Semimicro pH electrodes based on palladium–hydrogen system

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As a part of a programme studying the pH and potential variations inside artificial crevices, a number of semimicro pH electrodes based on the palladium–hydrogen system have been developed and characterized. Conventional hydrogen charged wire electrodes have been found to have a life of a few hours only, but by continually charging a palladium membrane from the rear, it has proved possible to prolong the life considerably. With palladium foil activated by anodization and palladization, and charged by contact with 1 atm hydrogen gas, behaviour essentially the same as that of the platinum–hydrogen electrode has been achieved, but without the need to saturate the solution with hydrogen.

INTRODUCTION

Hydrogen diffuses rapidly through palladium, and it has also been observed that large volumes of the gas are taken up by this metal. Hydrogen is absorbed spontaneously from the gas phase until the atomic ratio of hydrogen to palladium approaches a value of ~ 0.6.[1,2] The gradual incorporation of the hydrogen in the lattice involves significant physical changes, including expansion and distortion. Once immersed in solution the hydrogen charged palladium acquires the same potential as a platinized platinum electrode would in the presence of hydrogen. Thus the potential responds to pH changes in the same manner as a platinum–hydrogen electrode, but the solution may be free of added hydrogen gas (although some hydrogen will be introduced into the solution from the palladium). Hoare *et al.*[3] noted that palladium spontaneously absorbed hydrogen from $1 M$ H_2SO_4 solutions stirred with hydrogen at 1 atm pressure, but the process was retarded when the atomic ratio of hydrogen to palladium reached 0.025 ± 0.005. It was also established that the electrode potential of such a palladium–hydrogen alloy was equal to 0.0495 ± 0.005 V with respect to the platinum–hydrogen electrode.[4] Subsequent hydrogen uptake from aqueous solutions, up to a hydrogen/palladium ratio of ~ 0.6, occurred only when the palladium was cathodically polarized. Only when this concentration was reached did the palladium attain the same potentials as the platinum–hydrogen electrode. However, these electrolytically charged alloys were found to lose hydrogen spontaneously on open circuit, and the potential of $+49.5$ mV(NHE) was restored.[5,6] This behaviour has been explained in terms of the formation of a palladium–hydrogen β phase in the alloy at hydrogen/palladium ratios $\gtrsim 0.03$. The hydrogen activity in equilibrium with the $\alpha + \beta$ two phase mixture gives rise to an electrode potential of $+49.5$ mV with respect to platinum–hydrogen, and only when all of the initial α phase has been converted to β will more hydrogen dissolve in the β phase, allowing the hydrogen activity to rise to unity, and bringing the potential of the palladium to the same value as that of the platinum–hydrogen electrode. In the early experiments it was found that the spontaneous uptake of hydrogen from aqueous solutions was limited to saturation of the α phase. However, this has been found to be very sensitive to the surface state of the palladium, and other investigators have achieved unhindered absorption of hydrogen from aqueous solutions to form the β phase.[7,8]

In particular, the purity of the system is apparently very critical, since trace impurities are found to poison the palladium surface, leading to an arrest in the absorption. Flanagan and Lewis[9,10] found better reproducibility of hydrogen uptake and attainment of equilibrium in hydrochloric rather than sulphuric acid solutions. The results are also dependent on the state of activation of the electrode surface. Active palladium electrodes are obtained by palladization or by anodization. Anodization has been carried out at a current density of 40 A m^{-2} in $2 M$ HCl, and after 5 min the surface of the palladium was reported to become blackened and covered with bubbles of oxygen.[9] Palladization, on the other hand, has been performed in $1 M$ HCl solution containing 10 g l^{-1} of palladous chloride.[11,12] A current density of 400–500 A m^{-2} was applied for ~ 10 min to deposit a palladium black coating.

The mechanism of absorption of hydrogen by palladium from aqueous solutions has been proposed[9,13–15] to involve dissolution of the hydrogen gas, adsorption on the surface of the palladium, and finally dissociation into atomic hydrogen and absorption into the metal lattice. It has been proposed by Flanagan, Lewis, and Carson[9,13,14] that the rate limiting step in this process is that of chemisorption of hydrogen on the surface of the palladium, and that this step is readily blocked by other species adsorbed on the palladium.

The merits of the palladium–hydrogen electrode as a pH sensitive electrode have been studied by various workers,[11,12] and a system based on hydrogen charged palladium wire was applied by Lee *et al.*[16] to the study of pH in cavities on carbon steel and stainless steel.

EXPERIMENTAL: CONSTRUCTION OF ELECTRODES

Palladium–hydrogen wire electrode

Palladium wire (99·9% purity and 0·25 mm dia.) was cut to produce 30 mm long sections. Some of these were annealed at 900°C for 2–3 h to relieve stresses induced by the manufacturing process. Each section of palladium wire was soldered at one end to a length of copper wire of similar thickness. After cleaning to remove flux the joint and the bulk of the copper wire were coated with epoxy resin.

The surface of the palladium was activated by anodization in 1·19 M HCl solution. Analytical grade reagents and doubly distilled water were used to prepare this solution, and considerable care was taken to avoid contamination by impurities which might affect the adsorption of dissolved hydrogen on the palladium. A current density of 100 A m^{-2} was used for 30 s for the anodization, following which the wire was rinsed in doubly distilled water.
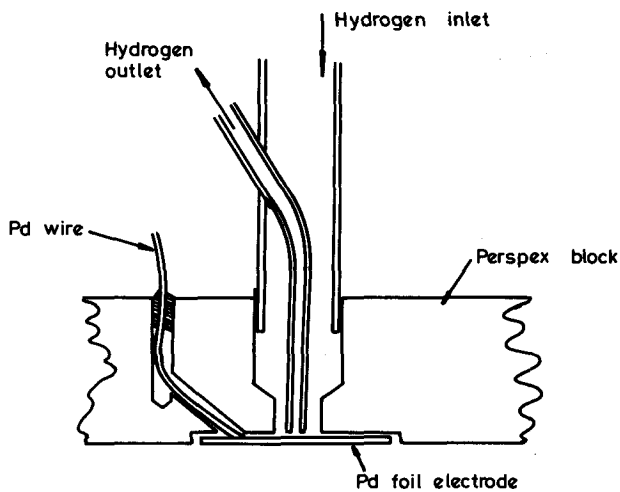
1 *Palladium foil micro pH electrode*
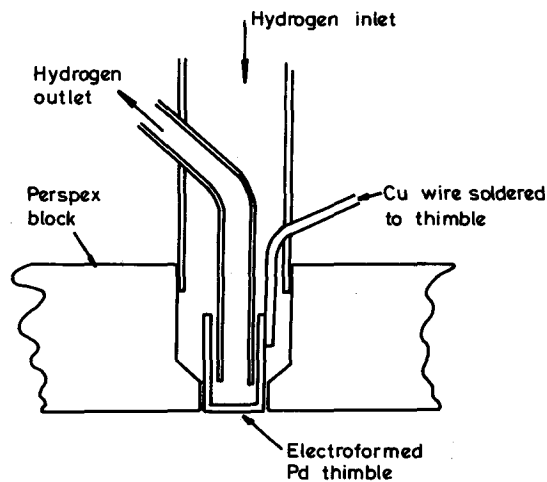
2 *Palladium thimble micro pH electrode*

Two possible methods of hydrogen charging were examined: the spontaneous absorption from solutions which were saturated with hydrogen gas, and cathodic charging. In both cases the electrolyte used was 1.19 M HCl prepared as for the anodization procedure. For the spontaneous absorption each activated wire was exposed for 24 h to solution through which hydrogen gas at 1 atm pressure was bubbled. For the cathodically charged wires the hydrogen bubbling through the solution was replaced by passing a cathodic current of 100 A m^{-2} into the wire for 1–2 h, using a platinum counter electrode.

Palladium foil and thimble electrodes
Because of the relatively short life observed for the hydrogen charged wire electrode, ways were sought of prolonging its life. This has been done for large scale electrodes by the use of palladium foil, and by electrolytically charging the palladium in service. The latter was felt to be difficult to control for semimicro electrodes, and consequently small electrodes based on hydrogen diffusion through thin palladium membranes have been investigated. While the previous work with large diffusion electrodes was based on the generation of hydrogen by electrolytic charging, it was felt to be easier for small electrodes to apply hydrogen to the back of the diffusion membrane in the form of a gas. Two designs of semimicro hydrogen diffusion electrode have been examined (Figs. 1 and 2). These are similar in principle, differing only in the way in which the palladium membrane is formed.

The palladium foil electrode (Fig. 1) was developed to lie flush with the wall of a simulated crevice, and was fabricated simply by punching a 3 mm dia. disc from a piece of 0.025 mm high purity palladium foil. Electrical connection to the disc was obtained by spot welding a 0.25 mm dia. palladium wire to the edge of the disc. The wire was then carefully bent so that it became perpendicular to the foil. The foil was degreased and treated first by anodization for a few seconds in 1 M HCl, then palladized by making it the cathode in a solution of 2–3% palladous chloride in 1 M HCl at a current density of 500–600 A m^{-2} for 2 min. Both faces of the foil became coated with a fine coating of palladium black. The electrodes were rinsed in distilled water for several hours, and then allowed to dry. When dry the assembly was sealed into a machined recess in a Perspex plate using epoxy resin. Great care was necessary to avoid coating the central region of the foil during this procedure.

The second form of hydrogen diffusion electrode was developed for insertion into holes of the order of 1 mm dia. (Fig. 2). It consists of a closed ended tube (or 'thimble') of palladium, the end of which acts as the hydrogen diffusion electrode. This was produced by electroforming palladium on a copper wire, the end of which had been carefully ground flat. The plating solution used consisted of 12 g l^{-1} of diamminodinitritopalladium plus 100 g l^{-1} of ammonium sulphamate, with the pH adjusted to and maintained at 8.3–8.5 by regular additions of ammonia. The wire was plated at a current density of 40 A m^{-2} for 24 h at a temperature of $40°C$. In order to improve the mass transport to the surface of the wire, the latter was mounted in a small stirrer motor and rotated during the plating process. After plating the specimens were rinsed with distilled water, and the copper wire cut just above the palladium plated end, which was ~ 10 mm long. In initial trials it was found that the palladium coating was very brittle after deposition, presumably because it contained a high concentration of dissolved hydrogen, and for subsequent attempts the plated wire was baked for 5 h at $350°C$ to remove the hydrogen and to relieve any internal stress in the deposit. The copper was removed from inside the palladium thimble using concentrated solutions of ammonium persulphate or cupric chloride. The former required very long immersion times (up to 3 weeks) to remove all the copper, but the cupric chloride, while dissolving the copper much more quickly, also caused corrosion of the palladium.

For testing purposes the thimbles were cast into a block of epoxy resin. In order to keep the working face of the electrode free of epoxy, this was coated with a solvent based lacquer (Lacomit) prior to the application of the epoxy. When the epoxy had cured, the block was ground back until the lacquer was exposed. Surplus lacquer was then removed with acetone. The palladium membrane was activated before making pH measurements by brief anodization in 1.19 M HCl solution.

For the calibration of the various types of electrode, a series of buffer solutions with pH values in the range 1–9 was prepared, together with a sample of 1.19 M HCl to provide a solution of pH 0. The potentials adopted by the electrodes were measured in the series of solutions, starting from pH 0 and moving in the alkaline direction. The electrodes were carefully rinsed in distilled water before each measurement.

RESULTS
Palladium–hydrogen wire electrode
The initial potentials adopted by the activated but uncharged palladium wires in 1.19 M HCl were strongly positive (700–800 mV(NHE)). After exposure in the solution saturated with hydrogen the potential fell until a

value of ~60 mV(NHE) was obtained after 3–4 h. The potential then remained unchanged, even after long periods of exposure (up to 24 h) to the hydrogen saturated solution. While the bulk of the measurements were made with respect to saturated calomel reference electrodes, a pair of platinized platinum electrodes were placed in the same cell and confirmed that the palladium wires were adopting a potential 60 mV above that of the platinum–hydrogen electrode. Once the spontaneously charged wires were removed from the hydrogen saturated solution and placed in a buffer solution, the potential remained 60 mV above that of the platinum–hydrogen electrode for about 5 h, after which the potential drifted in the positive direction. This electrode had a standard potential $E°$ of 60 mV(NHE), with a slope (at 20°C) of 58·0 mV/pH unit.

In contrast to the spontaneously charged wires, those which had been charged electrolytically quickly established an open circuit equilibrium potential of 0 ± 1 mV(NHE). However, when the charging was stopped the potential gradually drifted in the positive direction, and stabilized at +60 mV(NHE) after a few hours. Once this stable state had been reached the behaviour was essentially the same as the spontaneously charged wires, except that stable potentials were maintained for rather longer (~10 h) before the potential started to drift further in the positive direction.

For both electrodes it was found that the duration of the stable behaviour was reduced by bubbling nitrogen through the solution, suggesting that the transport of hydrogen away from the palladium surface was the rate controlling step in the depolarization process.

Palladium foil and thimble electrodes

It was found that the response of the electrodes depended critically on the surface treatment they had received before use. In the absence of palladization the electrode potential started to respond within a few minutes of the commencement of the supply of hydrogen to the rear of the foil. However, several hours elapsed before the potential stabilized at around −355 mV(NHE) in pH 7 solution. Thus, even after long exposure the foil was operating in the $\alpha + \beta$ range, rather than being fully saturated with hydrogen at 1 atm pressure. In contrast, the palladized foil rapidly attained an equilibrium potential of −420 mV(NHE) in the same solution. In part this may have been due to the generation of hydrogen during the palladization process, but a more rapid uptake of hydrogen by the palladium black surface must also have been involved for the foil to continue to operate as if fully saturated with hydrogen.

Two prototype foil electrodes were operated in several environments, including 3·5%NaCl solutions of varying pH, and a range of buffer solutions. The long term stability of the electrodes was monitored by recording changes in potential in a buffer solution. The calibration curve obtained by regression analysis of all of the results indicated an $E°$ value of −5 mV(NHE), and a slope of 58·8 mV/pH unit at ~23°C. The electrodes were reasonably stable, the potentials drifting by only ~10 mV over several days, and the original performance could be quickly restored by repeating the anodization and palladization steps. In respect of the palladization process, it was noticed that there was an optimum thickness for the palladium black coating, presumably because the transport of hydrogen to the outer surface of excessively thick coatings starts to become difficult, and other reactions, such as oxygen reduction, start to perturb the measured potential.

In comparison with the foil electrodes, which were very easy to prepare, the palladium thimble was very difficult and time consuming to construct. Despite the annealing of the thimble prior to the dissolution of the copper wire

former, cracks were still observed in all the finished thimbles, presumably arising from cracking of the palladium deposit during the plating operation. It was not certain whether these cracks penetrated the full thickness of the membrane, but the observed potential was ~60 mV more positive than that of the platinum–hydrogen electrode, suggesting that there may have been a film of liquid inside the thimble (although this may alternatively have been due to the difficulty of properly activating the internal surface of the thimble for hydrogen uptake). Despite these difficulties, the palladium thimble electrode is felt to represent a very promising technique for the construction of a robust semimicro pH electrode, and it is believed that a pH sensor of ~0·5 mm dia. could easily be developed, and, with proper attention to the surface activation processes, could measure pH to an accuracy of ~0·1 pH units.

DISCUSSION

The hydrogen charging results indicated that during the spontaneous absorption of hydrogen by the palladium wire electrodes, an arrest in hydrogen uptake was encountered which prevented these electrodes from reaching the same physical state as those produced by cathodic charging. This has also been noted by Hoare *et al.*,[3] and has been attributed to trace impurities poisoning the palladium surface and retarding the $\alpha \rightarrow \beta$ transition. However, this transformation has clearly occurred in part, as is evidenced by the stable potentials measured after charging. The latter are almost certainly due to the action of a two phase $\alpha + \beta$ alloy acting to buffer the hydrogen activity. The depolarization of the electrodes is clearly a direct result of the loss of absorbed hydrogen from the palladium. While spontaneous charging does not appear to succeed in producing a fully β structure (at least for the charging conditions used in this work), electrolytic charging clearly gives a fully β structure containing an excess of dissolved hydrogen. Once charging is stopped hydrogen is gradually lost to the environment, and the potential rises until the hydrogen concentration reaches that at which the α phase starts to form. The $\beta \rightarrow \alpha$ transition then provides a reservoir of hydrogen which results in a plateau in the potential–time relationship. Finally, when all of the β has transformed, the hydrogen in solution in the α gradually diffuses out of the palladium, with the potential rising again in consequence. For reasons which are as yet unknown, the plateau potential (corresponding to the $\alpha \rightleftharpoons \beta$ equilibrium) measured in this work was always in the region of 60 mV(NHE). This is ~10 mV more positive than that which has been reported by earlier workers.

With careful preparation and activation palladium foil electrodes in contact with 1 atm hydrogen behave as if saturated with hydrogen, while less well prepared electrodes (such as the thimbles) operate at the $\alpha + \beta$ plateau. In view of the buffering of the hydrogen activity provided by the $\alpha \rightarrow \beta$ transition, it seems possible that the controlled operation of the foil electrode in this region will provide an even more stable potential. This might be achieved by electrochemically charging at a controlled potential in a solution of known pH (e.g. +60 mV(NHE) in pH 0 solution), or by using a suitable gas mixture (e.g. 10% hydrogen in nitrogen). However, it should be appreciated that either of these options will create potential mass transport problems which do not arise with charging from pure hydrogen gas.

APPLICATIONS

Subsequent to the development work, a number of palladium foil electrodes were employed to monitor the pH inside an artificial crevice.[17,18] These electrodes gave calibration results which lay within ±15 mV of the original calibration line, corresponding to a pH measurement

accuracy of ± 0.25 pH units. It is believed that these errors were largely due to variations in the surface treatment of the foil, and could possibly be reduced by paying particular attention to the construction of the electrode. The use of electrolytic charging on the hydrogen uptake surface, rather than gas phase charging, might also assist in maintaining constant hydrogen activities. However, any hydrogen gas bubbles generated during the charging process might be expected to cause considerable problems in maintaining electrolytic conduction in the very small cell geometry. In addition to this research application of the electrode, a simple version of the palladium wire electrode has been incorporated into a laboratory class which demonstrates the techniques of measurement of electrochemical potential and pH.

REFERENCES

1. D. J. G. IVES and G. J. JANZ: 'Reference electrodes'; 1961, New York, Academic Press.
2. S. SCHULINDER, G. W. CASTELLA, and J. P. HOARE: *J. Chem. Phys.*, 1958, **28**, 16.
3. J. P. HOARE, S. SCHULINDER, and G. W. CASTELLAN: *J. Chem. Phys.*, 1958, **28**, 22.
4. J. P. HOARE and S. SCHULINDER: *J. Phys. Chem.*, 1957, **61**, 399.
5. G. W. CASTELLAN, J. P. HOARE, and S. SCHULINDER: *J. Chem. Phys.*, 1958, **28**, 20.
6. J. P. HOARE: *J. Electrochem. Soc.*, 1960, **107**, 635.
7. R. J. RATCHFORD and G. W. CASTELLAN: *J. Phys. Chem.*, 1958, **62**, 1123.
8. T. B. FLANAGAN and F. A. LEWIS: *J. Chem. Phys.*, 1958, **29**, 1417.
9. T. B. FLANAGAN and F. A. LEWIS: *Trans. Faraday Soc.*, 1959, **55**, 1400.
10. T. B. FLANAGAN and F. A. LEWIS: *Trans. Faraday Soc.*, 1959, **55**, 1409.
11. J. P. SCHWING and L. B. RODGERS: *Anal. Chim. Acta*, 1956, **15**, 379.
12. J. T. STOCK, W. C. PURDY, and T. R. WILLIAMS: *Anal. Chim. Acta*, 1959, **20**, 73.
13. A. W. CARSON, T. B. FLANAGAN, and F. A. LEWIS: *Trans. Faraday Soc.*, 1960, **56**, 363.
14. A. W. CARSON, T. B. FLANAGAN, and F. A. LEWIS: *Trans. Faraday Soc.*, 1960, **56**, 371.
15. R. J. FALLON and G. W. CASTELLAN: *J. Phys. Chem.*, 1960, **64**, 4.
16. Y. H. LEE, Z. TAKEHARA, and S. YOSHIZAWA: *Corros. Sci.*, 1981, **21**, (5), 391.
17. A. ALAVI: PhD thesis, University of Manchester Institute of Science and Technology, Manchester, 1983.
18. A. ALAVI and R. A. COTTIS: in 'Embrittlement by the localized crack environment', (ed. R. P. Gangloff), 75–88; 1984, Warrendale, PA, Metallurgical Society of AIME.