

The Hydrided Palladium Electrode

A REVIEW OF RECENT RESEARCH

By F. A. Lewis, Ph.D.

Chemistry Department, The Queen's University of Belfast

Changes in the electrical resistance and electrode potential of catalytically active Pd/H are valuable when studying rates of diffusion of reactants up to the electrode surface. In this article the results of experiments concerning the diffusion of hydrogen molecules and their correlation with hydrogen overvoltage are reviewed and possible sources of error in the measurements are discussed.

Because of their general excellent resistance to corrosive attack and since equilibria can be conveniently established on their surfaces between hydrogen ions and hydrogen molecules dissolved in solution, the platinum group metals may all be employed as hydrogen electrodes. The establishment of equilibria requires reversible chemisorption and dissociation of hydrogen molecules at the electrode surfaces which are also intermediate steps when hydrogen is electrolytically discharged at cathodes of platinum and related metals.

Although additional or alternative reaction steps have been suggested (1) perhaps the most condensed and idealised scheme of intermediate steps, in acidic solution, at hydrogen electrodes and cathodes is as follows:



where $\underset{*}{\text{H}}$ and $\underset{*}{\text{H}_2}$ are adsorbed species and H_2^\dagger and $\text{H}_2^{\dagger\dagger}$ are hydrogen molecules dissolved in solution within about 5 Å of the surface and beyond the limit of the Nernst diffusion layer respectively.

Conjointly with the formation of the chemisorbed intermediate $\underset{*}{\text{H}}$, there arises the

possibility of diffusion of hydrogen into the metal lattice, so that provided step 2 can proceed unhindered the equilibrium amount of hydrogen absorbed from hydrogen-saturated electrolytes should correspond to the amount absorbed when suitably activated surfaces are in direct contact with hydrogen in the gas phase at the same temperature and pressure. The amount of hydrogen absorbed by the platinum substrate of a standard (Pt/H/H₂) hydrogen electrode (1 atm H₂; 25°C) is however relatively small, extrapolation of pressure-concentration-temperature (P-C-T) data at higher temperatures (2) indicating the solid electrode to have the composition H/Pt ~ 0.1 × 10⁻⁴ atomic ratio. Moreover, few marked changes in conveniently measured physical properties of platinum result from the absorption of this amount of hydrogen (3).

The Pd/H/H₂ Electrode

Conflicting results have, until recently, still been reported, concerning the electrode potentials of the hydrided palladium electrode. A number of the major discordancies have now however been adequately resolved and, in particular, correlations between electrode potentials measured in solutions and the extensive P-C-T data available for the Pd/H system have been justified.

As an example, P-C-T data would indicate

that the hydrogen content of the palladium substrate of a standard equilibrium Pd/H/H₂ electrode (1 atm H₂; 25°C) to be H/Pd ~ 0.69 (atomic ratio) and this fact has now been verified experimentally (4, 5). This hydrogen content very greatly exceeds that of a standard Pt/H/H₂ electrode and although the other members of the platinum group of metals have not been so fully investigated as platinum and palladium the weight of present evidence (3) suggests that the Pd/H/H₂ electrode is unique in possessing such a large "sink" of hydrogen in the solid. An immediate consequence is that while hydrogen is absorbed into the "sink", palladium requires (volume for volume) longer to attain equilibrium in hydrogen saturated solutions than the other platinum group metals. Moreover, in contrast to platinum the increase in hydrogen content is reflected by changes, at rates which are conveniently measurable, of electrode potential, E, and of other physical properties such as electrical resistance (4, 5, 6, 7, 8). Furthermore, since diffusion of hydrogen within the solid electrode is relatively rapid (6, 9, 10) these changes can be utilised to measure either the kinetics of slower steps such as hydrogenation reactions catalysed at the electrode surface or alternatively to measure rates of diffusion of reactants up to the surfaces of electrodes which are very active catalytically.

Kinetics of Absorption of Hydrogen Dissolved in Solution

When a catalytically active palladium wire is immersed in efficiently stirred hydrogen-saturated dilute acid solutions, the time dependent changes of electrode potential, E, and electrical resistance (plotted as R/R₀ where R₀ is the resistance of the hydrogen-free specimen) are as shown in Fig. 1 where the time scale is dependent on the wire diameter (4, 7, 11). From relationships, which may be independently derived, between the hydrogen content of the specimen and both E and R/R₀, the increase of H/Pd can be measured simultaneously and is also shown

in Fig. 1. By alteration of the partial pressure of dissolved hydrogen (7, 8) as well as by a detailed analysis (4b, 8) of extensive measurements both with palladium and a series of palladium alloys it has been shown that the rates of hydrogen absorption are in very good accord with the equation

$$\frac{d(\text{H/Pd})}{dt} \propto k_0(P-p) \quad (5)$$

where k_0 has a value of $\sim 10^{16}$ molecules cm⁻² sec⁻¹ atm⁻¹ which is virtually independent of the hydrogen ion concentration in the electrolyte, P is the pressure under which the hydrogen molecules are dissolved in solution and p, the vapour pressure of the solid hydride, is related to E by the usual expression $\ln p = 2FE/RT$.

From the temperature dependence of the relationship between H/Pd and R/R₀ (5), the temperature dependence of k_0 indicated the activation energy of the rate controlling step to have a low value between zero and 2 Kcal/mole H₂ (4, 7, 8). All this evidence supports the view that this step is the permeation of the dissolved hydrogen molecules up to the electrode surface (step 4 above).

Poisoning of Catalytic Surface

The results in Fig. 1 may be excellently reproduced if the surface is activated by palladisation, but virtually identical results can be obtained with "bright" surfaces activated either by anodisation or even merely by pre-flaming (4, 12). However, the catalytic activity of pre-flamed or pre-anodised specimens is more readily negated by poisons (4). Poisonous species can be present in either insufficiently purified electrolytes or in the hydrogen or other gas streams or be leached from the electrolyte container or specimen holder. There is also the possibility of copper, zinc or mercury being introduced into the electrolyte from electrical connections.

It should however be noted that despite the elimination of catalytic poisons from the sources listed, extremely misleading data can be obtained if specimens are not effi-

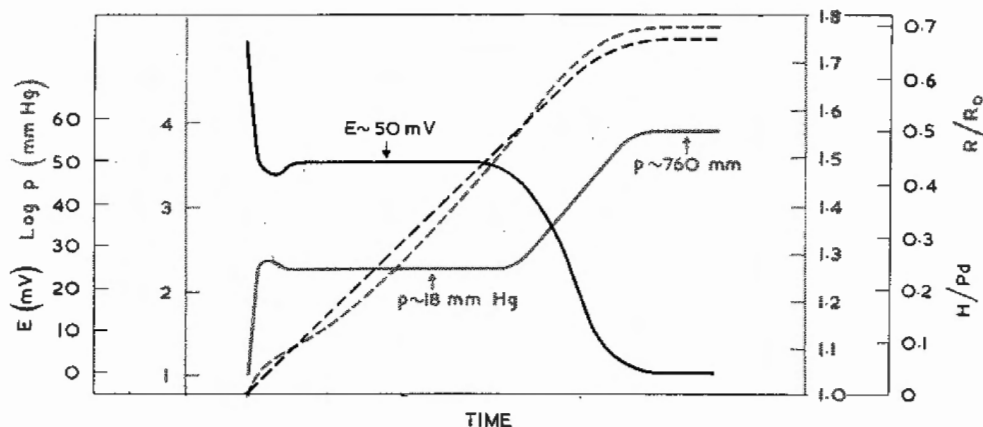


Fig. 1 Time dependence of R/R_0 , electrode potential and derived parameters for palladium immersed in hydrogen saturated dilute acids. Time for equilibrium ($E=0$) ca. 2 hours with .012 cm diam. wire and ca. 7 hours with .027 cm diam. R/R_0 and H/Pd are shown by broken lines

ciently cleaned before introduction into solution since subsequent activation procedures, such as anodisation or cathodisation, may not thereafter be entirely successful.

Study of Hydrogen Overvoltage

Although Fig. 1 illustrates the increase of H/Pd by absorption of molecules from a hydrogen saturated solution, hydrogen may of course also be introduced when the specimen is cathodised, the current density required to discharge $\sim 2 \times 10^{16}$ hydrogen ions $\text{cm}^{-2} \text{sec}^{-1}$ (i.e. k_0P where $P=1 \text{ atm}$) being $\sim 3 \text{ mA cm}^{-2}$. Moreover if electrolytic charging is carried out subsequent to attainment of $E=0$ ($p=1 \text{ atm}$, see Fig. 1) in a hydrogen saturated electrolyte and time is allowed for a steady state to be established, the number of molecules of hydrogen ($\text{cm}^{-2} \text{sec}^{-1}$) thereafter being evolved at the cathode

will be $\frac{Ni}{2F}$ where i is the current density (A.cm^{-2}), N is Avogadro's number and F the Faraday Constant. Provided diffusion of molecules from the surface continues to be rate controlling:

$$\frac{Ni}{2F} = k_0(P-P) \quad (6)$$

Now the resulting increase of p should be reflected in a potential difference between

Pd/H and an equilibrium hydrogen electrode in the same solution. This difference in potential constitutes a component of overvoltage which has been termed (9, 12, 13) η_2 . It can then be shown that η_2 should be related to current density by the equation

$$-\eta_2 = \frac{RT}{2F} \ln \left(i + \frac{2P.F.k_0}{N} \right) - \frac{RT}{2F} \ln \left(\frac{2P.F.k_0}{N} \right) \quad (7)$$

The experimental measurement of η_2 during cathodisation in the steady state is complicated by the fact that the actual potential, i.e. total apparent overvoltage η , contains additional terms (12, 14). Thus there is an I.R. drop (often written η_R) between the Pd/H cathode and the reference electrode. In addition, even with vigorously stirred solutions there can remain a concentration overvoltage term η_c due (12, 14, 15) to the concentration of hydrogen ions at the electrode surface being limited by diffusion through the Nernst layer.

Once again the large sink of hydrogen in Pd/H proves its experimental value. Following interruption of cathodisation the time dependent change of electrode potential E (now entirely characterised by H/Pd —except for retention of an η_c term at very small times) can be conveniently and accurately measured: this is only approximately logarithmic but linearly time dependent expressions can be derived, by using appropriate

relationships between E , H/Pd and p , and these can be extrapolated back to zero to give reliable values of E during steady state cathodisation, i.e. η_2 . Values of η_2 so obtained (12) have been shown, for both palladised and catalytically active "bright" cathodes, to fit relation 7 very satisfactorily in the range of current densities from zero to ca 50 ma. cm^{-2} confirming that in this range of current densities the magnitude of η_2 is controlled by the diffusion of dissolved molecules. Present evidence suggests that at higher current densities hydrogen evolution by molecular diffusion becomes increasingly supplemented by bubble formation and η_2 then tends to a limiting value (12, 13) as shown in Fig. 2. These more recent results in which resistance and electrode potential measurements have been employed in conjunction appear excellent confirmation of the earlier experiments and conclusions of Knorr and his collaborators (13, 16) who have also presented evidence that relationships complementary to relation 7 apply equally well to the overvoltage at catalytically active platinum electrodes. In principle, the relationships between current density and overvoltage should also be capable of yielding information concerning the kinetics of proton discharge and chemisorbed hydrogen atom recombination (steps 1 and 2 above). It is therefore

unfortunate that there has latterly been a general lack of emphasis accorded to Knorr's work since this clearly indicated the limitations which are generally imposed by diffusion controlled kinetics for obtaining data concerning steps 1 and 2 from overvoltage studies.

Possible Errors in Measurement of R/R_0

In the course of our measurements of electrical resistance in aqueous solutions careful re-examination has been made (8, 10, 12, 17) of the relative magnitude of parallel conduction of the bridge measuring current through the electrolyte, a factor which had been generally underestimated. The proportion of this "co-conduction" through solution is a function not only of the composition of the electrolyte and of the dimensions of the specimen but also of the catalytic activity of its surface; those surfaces of high catalytic activity possessing a lower impedance to current flow. In the course of these experiments and of complementary study of current flow (and of its polarisation) between pairs of Pd/H electrodes, progress has also been made (12, 18) in obtaining quantitative data regarding both the capacitance and resistance components of the total impedance close to the electrode surface. Furthermore,

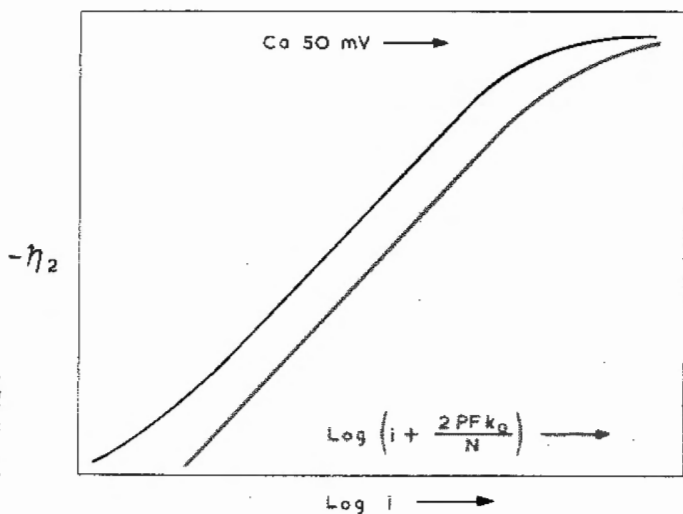


Fig. 2 Relationships between diffusion (or hydride) overvoltage, η_2 , and logarithmic functions of current density i and the rate constant, k_0 , for diffusion of hydrogen molecules to the electrode surface

it has also been found possible to utilise such studies as a further method of obtaining P-C-T data for the hydrides of palladium and also of its alloys (10).

Sources of Error in Electrode Potential Measurements

Palladium electrodes are generally connected to platinum leads, and exposed platinum if catalytically active can attain a zero volt potential in hydrogen saturated solutions (and exhibit analogously differing potentials under alternative experimental conditions) more rapidly than palladium, thus giving rise (7) to a mixed potential which can be varyingly misleading as a measure of H/Pd. In addition, the "local cell" then set up can cause proton transfer from the exposed Pt/H regions of Pd/H regions. However unless comparatively large regions of platinum are exposed, experiments have shown (7, 19) that such a local cell effect should not cause marked errors in the measurement of diffusion controlled kinetics.

The platinum may be shielded from solution by covering the leads and an adjoining small area of palladium with soda glass, which bonds intimately to both metals. The entire specimen may thereafter be readily cleaned by flaming, so that subsequent activation procedures are then more likely to be uniformly effective over the whole surface. Polythene and Teflon have also been widely used (7, 19) to cover the leads but extra care is required with these materials to shield both the platinum, and particularly base metal connections beyond the platinum, from the solution. As against this objection to polythene the expansion of palladium which results from hydrogen absorption may cause fracture of the glass and expose the platinum during an experiment, although using fine wires as specimens both increases the probability of completing an experiment before fracture and decreases the general risk of its occurrence. Although specimens with glass insulated leads may be conveniently re-employed after they have been outgassed and any fractured

glass repaired with a small flame, mixed potential effects, similar in principle to those resulting from exposed platinum, may arise if the diameter of the specimen close to the glass insulation is unduly decreased by oxidation.

The Palladium Bi-electrode

A further feature of palladium, which follows from the rapid rate at which hydrogen can permeate the solid, is its utility in the form of a bi-electrode consisting of a palladium membrane separating two solutions or a gaseous atmosphere and an electrolyte (20, 21). Hydrogen entering at the "absorption" side of the membrane diffuses to, and is released at, the diffusion side. Provided both sides are carefully activated and the stirring of the solution is carefully controlled at both interfaces, the electrode potential at the diffusion side can be controlled from the "absorption" compartment. A valuable synopsis of earlier studies is available in a paper by Frumkin and Aladjalova (9) and there is growing interest (20, 21, 22, 23) in the practical value of the Pd/H electrode in this form. Once again the technical problems (arising from expansion of the membrane on absorption of hydrogen) of sealing the bi-electrode into its container, while preventing electrical connections from contacting the solution, have been tackled in several ways but no method so far suggested is without some disadvantages.

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Platinum Metals in Photographic Emulsions

A STUDY OF THEIR EFFECTS ON SENSITIVITY

During the last few years a considerable increase has been made in the sensitivity of photographic emulsions with little increase in grain size. Some at least of this improvement is due to the use of noble metals as sensitizers and general emulsion improvers.

In the course of a symposium on "The Ultimate Sensitivity in Photography—Today and Tomorrow" organised last year by the Royal Photographic Society, a contribution on this subject was presented by two independent workers in the field, A. Narath and A. Tiilikka, of the Institut für angewandte Photochemie und Filmtechnik, Technische Universität, Berlin. Their paper, now published in *The Journal of Photographic Science*, 1961, **9**, 303-311, describes their investigation by potentiometric methods of reactions between gelatin and the noble metals.

In a review of the literature, the authors point out that although the sensitivity of silver bromide suspensions is increased by the addition of gold, platinum and palladium, much of this is lost in the presence of gelatin and other colloid vehicles, which at present are essential emulsion constituents. This restraining effect is apparently due to interaction in the emulsion between the noble metals and gelatin or its microcomponents, with the result that the metals cannot completely penetrate the adsorbed gelatin layer on the silver halide grains to increase their sensitivity.

In their investigation the authors simulated photographic emulsions, but excluded silver

halides. The reactions were followed potentiometrically using gold, platinum and palladium electrodes and a saturated calomel reference electrode. Concentrated gelatin, polyvinyl alcohol control solutions, gold thiocyanate complex and K_2PtCl_4 and K_2PdCl_4 solutions were used.

The results of the titrations were compared with emulsion sensitising tests, using a simple bromo-iodide emulsion employed in earlier work. This contained 0.088 moles silver and about 25 grammes gelatin in 250 millilitres emulsion at the beginning of digestion. All titrations and emulsion digestions were made at pH 6.

The gelatins giving the greatest sensitivity with silver halides were found to have the strongest reaction with the noble metals, preventing them from sensitising the silver. Platinum and palladium react more strongly than gold, and consequently have a greater restraining effect on sensitivity. The metals also react with many organic sulphur-containing sensitizers and ripening restrainers used in emulsions.

The authors suggest that platinum and palladium (and also iridium and rhodium) might be used to increase emulsion sensitivity and/or contrast, providing that low concentrations of gelatin are used and that the gelatin contains reducing agents, or alternatively that colloid vehicles are used which do not form strong complexes with the platinum metals. They propose to continue their investigation in these directions.

F. E. K.