose pH is being measured . It is well established that the potential for an ideal oxide electrode system in aqueous solution at 25ºC, decreases with increasing pH by ca. 59 mV/pH unit, with respect to a pH independent reference electrode such as the NHE or the saturated calomel electrode (SCE).

Regular Nernstian pH shift

We consider a metal oxide/hydroxide electrode system described by the general equation:

$$MO_n + nH_2O + 2ne^- \leftrightarrows M + 2nOH^- \qquad (A1)$$

The solubility constant, K_S, for the hydroxide is defined by reference to the equation,

$$M(OH)_n \leftrightarrows M^{n+} + nOH^- , \qquad (A2)$$

and is given by:

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[1] Based on paper presented at EIRELEC '11: Electrochemistry – The future?, Dun Raven Arms Hotel, Adare, Co. Limerick, 16-18 May, 2011.

$$K_S = a_{M^{n+}} a_{OH-}^{n} \qquad \text{(A3)}$$

Rearranging for the metal ion activity achieves,

$$a_{M^{n+}} = \frac{K_S}{a_{OH-}^{n}} = \frac{K_S a_{H_3O+}^{n}}{K_w^{n}} \ , \qquad \text{(A4)}$$

where, K_w $(= a_{H_3O+}.a_{OH-})$ is the ionic product of water. The Nernst equation for the redox process, $M^{n+} + ne^- \leftrightarrows M$, can be written as:

$$E = E^0 - \frac{RT}{nF}\ln\frac{a_M}{a_{M^{n+}}} \qquad \text{(A5)}$$

Substituting for $a_{M^{n+}}$ from equation (A4) and following the usual convention that $a_M = 1$ yields the following expression:

$$E = E^0 + \frac{RT}{nF}\ln\frac{K_S . a_{H_3O+}^{n}}{K_w^{n}} \qquad \text{(A6)}$$

Equation (A6) can be re-written as:

$$E = E^0 + \frac{RT}{nF}\ln\frac{K_S}{K_w^{n}} - \frac{2.303RT}{F}pH \qquad \text{(A7)}$$

The potential variation with pH, for the redox transition $M^{n+} + ne^- \leftrightarrows M$, at 25ºC is then given by:

$$\frac{\partial E}{\partial pH} = -\frac{2.303RT}{F} = -0.059\,\text{V} \qquad \text{(A8)}$$

According to equation (A8), the potential for an ideal oxide electrode system in aqueous solution at 25ºC, decreases with increasing pH by ca. 59 mV/pH unit, with respect to a pH independent reference electrode such as the NHE or the saturated calomel electrode (SCE). Such a shift in potential with pH, is referred to as a *Nernstian shift*, since it is predicted by the Nernst equation. It should be noted that if the reference electrode is pH dependent, such as the reversible hydrogen electrode (RHE) or the Hg/HgO electrode, no potential pH shift will be observed, since the potential of this type of electrode also alters by ca. 59 mV per unit change in pH at 25ºC.

Appendix B

Super-Nernstian pH shift

The large potential/pH shift of ca. – 0.089 V/pH unit obtained for the charge storage reaction corresponding to the A_3/C_2 peak set can be rationalized in terms of simple thermodynamic arguements. The use of thermodynamics is justified in this case since it has been shown that the peak potentials do not shift appreciably with changes in sweep rate at least in the range 1- 200 mV/s which is within the timescale of the voltammetry experiments under which the peak potentials were recorded as a function of solution pH.

We initially consider the reduction of the hydrous oxide layer on gold, a reaction which exhibits an essentially similar potential vs pH response (- 88.5 mV/pH) as the case for the Fe(II)/Fe(III) redox transition within the hydrous oxide layer. The observed response can be rationalized if it is assumed that the cations in the film can co-ordinate to a given number q of hydroxide ions. This concept is in close analogy with polarography where the reduction potential of a cation may be decreased by addition of a complexing agent. The complex formation reaction in the hydrous film may be represented in this case by the following expression:

$$Au^{3+} + q\,OH^- \leftrightarrows Au(OH)_q^{(q-3)-} \qquad (B1)$$

The stability constant K for the latter reaction is given by the equation:

$$K = \frac{a_{Au(OH)_q}{}^{(q-3)-}}{a_{Au^{3+}}\,a_{OH^-}{}^{q}} \qquad (B2)$$

The electrode reaction is given by:

$$Au^{3+} + 3e^- \rightarrow Au \qquad (B3)$$

And it is assumed to behave in a reversible manner so the Nernst equation pertains:

$$E = E^0 + \frac{RT}{3F}\ln a_{Au^{3+}} \qquad (B4)$$

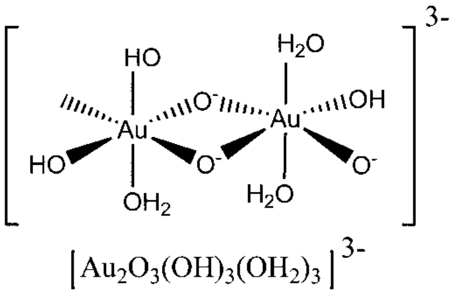
An expression for $a_{Au^{3+}}$ may be obtained from eqn.B2 and substituting into eqn.B4 yields:

$$E = E^0 + \frac{RT}{3F}\ln\frac{a_{Au(OH)_q^{(q-3)-}}}{K_W^q K^q} - \frac{2.303RT}{F}\left(\frac{q}{3}\right)pH \qquad \text{(B5)}$$

Hence the sensitivity of the potential to changes in pH is given by

$$\frac{dE}{dpH} = -\frac{2.303RT}{F}\left\{\frac{q}{3}\right\} = -0.059\left\{\frac{q}{3}\right\}V \qquad \text{(B6)}$$

According to the observed experimental data $dE/dpH \cong -0.0885\,V$. Comparing with the result derived in eqn.B6 we can assign q = 4.5. Thus it is assumed that the complex present in the hydrated oxide layer on gold is $Au(OH)_{4.5}^{1.5-}$ or $Au_2(OH)_9^{3-}$. The latter composition corresponds to the molecular formula $[Au_2O_3(OH)_3(OH_2)_3]^{3-}$. The latter is illustrated in scheme B1.



Scheme B1

It is obvious that with the type of complex shown in scheme B1 proton transfer processes can lead to alteration of the type of ligand at quite a number of coordination sites, and consequently the configuration illustrated in scheme B1 is only one of several possible for this species. The basic unit of the hydrous film is therefore assumed to be dimeric comprising of two edge sharing octahedral; oxygen bridging between dimers is assumed to produce relatively stable, probably nonlinear polymer chains (alternatively it may be taken as evidence that the degree of crosslinking is low)- hence the open structure of these hydrated films. The negative charge on the dimer units is assumed to be balanced by electrostatically bound cationic species such as H_3O^+ and Na^+.

The approach presented has application in the related but more complex Fe(II)/Fe(III) redox transition in hydrated iron oxide films. If the Fe metal is regarded as relatively inert then the electrode during the course of the Fe(II)/Fe(III) transition (peak A_3) may be regarded as displaying behaviour analogous to that exhibited by a conventional redox electrode such as Pt/Fe^{2+},Fe^{3+} - the Fe(II) and Fe(III) species existing at equilibrium in the hydrous oxyhydroxide film, rather than in the bulk solution. Hence the gel like hydrous oxide layer is analogous to a standard redox electrode in contact with an aqueous solution containing the electroactive ions.

The basic electrode reaction is given by:

$$Fe^{3+} + e \leftrightarrows Fe^{2+} \tag{B7}$$

The corresponding Nernst equation is:

$$E = E^0 - \frac{RT}{F} \ln \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \tag{B8}$$

For the ions in the hydrous regions of the film the activity values may be expressed in terms of the stability constants K_2 and K_3 of the hydroxyl species. The latter quantities are obtained by reference to the expressions:

$$Fe^{2+} + q\,OH^- \leftrightarrows Fe(OH)_q^{(q-2)-} \tag{B9}$$

$$Fe^{3+} = r\,OH^- \leftrightarrows Fe(OH)_r^{(r-3)-} \tag{B10}$$

Hence the stability constants are given by:

$$K_2 = \frac{a_{Fe(OH)_q}{}^{(q-2)-}}{a_{Fe^{2+}}\,a_{OH^-}{}^{q}} \qquad K_3 = \frac{a_{Fe(OH)_r}{}^{(r-3)-}}{a_{Fe^{3+}}\,a_{OH^-}{}^{r}} \tag{B11}$$

Substitution for the iron (II/III) ion activities using eqn.B11 into the Nernst equation eqn.B8 yields on simplification that

$$E = E^0 - \frac{2.303RT}{F} \log\left\{ \frac{a_{Fe(OH)_q}{}^{(q-2)-}}{a_{Fe(OH)_r}{}^{(q-3)-}} \frac{K_3}{K_2} \right\} - \frac{2.303RT}{F} \log a_{OH^-}{}^{(r-q)} \tag{B12}$$

Noting that $a_{OH^-} = K_W \big/ a_{H_3O^+}$ then eqn.B12 becomes:

$$E = E^0 - \frac{2.303RT}{F} \log\left\{ \frac{a_{Fe(OH)_q}{}^{(q-2)-}}{a_{Fe(OH)_r}{}^{(q-3)-}} \frac{K_3}{K_2} \frac{1}{K_W{}^{(r-q)}} \right\} - \frac{2.303RT}{F} (r-q)\, pH \tag{B13}$$

If the activities of the surface species are assumed to be pH independent (this means effectively that the hydrous film does not alter in composition with change in pH) then at 298 K one has:

$$\frac{dE}{dpH} = -\frac{2.303RT}{F}(r-q) = -0.059(r-q)\,V/pH \qquad \text{(B14)}$$

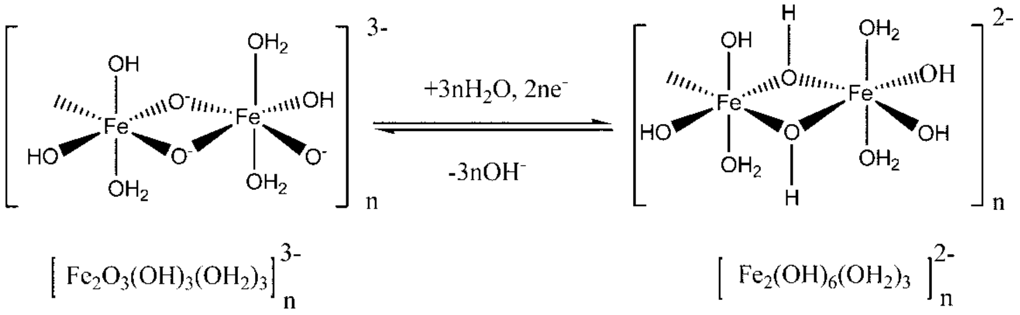
Experimentally, one finds that $dE/dpH \cong 0.088\,V$ and so we assign 0.059 (r-q) = 0.088 and hence $r - q \cong 3/2$. This suggests that the charge storage reaction for the film should be written as

$$Fe(OH)_r^{(r-3)-} + e^- \leftrightarrows Fe(OH)_q^{(q-2)-} + (3/2)\,OH^- \qquad \text{(B15)}$$

Now comes the important approximation. Since values for r and q cannot be determined explicitly by the present calculation, the assumption must be made that *the hydroxyl complex of Fe(III) is similar to that previously proposed for Au(III)*. The composition of the oxidized state is therefore written as $Fe_2(OH)_q^{3-}$ or indeed $[Fe_2O_3(OH)_3(OH_2)_3]^{3-}$. On this basis the net charge storage reaction may be written as:

$$[Fe_2O_3(OH)_3(OH_2)_3]_n^{3-} + 3\,nH_2O + 2ne^- \leftrightarrows [Fe_2(OH)_6(OH_2)_3]_n^{2-} + 3\,nOH^- \qquad \text{(B16)}$$

The oxidized and reduced forms may be represented in structural terms in scheme B2.



Scheme B2

Although the structures proposed here have not been derived in a rigorous manner, they provide a reasonable interpretation of the behaviour of the hydrous layer- even apart from the unusual pH effects.

Appendix C

Electrode kinetics of compact oxide formation at low potentials.

We assume that the peaks A_1 and A_2 can be largely attributed to the initial oxidation of iron to form the anhydrous compact Fe(II) layer of $Fe(OH)_2$ according to the following mechanism:

$Fe + OH^- \rightarrow FeOH_{ads} + e^-$ (C1)

Followed by:

$FeOH_{(ads)} \rightarrow HOFe$ (fast) (C2)

$HOFe + OH^- \rightarrow HOFeOH_{(ads)}$ (slow rds) (C3)

$HOFeOH_{(ads)} \rightarrow Fe(OH)_2 \rightarrow FeO + H_2O$ (C4)

If we assume that the heat of adsorption of the OH$^-$ ions on the iron surface decreases linearly with coverage then the rate equation corresponding to eqn.(C3) above describing film formation under Temkin conditions is given by the following expression:

$$i = k'a_{OH^-} - \theta_{HOFe} \exp\left[-\frac{\beta f(\theta_\Sigma)}{RT}\right] \exp\left[\frac{\beta F}{RT}\eta\right] \qquad \text{(C5)}$$

In the latter expression θ_Σ denotes the total surface coverage, k' is a constant, and $f(\theta_\Sigma)$ is a function of surface coverage to be further specified. From eqn.C2 it is possible to write

$$\theta_{HOFe} = k''\theta_{FeOH} \qquad \text{(C6)}$$

Where k'' denotes another constant. If it is furthermore assumed that the process described by eqn.C1 is in equilibrium then one may show that:

$$\theta_{FeOH} = Ka_{OH^-}(1-\theta_\Sigma)\exp\left[-\frac{f(\theta_\Sigma)}{RT}\right]\exp\left[\frac{F\eta}{RT}\right] \qquad \text{(C7)}$$

In the latter expression $K = k_1/k_{-1}$ is the equilibrium constant and k_1, k_{-1} denote the rate constants for the forward and reverse steps of the initial hydroxyl ion discharge step. Consequently combination of eqn.C5, eqn. C6 and eqn.C7 yields the following expression for the film formation current:

$$i = ka^2_{OH^-}(1-\theta_\Sigma)\exp\left[\frac{(1+\beta)f(\theta_\Sigma)}{RT}\right]\exp\left[\frac{(1+\beta)F}{RT}\eta\right] \qquad \text{(C8)}$$

In the latter expression we note that $k = k'k''K$. Assuming that the symmetry factor $\beta = 0.5$ yields that

$$i = k a^{2}_{OH^-}\left(1-\theta_\Sigma\right)\exp\left[\frac{3f\left(\theta_\Sigma\right)}{2RT}\right]\exp\left[\frac{3F\eta}{2RT}\right] \tag{C9}$$

In general $f\left(\theta_\Sigma\right)=g\theta_\Sigma$ where g denotes the Temkin interaction parameter. At constant total surface coverage, the Tafel slope for the oxide formation process is theoretically given by:

$$b=\left(\frac{d\eta}{d\log i}\right)_{\theta_\Sigma, a_{OH^-}}=\left(\frac{dE_P}{d\log\upsilon}\right)=2.303\left\{\frac{2RT}{3F}\right\} \tag{C10}$$

This prediction yields a value of 0.040 V/dec at 298 K. The latter value is in excellent agreement with the experimentally obtained value of 39 mV obtained from measurements of the sweep rate variation of the potentiodynamic A_2 peak potential outlined in fig.10.