

ELECTROCATALYSIS AND FUEL CELLS

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Electrocatalysis may be defined as the relative ability of different substances, when used as electrode surfaces under the same conditions, to accelerate the rate of a given electrochemical process.

Unlike catalytic effects in the conventional sense, the relative electrocatalytic properties of a group of materials at a given temperature and concentration of reactant and product are not necessarily constant. They may vary owing to the different dependence of rates on electrical potential; that is, variation in Tafel slope with substrate, for the same electrochemical reaction. These differences in Tafel slope may come about by variation of the symmetry factor from one substrate to another, or by changes in the adsorption isotherm of reaction intermediates. A problem of fundamental importance in assessing electrocatalytic behavior is, therefore, the rational potential at which relative reaction rates should be compared. It is generally considered that this potential should be the potential of zero charge (p.z.c.) of the particular substrate, as under these conditions there is no charge-dependent electric field to influence electron transfer rates (1).

It is more convenient in practice to measure rates at constant potential with respect to a standard electrode. Under these conditions, electronic factors which are involved in the chemical (p.z.c.) rate equation cancel, so that a simplified dependence of relative rate on free energies of adsorption of reaction intermediates results provided the symmetry factor is constant (2,3). This point will be more completely discussed below.

The concept of electrocatalysis is rather recent, and has arisen since the advent of research into fuel cells as a practical means of energy conversion. The performance of such devices depends, at the present stage of technology, almost entirely on problems concerning electrode reaction rates rather than, for instance, mass-transport processes. Typical H_2/O_2 fuel cells, working at low temperatures in acid electrolyte, are limited by the intrinsic rate of the oxygen electrode. To date, platinum is the most effective material for both hydrogen oxidation and oxygen reduction in acid medium. There is, however, a considerable difference in the relative rates at a given overpotential that can be maintained on a platinum electrode for these two processes. Under ordinary conditions, the hydrogen oxidation rate is approximately 10^7 times more rapid than that of oxygen reduction. This difference results in an effective loss in efficiency, due to cathode polarization, of perhaps 30 percent, and requires the use of platinum metal catalysts in high loadings. This slow rate of the oxygen-reduction reaction is well known, and is manifested in practice by the low open-circuit potential of the cathode which corresponds to rate control by an alternative process, the electrode potential being determined by platinum oxidation (4), or impurity oxidation (5), or by some parasitic redox process.

The hydrogen electrode process on platinum has one of the fastest specific rate constants known (apart from metal-metal ion reactions of reactive metals and some redox processes) in aqueous solutions, whereas oxygen reduction on platinum must by comparison be considered a very slow process, though it is by no means the slowest reaction that has been observed.*

One striking fact about reaction rates on different metal substrates is the wide range of rate constants that are encountered for the same process - for instance, some 10 orders of magnitude for the hydrogen electrode reaction (6), and at least 5 orders of magnitude for oxygen evolution on oxidized platinum (7). Recent work conducted in this laboratory has shown that rate constants for oxygen reduction on oxide-free noble metals in acid electrolyte vary by approximately 7 orders of magnitude. Wide rate variations for other types of reactions, for instance hydrocarbon oxidation, have been noted.

In this paper, past work on electrocatalysis will be briefly reviewed and correlated with some recent work on the electrocatalytic properties of Group VIII and Ib metals and alloys for the oxygen reduction reaction in acid solution. Some of the consequences of this study concerning the fuel cell oxygen electrode are discussed. In particular, the electrocatalytic mechanisms of the hydrogen and oxygen electrodes will be explored in detail, to determine the likelihood of future increase in O_2 electrode exchange currents.

The Mechanism of Electrocatalysis

In general, the study of specific reactions has given some insight into the factors controlling rates on different electrode substrates. The reactions most broadly studied for this purpose have been -

1. Hydrogen evolution in acid solution (6, 9, 10).
2. Oxygen evolution on noble metal oxides in acid solution (11,12).
3. Certain hydrocarbon reactions, for example, ethylene oxidation (13, 14).

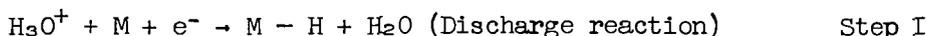
In comparing reaction rates for a specific process on different metals, it is important to first ascertain that two necessary conditions are met:

1. The process in question must be the same on the group of metals - that is, the rate-determining step must be the same in each case, and the reaction path, at least as far as the rate-determining step, must also be the same.
2. The process has been compared on the different metals under the same conditions - that is, with the same surface preparation in solutions of the highest possible purity, so that poisoning of the electrode surface by adsorption of capillary-active matter is avoided.

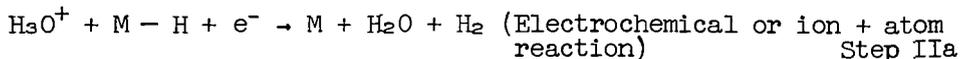
* Oxygen reduction on gold (8), and hydrogen evolution on lead or mercury (6) are several orders of magnitude worse.

The Hydrogen Evolution Reaction

It is generally considered (15-22) that the mechanism of the hydrogen evolution reaction in acid solution on the majority of metals studied involves the sequence



which is then followed by either



or



where M is a surface site on the metal.

Attempts to correlate the overpotential of hydrogen evolution with the properties of the electrode substrate date back several decades. Bonhoeffer (23) in 1924 noted a connection between hydrogen overvoltage and the rate of catalytic hydrogen combination. Correlations between exchange current and interatomic distance (24-27), metal surface energy (28,29), cohesion energy (30), melting point (26), and compressibility (31), have been discussed by a number of authors. In a similar way, Bockris and co-workers (6,32-34) showed that the thermionic work function of the metal and its hydrogen overvoltage were empirically related. Horiuti and Polanyi (35), followed by other authors (36,37) had previously pointed out that the rate of the discharge reaction (I) should be increased (that is, the activation energy decreased assuming a constant entropy of activation) if the heat of adsorption of atomic hydrogen on the metal surface were high. Rüetschi and Delahay (9,38) attempted to establish this relationship by considering an approximate calculation of the S - H bond energy, based on the Pauling equation (39) as used by Eley (40) for chemisorption phenomena, i.e.,

$$D_{\text{M} - \text{H}} = \frac{1}{2} \left(D_{\text{M} - \text{M}} + D_{\text{H} - \text{H}} \right) + 23.06 \left(X_{\text{M}} - X_{\text{H}} \right)^2 \quad (1)$$

where $D_{\text{M} - \text{H}}$ is the M - H bond strength, $D_{\text{M} - \text{M}}$ is the metal-metal atom bond strength, $D_{\text{H} - \text{H}}$ is the adsorbate bond strength, and X_{M} , X_{H} are the electronegativities of the metal and adsorbate respectively. As metal-metal atom forces are short range, $D_{\text{M} - \text{M}}$ is equated to $L_s/6$ for close-packed metals (9), where L_s is the latent heat of sublimation. These authors (9) established that a good dependence of log rate on $D_{\text{M} - \text{H}}$ existed, but they calculated the latter value neglecting the electronegativity terms; that is, they showed that for certain metals a correlation between L_s and the rate of the hydrogen electrode reaction existed. As L_s is closely related to hardness, cohesion energy, melting point, compressibility and surface energy, this relationship is in good agreement with other correlations based on these parameters (26,28-31). Conway and Bockris (6) developing earlier ideas of Bockris and his coworkers (32,34) showed

that an approximately linear relationship exists between $\log i$ and electronic work-functions for many metals with a second (inverse) relationship apparent for a few metals (Tl, Hg, Pb) with very low hydrogen evolution rates ($i_0 \sim 10^{-11} - 10^{-13}$). They also point out that, because of the empirical linear relationships between work function and L_S , and work function and X_M , which hold for many metals, D_{M-H} can be written in the form

$$A \phi^2 + B \phi + C \quad (2)$$

where ϕ is the work function, and A, B, and C are constants. In consequence of this relation, and as $\log i_0$ and ϕ are linearly dependent, a quadratic expression connects $\log i_0$ and the calculated (or experimental*) values of D_{M-H} (41, 42).

The same authors show that other relationships exist between ϕ and the percentage d character (% d contribution to intermetallic dsp single-bond orbitals) (43) which is a function of atomic number and interatomic distance (43, 44). This serves to correlate earlier observations of rate dependence on the latter quantity (32). Similarly, a linear % d character- $\log i_0$ relation is observed for the transition metals.

The quadratic plot of $\log i_0$ (or overpotential) against D_{M-M} has, like the $\log i/\phi$ plot, two distinct approximately linear regions, with a positive slope for the transition metals and Group Ib, together with Al, Be, and Ga, whereas a negative slope appears for Hg, Tl, and Pb. Conway and Bockris (6) attribute this to the fact that on the latter three metals, which probably have much lower D_{M-H} values than calculated owing to their electronic structures, reaction I is rate determining, whereas on the remaining metals reaction IIIa is rate determining.

Volcano Plots

We may, in principle, write the forward rate equations for Reactions I and IIIa as follows:

$$(I) \quad \vec{i} = F \cdot \frac{kT}{h} [M] [H^+] \exp - \frac{\Delta G_o}{RT} - (1 - \beta) \frac{\Delta G_H}{RT} - \frac{\beta F \phi}{RT} \quad (3)$$

$$(IIIa) \quad \vec{i} = F \cdot \frac{kT}{h} [H] [H^+] \exp - \frac{\Delta G_o'}{RT} + \frac{\beta \Delta G_H}{RT} - \frac{\beta F \phi}{RT} \quad (4)$$

where $[M]$, $[H]$ and $[H^+]$ are the activities of metal sites, adsorbed hydrogen, and hydroxonium ions, ΔG_o and $\Delta G_o'$ are metal independent (i.e., adsorption independent) free energies of the activated complex at $\phi = 0$. ΔG_H is the free energy of adsorption of H, and ϕ is the potential with reference to an arbitrary reference electrode. The other symbols have their usual meanings. Following Frumkin (2), no expression for ϕ , the work function, appears in the rate equation, as this quantity is self-cancelling (2, 3, 46).

* Experimental and calculated (metal-hydride) values of D_{M-H} are in relatively good agreement, but differ by about 15 kcal, due to the surface "image potential" (45).

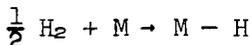
Putting $\theta = [H]$ and $1 - \theta = [M]_2$, we have

$$(I) \quad \bar{i} = F \cdot \frac{kT}{h} (1 - \theta)[H^+] \exp - \frac{\Delta G_o}{RT} - (1 - \beta) \frac{\Delta G_H}{RT} - \beta \frac{F_0}{RT} \quad (5)$$

$$(IIa) \quad \bar{i} = F \cdot \frac{kT}{h} \theta [H^+] \exp - \frac{\Delta G_o'}{RT} + \frac{\beta \Delta G_H}{RT} - \beta \frac{F_0}{RT} \quad (6)$$

$$\text{Assuming that } \frac{\theta}{1 - \theta} = (pH_2)^{1/2} \cdot \exp - \frac{\Delta G_H}{RT} \quad (7)$$

That is, the Langmuir isotherm applies for the equilibrium process IIb,



$$\text{We can write } \theta = \frac{(pH_2)^{1/2} \exp - \Delta G_H/RT}{1 + (pH_2)^{1/2} \exp - \Delta G_H/RT} \quad (8)$$

Substituting for θ , we obtain

$$I \quad \bar{i} = F \cdot \frac{kT}{h} \exp \left(- \frac{\Delta G_o}{RT} - \beta \frac{F_0}{RT} \right) \frac{[H^+] \exp - (1 - \beta) \Delta G_H/RT}{1 + (pH_2)^{1/2} \exp - \Delta G_H/RT} \quad (9)$$

$$II \quad \bar{i} = F \cdot \frac{kT}{h} \left(\exp - \frac{\Delta G_o'}{RT} - \beta \frac{F_0}{RT} \right) \frac{(pH_2)^{1/2} \cdot \exp (1 - \beta) \Delta G_H/RT}{1 + (pH_2)^{1/2} \exp - \Delta G_H/RT} \quad (10)$$

These equations are similar to those developed by Parsons (4) and Gerischer (48), and indicate that rates for both reactions have, under these conditions, the same dependence on ΔG_H . They indicate that $\log i$ would be, at fixed potential and fixed pH_2 and $[H^+]$, an ascending and descending linear function of ΔG_H with a maximum at $\Delta G_H = 0$. If ΔG_H is linearly coverage dependent, that is, if the Temkin isotherm applies, a development of these equations show that a similar relation between i , and ΔG_H , but with a plateau-like rather a sharp maximum around $\Delta G_H = 0$, should occur. Such plots were given the name "volcano plots" by Balandin (49), though he discussed catalytic rather than electrocatalytic cases.

It has been claimed (50) that this approach will explain the fact that metals such as Pb, Hg and Tl have low exchange currents ($\Delta G_H > 0$), whereas metals such as Pt or Pd (ΔG_H presumed to be ~ 0) have high values. In a similar way, metals with $\Delta G_H < 0$ (W, Mo, Ta) also have low exchange currents.

As ΔG_H values are not generally known, the general trend of this parameter is equated to the experimental (or calculated) ΔH_H (i.e., $D_M - H$) values (6,9) assuming that the standard entropy of adsorption is metal independent - that is, it corresponds only to the loss of 3 translational degrees of freedom (9). This assumption is, however, probably not justified, as there is evidence that a compensation effect between ΔS_H and ΔH_H exists. This implies that on surfaces where

D_{M-H} is high, ΔS_H is low owing to the high degree of order in the adsorbate. Similarly, on surfaces with a low D_{M-H} , increased adsorbate mobility and hence increased ΔS_H results. This is well illustrated by Breiter's (51) experimental correlation of ΔH_H and ΔS_H on platinum in different electrolytes where D_{M-H} is modified by differing degrees of anion adsorption.

A second, more important objection involves Parsons' (47) assumption that the adsorbed hydrogen on the surface of the electrode is in equilibrium with gaseous hydrogen via the combination reaction (Equation 7). On platinum, Parsons (47) has estimated the i_0 of this reaction to be $\sim 10^{-2}$. As the process is non-electrochemical, it is hard to see how the $H_2 \rightarrow 2H$ equilibrium can be maintained in the Tafel region ($i > 10^{-1}$ A/sq cm). On this basis, it would therefore seem that this thermodynamic equilibrium is not the origin of the volcano-type $i - D_{M-H}$ relationship noted by Bockris and Conway (i increasing with D_{M-H} for Pb, Hg, Tl, decreasing with D_{M-H} for transition metals (6)). The relative rates seem best explained by the exponential dependence of i on increasing D_{M-H} for the discharge reaction (Equations 5, 9) as suggested by Conway and Bockris (6, 41, 42, 52), for Pb, Hg, and Tl, where low coverages of molecular hydrogen are encountered, and where ΔG_H is large and positive. For the Group Ib and transition metals (except platinoid metals at low overpotentials (53, 55), and perhaps Fe (1)), the ion and atom reaction is considered to be rate determining (56). In this case, we can assume that the previous step, the discharge reaction (I) is in pseudo-equilibrium. The equilibrium condition for this process (assuming Langmuir conditions) is

$$\frac{\theta}{1-\theta} = [H^+] \exp - \Delta G_H / RT \exp - F\phi / RT \quad (11)$$

Hence

$$\theta = \frac{[H^+] \exp - \Delta G_H / RT \exp - F\phi / RT}{1 + [H^+] \exp - \Delta G_H / RT \exp - F\phi / RT} \quad (12)$$

where θ is the surface coverage in [H].

Substituting this in Equation 6 we obtain

$$\bar{i} \propto \frac{FkT}{h} [H^+]^2 \frac{\exp - (1 + \beta) F\phi / RT - \beta \Delta G_H / RT}{1 + [H^+] \exp - \Delta G_H / RT - F\phi / RT} \quad (13)$$

This expression has exactly the same form as Equation 10, and implies again that a volcano-type relation should occur, with i decreasing with decreasing ΔG_H (increasing D_{M-H}) for $\Delta G_H < 0$ (52, 57). The latter condition implies a high coverage of H, and hence favors the ion and atom rate-determining step, as suggested by Conway and Bockris for these metals (6, 52, 56, 57).

Heats of Activation and Frequency Factors

Heats of activation for the hydrogen evolution reaction are only available for a few metals. Glasstone, Laidler, and Eyring (58) quote some early values, which indicate general similarity of preexponential terms. Later values, obtained under conditions of high purity by Parsons (55) for the combination and discharge reactions on platinum, indicate that for both the heat of activation is about 5.2 kcal/mole at the reversible potential. In the same work, Parsons (55) (see also Temkin (59)) derives theoretically the preexponential terms of the combination, ion, and atom and discharge reactions. For the discharge reaction, the quantities are about 2×10^6 A/sq cm ($\theta \rightarrow 0$), and 2×10^7 A/sq cm ($\theta \rightarrow 1$); for the combination reaction 3×10^2 A/sq cm ($\theta \rightarrow 0$) and 2×10^7 A/sq cm ($\theta \rightarrow 1$); and for the ion plus atom reaction (assuming a mobile activated complex) 40 A/sq cm ($\theta \rightarrow 0$) and 10^4 A/sq cm ($\theta \rightarrow 1$). These values are in reasonable agreement with experiment (55).

Conway, Beatty, and DeMaine (60) measured activation energies on a series of copper-nickel alloys. They found that in each case the activation energy was temperature dependent, but that the value for copper was less than that for nickel (in agreement with other workers (61, 62)). The values for the alloys were nonlinearly dependent on the atom percentage of the components. However, at constant overpotential, the difference in the heats of activation on copper and nickel was shown to be reasonably consistent with experimental values of D_{M-H} on these metals, assuming Equation 13 applies in its simplified form for ΔG_H negative ($i \propto \exp + (1 - \beta) \Delta G_H/RT$), hence energy of activation $\propto (1 - \beta) \Delta H_H$. Hence, the fact that i_0 on Ni is greater than that on copper indicates that in all probability the Arrhenius preexponential terms for these two metals are very different, and perhaps implies a higher coverage of H on nickel. Similarly, if coverage is markedly temperature-dependent, the nonlinearity of the Arrhenius plots is accounted for.

On the basis of Parsons' (55) and Temkin's (59) theoretical calculations and the experimental data of Conway et al. (60) the assumption of a constant ΔS_{act} (or preexponential factor, assuming θ to be constant) over a series of metals is improbable. It is clear from Equation 13, assuming ΔG_H is large and negative, that

$$i \propto \exp (1 - \beta) \Delta G_H/RT$$

Hence, assuming that the preexponential factor is independent of the metal, we may write

$$2.303 \log i \propto (1 - \beta) \Delta H_H/RT$$

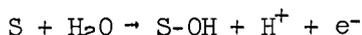
Hence, with $\beta = \frac{1}{2}$, the slope of the linear $\log i - \Delta H_H$ plot should be $1/4.6 RT$ (about 0.36). Data of Conway and Bockris (6,41) show that for metals with a large ΔH_H , the slope is appreciably less than this, again suggesting that the preexponential factor is important in determining the overall rate, and that a "compensation effect" between ΔH_{act} and the preexponential factor, as is often noted in gas-phase catalytic processes, appears to apply in this case.

Recently, Bockris, Damjanovic, and Mannan (10) have reexamined the hydrogen electrode reaction on a number of pure metal and alloy systems. The systems were chosen to maximize the change in one particular parameter - for instance, d-orbital vacancies or internuclear distance. The results obtained again show the dependence of rate constants on % d character and d-orbital vacancies. In addition, i_0 appears to be linearly dependent on internuclear distance (which depends on L_d and electronegativity when other electronic characteristics are constant). Essentially, these results confirm that for similar systems, i depends on those characteristics which determine the strength of the M-H bond.

The general picture that emerges is an approximate dependence of $\log i_0$ on the heat of adsorption of atomic hydrogen, but experimental evidence of the effect of the preexponential factor in the rate expression is not at present available.

Electrocatalysis in Other Systems

Rüetschi and Delahay (63) have examined Hickling and Hill's (64) oxygen evolution overpotential data in terms of the strength of the M-OH bond, using arguments similar to those for the hydrogen evolution electrode. The rate-determining step for the oxygen evolution reaction in acid solution is generally accepted to be the water discharge reaction (65,66).



where S is an active surface site on the (oxidized) metal surface. On this basis, the heat of activation of the oxygen evolution reaction should depend on the strength of the S-OH bond. Rüetschi and Delahay (63) assumed that this could be equated to the bond strength of the metal hydroxide, which is reasonable in view of the fact that at oxygen evolution potentials, metallic electrodes are always covered with a superficial oxide layer, which reaches a thickness of several Angströms on Pt (67).

Dahms and Bockris (13), and Kuhn, Wroblowa and Bockris (14) have examined ethylene oxidation in acid solution on a series of noble metals and alloys. The latter workers established that a volcano-type relationship existed when $\log i$ at constant overpotential was plotted against d-orbital vacancies or L_d . Approximately two orders of magnitude positive change in i was noted in going from Au to Pt, with a further negative change of approximately three decades through iridium, rhodium and ruthenium to osmium.

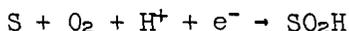
Ethylene oxidation was shown to have a negative reaction order on platinum, and this was interpreted by postulating that increasing ethylene coverage reduces the coverage of adsorbed OH radicals on the electrode (13). The OH is derived from the oxidation of water, and is directly involved in the chemical rate-determining step. This rate, on the ascending side of the volcano, is controlled by increasing metal-adsorbate bonds, whereas in the descending side the major influence is in the preexponential term of the rate expression - that is, the decreasing coverage of ethylene in the face of increasing -O or -OH adsorption.

A process of this type indicates a special case of electrocatalysis where increasing rate as the metal-adsorbate bond-strength increases is compensated by decreasing coverage due to competitive adsorption. This effect would be expected to be even more marked under the Temkin conditions of adsorption, where the strength of the metal-adsorbate bond falls as the total coverage of the adsorbate increases.

Oxygen Reduction on Phase Oxide-Free Precious Metals in Acid Solution

Recent work in this laboratory on the oxygen reduction reaction carried out on a range of precious metals and alloys in 85% orthophosphoric acid solution under high purity conditions indicates that initial electron transfer to an adsorbed oxygen molecule is rate determining on Group Ib and Group VIII metals and alloys, provided the metal surface was initially in the reduced condition - that is, it carried no phase oxide.

In all probability the rate-determining step also involves a proton, thus:



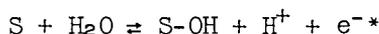
This is in agreement with pH dependence work carried out on platinum electrodes in dilute perchloric acid at constant ionic strength (68) and is in general agreement with mechanisms suggested for other metals in acid electrolyte (69,70). At potentials above about 800 mV on platinum, 650 mV on rhodium, and 750 mV on palladium, intermediate coverages of adsorbed oxygenated species derived from water oxidation are present on these metals (71,72,73). The coverage of these species is linearly potential dependent, and can be approximately described by the Temkin isotherm (72,73). On iridium (73), ruthenium (74), and osmium (75), high coverages of oxygenated compounds are present, and the coverage-potential relationship seems to be more nearly Langmuirian. On gold, very low coverages of the oxygenated compounds are noted (71), and again the appropriate isotherm is Langmuirian.

The rate of the forward reaction in oxygen reduction may be written

$$\bar{i} = \frac{kT}{h} \theta^* [H^+] \exp \frac{-\bar{\Delta}G_o - (1 - \beta) \Delta G_p + \beta \Delta G_r}{RT} \exp \frac{-\beta E_a}{RT} \quad (14)$$

where θ^* is the coverage with molecular oxygen, $\bar{\Delta}G_o$ is metal independent, ΔG_p is the standard free energy of adsorption of the reaction product (SO_2H), ΔG_r is the standard free energy of adsorption of oxygen molecules, and β is the symmetry factor. It is assumed that the standard state for θ is $\theta = 1/2$. If ΔG_p and ΔG_r are not potential dependent (that is, the Langmuir isotherm applies), the Tafel slope for this process will be $2RT/F$, if $\beta = 1/2$. This is experimentally observed on gold, silver, osmium, ruthenium, and iridium.

Oxygenated compounds are adsorbed on the electrode according to an equilibrium of the type (5,68)



The equilibrium condition for this reaction is

$$\frac{\theta}{1 - \theta^* - \theta} = k[H_2O] [H^+]^{-1} \exp\left\{-\frac{\Delta G_{OH}}{RT}\right\} \exp(F_0/RT) \quad (15)$$

where again θ^* is the coverage of molecular oxygen by direct absorption, ΔG_{OH} is the free energy of adsorption of $-OH$, and k is a metal-independent constant.

If we assume θ^* to be small compared with θ in the intermediate coverage range ($0.2 < \theta < 0.8$) where Temkin adsorption might be expected to apply, with $\theta/1-\theta$ approximately constant in this range of θ , we can write

$$\log [H^+] + \frac{\Delta G_{OH}}{RT} = \frac{F_0}{RT} + \text{const.} \quad (16)$$

If we assume that the heat of adsorption of O_2H is similarly affected (68) by the changes in coverage, and heat of adsorption of OH , then with $\beta = 1/2$, and substituting Equation 16 in Equation 14 we obtain

$$i \propto [pO_2] [H^+]^{3/2} \exp(-F_0/RT) \quad (17)$$

which is in agreement with experimental data on platinum (68), palladium and rhodium. This equation assumes that $\theta^* \propto pO_2$ (that is, θ^* is small, and ΔG_r is small and independent of changes in θ). Under Temkin conditions of adsorption of $-OH$ the effective rate constant of the reaction falls as θ , hence potential, rises and the reaction can be considered to be progressively poisoned by adsorbed oxygen atoms or OH radicals.

It is of interest to consider the type of relation we would expect between the forward reaction rate of the reduction reaction and ΔG_p .

Assuming that molecular oxygen is adsorbed following the Langmuir isotherm, we can write

$$\frac{\theta^*}{1 - \theta^* - \theta} = [pO_2] \exp - \frac{\Delta G_r}{RT} \quad (18)$$

where $1 - \theta^* - \theta$ is the available activity of vacant metal sites.

Hence, from Equations 18 and 15, at constant pO_2 , H_2O and H^+

$$\theta^* = \theta k^{-1} \exp (\Delta G_{OH} - \Delta G_r - F_0)/RT \quad (19)$$

* The $S-OH$ is probably oxidized further to $S-O$, but this causes no further change in the total coverage.

From Equation 15, assuming that θ^* is small compared with θ

$$\theta = \frac{k \exp \left(\frac{F\phi - \Delta G_{OH}}{RT} \right)}{1 + k \exp \left(\frac{F\phi - \Delta G_{OH}}{RT} \right)} \quad (20)$$

From Equations 14, 19, and 20 assuming $\beta = 1/2$

$$i \propto \frac{\exp - \Delta G_T / 2RT \exp - \Delta G_P / 2RT}{1 + k \exp \left(\frac{F\phi - \Delta G_{OH}}{RT} \right)} \exp - F\phi / RT \quad (21)$$

As ΔG_P (free energy of adsorption of O_2H) and ΔG_{OH} (free energy of adsorption of OH) should change by similar amounts from metal to metal, Equation 21 can be written at constant θ

$$i \propto \frac{\exp - \Delta G_T / 2RT \exp - \Delta G_{OH} / 2RT}{1 + k \exp - \Delta G_{OH} / RT} \quad (22)$$

This expression again has a maximum at $\Delta G_{OH} = 0$; increasing with ΔG_{OH} for $\Delta G_{OH} > 0$, and decreasing for $\Delta G_{OH} < 0$.

Experimental Data on Oxygen Reduction

Figures 1-5 show data for a range of metals and alloys for the oxygen reduction reaction of 85% orthophosphoric acid. Volcano plots are observed when i (at 25°C) at a potential of 800 mV with respect to a hydrogen electrode in the same solution are plotted against metal parameters that are known to influence heat of adsorption (L_S , d-orbital vacancies, d character). In addition, a plot of i against the heat of adsorption of the oxygenated reaction intermediate is shown.

The latter has been calculated relative to the value for gold, assuming that Paulings' equation for heat of adsorption holds for the adsorbed product in the rate-determining step ($-O_2H$) and assuming that the electronegativity of oxygen in the adsorbate can be put equal to 3.5. Electronegativity values for the metals are derived from Gordy and Thomas (78) and L_S values are from Bond (76). Data are included here for a range of platinum-ruthenium alloy electrodes. In this case, each parameter plotted has been assumed to be directly dependent on the atomic composition of the solid solution.

Published polarization data on platinum-rhodium alloys in dilute sulfuric acid (79) make it appear that they could be accommodated on the rising side of the volcano in the same way as the Pt-Ru alloys and similarly, data on the platinum-gold and palladium-gold alloys (60) suggest that they would fall on the opposite side of the volcano.

In the present work it was possible to compare the heat of activation measured for each metal or alloy system with a calculated value (relative to platinum).† The S-O₂H bond strength (ΔG_p) calculated from Pauling's equation relative to that for platinum was substituted in Equation 14, assuming $\beta = 1/2$, and ignoring changes in ΔG_p over the series of metals. A plot of this value against experimental activation energy at $\eta = -460$ mV is shown in Figure 6. For the materials exhibiting Temkin adsorption (Pt, Rh, Pd and some Pt-Ru alloys) a small correction had to be made to the experimental energy of activation because of the different value of the Tafel slope under those conditions. Horizontal lines on the plot indicate the uncertainty in the calculated values of heat of activation corresponding to ± 0.1 unit uncertainty in metal electronegativity, whereas vertical lines are estimated experimental uncertainties in heats of activation. It can be seen that a satisfactory agreement exists between calculated and experimental values, thus confirming earlier suppositions that this should be the case. It should be noted that no satisfactory correlation was obtained for silver, whose Pauling electronegativity (1.9) predicts a much higher bond strength than would seem to be the case here.‡

It is clear that for this electrode system, the major differences in the rate over the series of metals studied are due to changes in preexponential factors rather than in heat of adsorption. In Figure 7, the experimental value of the preexponential factor for each metal or alloy has been plotted against the experimental heat of activation. For the Group VIII metals and alloys a very good "compensation effect" is exhibited with the preexponential factor increasing over more than five decades from osmium to platinum. Gold and silver have similar preexponential values, but substantially greater heats of adsorption, than those on platinum. From Equations 19 and 20, assuming ΔG_p

not to vary substantially over the series of metals examined (as implied in Figure 6), the coverage of molecular oxygen θ^* can be expected to be proportional to $(1 + k \exp - \Delta G_{OH}/RT)^{-1}$. It will therefore be low for metals of high negative ΔG_{OH} (e.g., osmium), and will rise as ΔG_{OH} increases. The rise will be slow, however, after $\Delta G_{OH} \sim 0$ (platinum). At least part of the variation in preexponential factors may be explained in this manner. It is also apparent that the entropy of the adsorbate may not be metal-independent, but may depend on the heat of adsorption. The experimental values of the preexponential factor on platinum, palladium, gold, and silver are high - of the same magnitude as those calculated by Parsons (55) for mobile adsorbates in the hydrogen reaction. Thus, it is probable that the loosely bound adsorbate on these metals is relatively mobile. Increasing heat of adsorption on going from platinum to osmium should decrease adsorbate mobility so that the adsorbate entropy, hence the standard free energy of the activated complex, is decreased.

‡ The observed difference between the activities of gold and silver in acid and alkaline solution is very striking.

† The absolute value of the O₂H bond strength cannot be determined, as the D_{X-X} value - that is, the strength of the O-O bond in a hypothetical diperoxy compound - is indeterminate.

Summary and Application to Fuel Cells

It thus appears that the oxygen electrode reaction is thermodynamically limited on the noble metals. Preexponential factors of the rate-determining oxygen reduction reaction are close to those of the hydrogen electrode reaction, but heats of activation are very much higher. Attempts to reduce the heats of activation by increasing the heat of adsorption of reaction intermediates simply result in lowered rates due to compensating changes in the preexponential factor. The rate of the oxygen electrode reaction under Langmuir adsorption conditions is an ascending and descending function of the standard free energy of adsorption of $-O_2H$ (or similar oxygenated species), with a maximum when this quantity is equal to zero. This occurs approximately at platinum as is the case for $-H$ in the hydrogen electrode reaction. Consequently, it seems to be highly improbable that the rate constants of the oxygen reduction mechanism on the noble metals in acid solution can be substantially increased from present levels.

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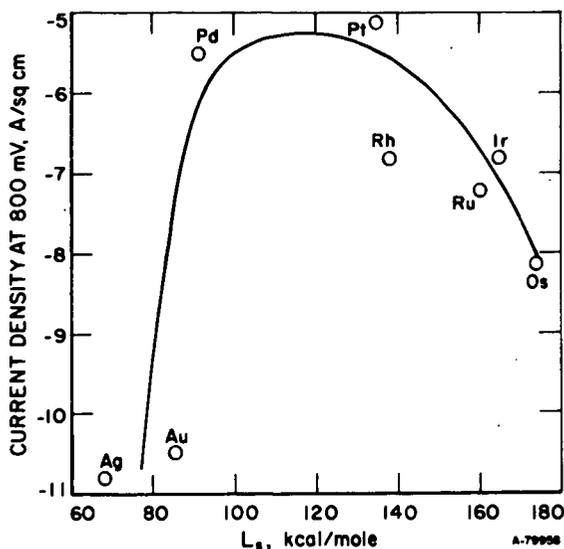


Figure 1. O₂ Reduction in 85% Orthophosphoric Acid: Plot of i at $\eta = -460$ mV at 25°C Against Latent Heat of Sublimation of Electrode Metal. (Latent heat of sublimation values are from Bond (77):)

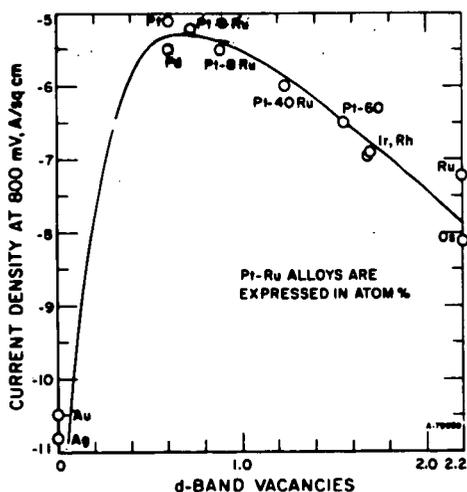


Figure 2. O₂ Reduction in 85% Orthophosphoric Acid: Plot of i at $\eta = -460$ mV at 25°C Against d-Orbital Vacancy Value of Electrode Metal. (For d-orbital vacancy values, see Ref. 18. The value for osmium has been considered to be the same as that for ruthenium and iron.)

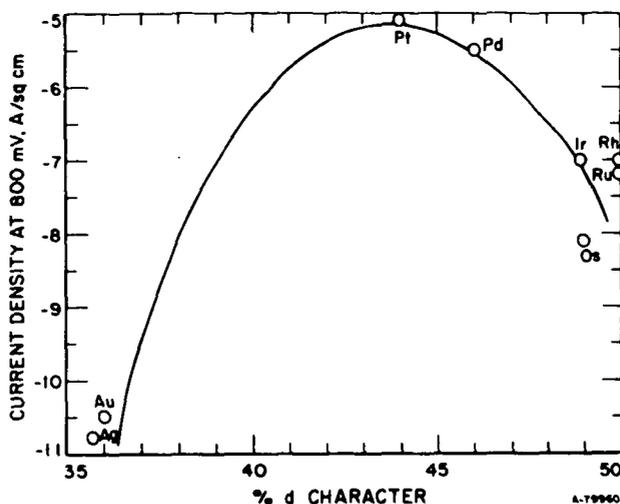


Figure 3. O_2 Reduction in 85% Orthophosphoric Acid: Plot of i at $\eta = -460$ mV at $25^\circ C$ Against % d Character of Electrode Metal. [% d character values (calculated where necessary) from Ref. 43.]

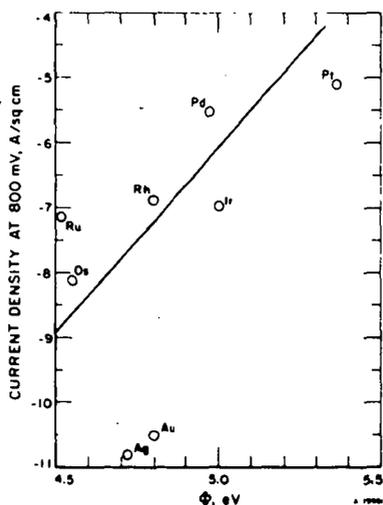


Figure 4. O_2 Reduction in 85% Orthophosphoric Acid: Plot of i at $\eta = -460$ mV at $25^\circ C$ Against Electronic Work Function of Substrate Metal. ϕ Values are "Preferred" Values, Except Ru, Os, Ir. Values for Pt (C. W. Oatley, Proc. Phys. Soc. 51, 318 (1939)), Ru and Os (O. Klein and E. Lange, Z. Electrochem. 44, 542 (1938)) are by Contact Potential Method. Value for Rh (H. B. Wahlen and L. V. Whitney, J. Chem. Phys. 6, 594 (1938)) is by Thermionic Emission. Values for Pd (L. A. Dubridge and W. W. Roehr, Phys. Rev. 37, 1269 (1931)), and Au (L. W. Morris, Phys. Rev. 37, 1263 (1931)) are by the Photoelectric Method. The Value for Ir is From Ref. 13

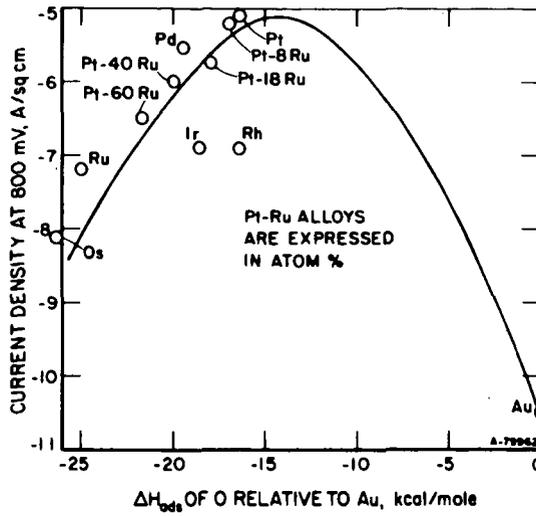


Figure 5. O_2 Reduction in 85% Orthophosphoric Acid: Plot of i at $\eta = -460$ mV at $25^\circ C$ Against Calculated M-O Adsorbate Bond Strength (Relative to Au).

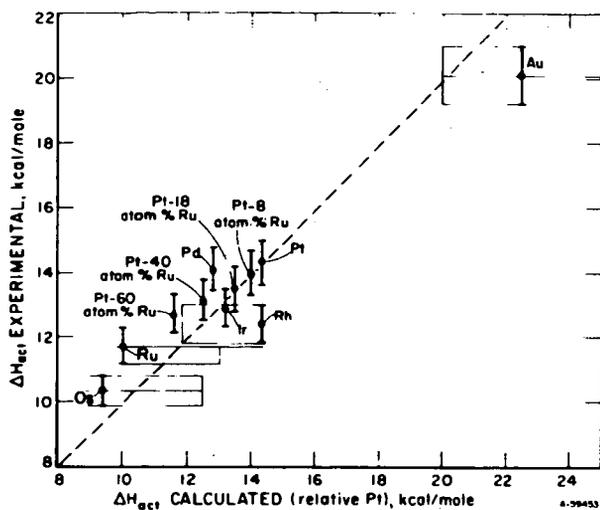


Figure 6. O_2 Reduction in 85% Orthophosphoric Acid: Plot of Experimental Heat of Activation (at $\eta = -460$ mV) Against Calculated Value (Relative to Pt).

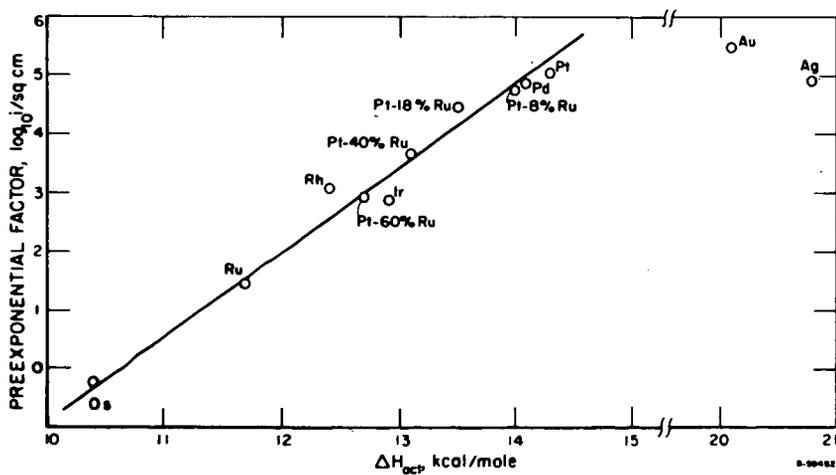


Figure 7. O_2 Reduction in 85% Orthophosphoric Acid: Plot of Experimental Heat of Activation (at $\eta = -460$ mV) Against Preexponential Factor.