

ELECTROLYTIC HYDROGEN-METAL INTERACTIONS

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ABSTRACT

The electrolyte composition and the electrodic conditions have a major effect on the entry of electrolytic hydrogen into metals. In the case of ferrous metals there is a large body of literature and various promoters have been identified. Only a few inhibitors have been found, such as organic nitriles. This paper reports the complete inhibition of the entry of hydrogen into iron by UPD Zn in concentrated alkali solutions. Less is known about the effect of electrolyte on the entry of hydrogen into palladium. The present work shows that many of the known promoters for ferrous metals actually inhibit the entry and egress of hydrogen from palladium. Permeation results on a Pd membrane in pure 0.1 M NaOH indicate that only 20% of the surface is used for the entry of hydrogen into the metal. In 0.1 M NaOH + 10^{-3} M NaCN it drops to 5%. The fraction of the surface used strongly depends on electrolyte purity. Impurity effects can account for the discrepant results for electrochemical hydrogen loading of Pd.

INTRODUCTION

The effect of the electrolyte and electrodic conditions on the entry of hydrogen into palladium and ferrous metals is the subject of an extensive literature and several reviews (1-4). As early as the mid thirties, several groups working on the entry of hydrogen from the gas phase realized the relevance of adsorption and surface coverage to the kinetics of the entry of hydrogen into metals (5-7). Also around the same time, Kobosev and Montblanova (8-9) deduced the relationship between the energetics of adsorption and the ingress of hydrogen into the metal. The energetics of the entry of hydrogen into metals from the gas phase has been treated, more recently, by Pick and Sonnenberg (10).

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It was only in the sixties that many of these important concepts were developed and applied, by Bockris and his co-workers, to the entry of electrolytic hydrogen into metals (11-13). The delay in application of these concepts to the entry of hydrogen into metals was caused mainly by the slow development and acceptance of the concepts electrode kinetics. Another contributor was the two conflicting kinetic models have been proposed for the entry of electrolytic hydrogen into metals. One view of the entry of electrolytic hydrogen into metals is that hydrogen enters the metal in the same elementary act in which it is discharged, and the intermediate state through which hydrogen enters the metal lattice is not the same as the adsorbed intermediate which leads to the evolution of molecular hydrogen (1, 14, 15). The other view is that the electrolytic hydrogen on entering the metal must go through an adsorbed state which is identical to the intermediate that leads to hydrogen evolution (12). The only experimental work that supports the first mechanism is the work of Palczewska on the entry of hydrogen into nickel from gas phase in the presence of a radio-frequency hydrogen plasma (16). From the effects of applied electric field on the plasma it was concluded that H^+ ions, not H atoms, entered the metal. The current and the potential dependence of the entry of hydrogen into iron agrees with second mechanism. Also the analysis of Pumphrey (17) of permeation transients has shown that the boundary condition at the input side is one of constant surface coverage rather than surface concentration. Furthermore he deduced that the flux entering the metal is limited by the finite rate constants for the transfer of hydrogen between the adsorbed and absorbed states. There is general agreement that in the gas phase hydrogen goes through an adsorbed intermediate and that the hydrogen coverage is an important parameter in the kinetics of the entry of hydrogen into the metal. More recently the work of Graham and his co-workers, using analysis potentiostatic desorption current transients, confirmed that this is true in the case of iron in pure H_2SO_4 electrolyte (18). In this case about 2% of the discharged hydrogen enters the metal. The remainder is evolved as hydrogen gas. In electrolytes containing promoters such as H_2S as much as 25% of the discharged hydrogen can enter the metal. In this case the current transients indicated that the process was controlled by diffusion in the metal and not interfacial processes. The earlier work of Bockris and co-workers has shown that high concentrations of hydrogen in iron can damage the metal and affect diffusion measurements (19). So any conclusions from current transients obtained under such conditions have to be treated with care. At present it can be concluded that surface coverage and interfacial processes are important in

determining the ingress of electrolytic hydrogen into metals.

It is well known that additions of S^{2-} to acids and CN^- to alkaline electrolytes promote the entry of hydrogen into ferrous metals. The early work on the effect of anions on the entry of hydrogen into palladium has been reviewed (1). Recent work indicates that the effect of the electrolyte is different for ferrous metals and palladium (20). In this paper these differences are reviewed and new results are presented on the effect of the electrolyte on the entry of hydrogen into palladium and the effect of UPD Zn on the entry of hydrogen into iron.

EXPERIMENTAL

The effect of electrolyte on the entry of hydrogen into palladium was investigated by cyclic voltammetry and permeation methods. Permeation methods were used to study electrolyte effects on the entry of hydrogen into iron. Details of the experimental methods are given elsewhere (19, 20). Permeation measurements were made using the bi-electrode coulometric technique of Devanathan and Stachurski (11). The cell is shown in Fig. 1. The electrolyte on the diffusion side of the membrane was 0.1 M NaOH. The potential on the diffusion side was held at -0.5 V vs. Hg/HgO.

RESULTS AND DISCUSSION

Effect of Electrolyte

The interaction of electrolytic hydrogen with palladium in pure electrolytes is illustrated by the cyclic voltammograms for 0.1 M NaOH that are shown in Fig. 2. The general features of the voltammogram that extends into the hydrogen region is very similar to that reported for 0.3 M NaClO₄ (21). Arresting the potential at -1.0 V for 5 s greatly increases the hydrogen desorption current. In all cases complete desorption of the hydrogen occurred before the onset of oxide formation at -0.3 V.

Most of the common electrolyte additives that are known to promote the entry of hydrogen into ferrous metals actually inhibit the entry of hydrogen into palladium. This effect can be seen in Fig. 3 which shows cyclic voltammograms for 0.1 M NaOH + 10^{-3} M NaCN. Results in the oxide region show that the oxide formation process is

inhibited by CN^- . There was no indication of Pd dissolution. In the hydrogen region the absorption process is greatly inhibited. The major effect, however, is on the hydrogen desorption process. Most of the hydrogen appears to be desorbed in a narrow potential region around 0.05 V. This is more clearly seen after the potential arrest at -1.0 V. Similar, though less striking, effects were observed for 5×10^{-5} M additions of TeO_2 , As_2O_3 and Na_2S to 0.1 M NaOH. In the case of ferrous metals all of these additives promote the entry of hydrogen into the metal.

A major problem in the control of hydrogen embrittlement of steel during pickling or electroplating operations is that there is the lack of inhibitors for hydrogen ingress to the metal. Till now the only reported inhibitors were organic nitriles (12). Dražić and Vorkapić have reported that the addition of zinc ions to the electrolyte inhibits the hydrogen evolution reaction on iron (22). They speculated that the effect may be due to underpotential deposition of zinc on the metal. In the present study the UPD process and the entry of hydrogen into iron was investigated in pure KOH and zincate electrolyte. In dilute solutions of KOH and zincate no UPD process could be observed. This may be due to the high hydrogen evolution currents in these electrolytes. However in concentrated electrolyte (8.4 M KOH + 0.74 M ZnO) a clear UPD pattern could be seen in the voltammogram shown in Fig. 4. Figure 5 shows the effect of zincate on the hydrogen evolution reaction and on the permeation rate through a 1.0 mm iron membrane. In pure KOH the Tafel slope is $2RT/F$ and the corresponding variation of the permeation current is $4RT/F$. In the zincate containing electrolyte the inhibition of the hydrogen evolution reaction can be clearly seen. There is some hysteresis, depending on whether the measurements are made with increasing or decreasing overvoltage. The most striking feature, though, is the complete inhibition of hydrogen permeation by the UPD zinc. The fact that the UPD process can only be observed in concentrated electrolytes may be due to a chemisorption process, prior to UPD, that does not involve a net Faradaic current. Recent electrochemical quartz balance studies of UPD of Pb indicate that such processes can indeed occur (23). There is always the trivial explanation that the effect is due to some impurity in the zinc oxide. However, it is too much of a coincidence that the observed underpotential shift is about that expected for zinc on iron.

Uniformity of the Surface Process

Figure 9 shows plots of the cathodic current and the permeation current for a 0.025 mm Pd membrane in pure NaOH, and in alkaline cyanide electrolyte. Over most of the hydrogen adsorption region the currents balance. In other words, all discharged hydrogen permeates through the membrane and arrives at the other side. There are deviations from current balance at extreme negative and positive potentials. The deviations can be caused by the occurrence of a parasitic cathodic process (e.g. oxygen reduction), hydrogen evolution, hydride formation or hydrogen trapping in the metal. The deviation from current balance at low currents can be ascribed to either the occurrence of another cathodic process such as oxygen reduction or to hydrogen trapping in the metal. Trapping is the more plausible explanation. The calculated C_0 ($C_0 = H$ concentration on input side) for the convergence of the cathodic and permeation current indicate that the traps can hold about 5×10^{-6} g-atom of H/cm³ of Pd. The divergence in the cathodic current at higher potentials is due to a combination of hydrogen evolution and formation of the β -phase. The formation of the β -phase is associated with slow permeation decay transients. These slow decay transients, obtained at negative potentials, indicate a process governed by decomposition of the β -phase rather than diffusion. These are characterized by an initial very slow decay followed by a faster decay process. The time for completion of the slow process depends on the cathodic potential and the time of polarization. The slow process corresponds to hydride decomposition and the fast process is completion of the diffusion process. The calculated C_0 at which the slow decay transients were observed in pure NaOH was about five times lower than the terminal solubility of the α -phase. In 0.1 M NaOH + 10^{-3} M NaCN it was about twenty times lower. A possible explanation is that certain regions of the α -phase transform to the hydride more readily than others (24). This also strongly suggests that only a fraction of the surface is used for the entry of hydrogen into the metal. If this is true then only 20% of the surface is used in pure NaOH and a mere 5% is used in the cyanide containing electrolytes. The recent electron microscopy results of Rolison support this hypothesis (25). These results indicate that the fraction of the surface used for the ingress of hydrogen into palladium depends on the purity of the electrolyte. Apart from electrolyte effects metallurgical effects may also be involved, which could account for the low surface utilization in the pure electrolyte. All these effects could be a contributing factors in the lack of reproducibility of the Pons-Fleischman effect.

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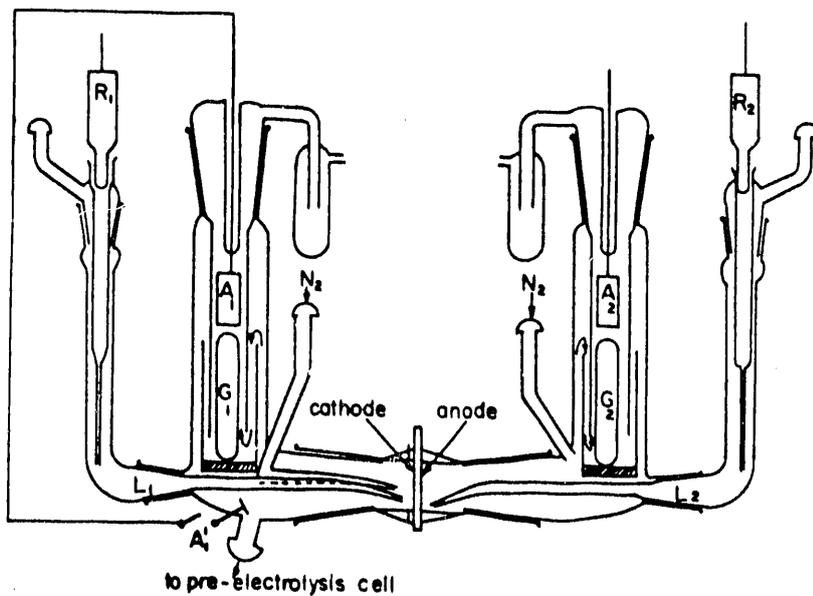


Fig. 1. Cell for permeation measurements (11).

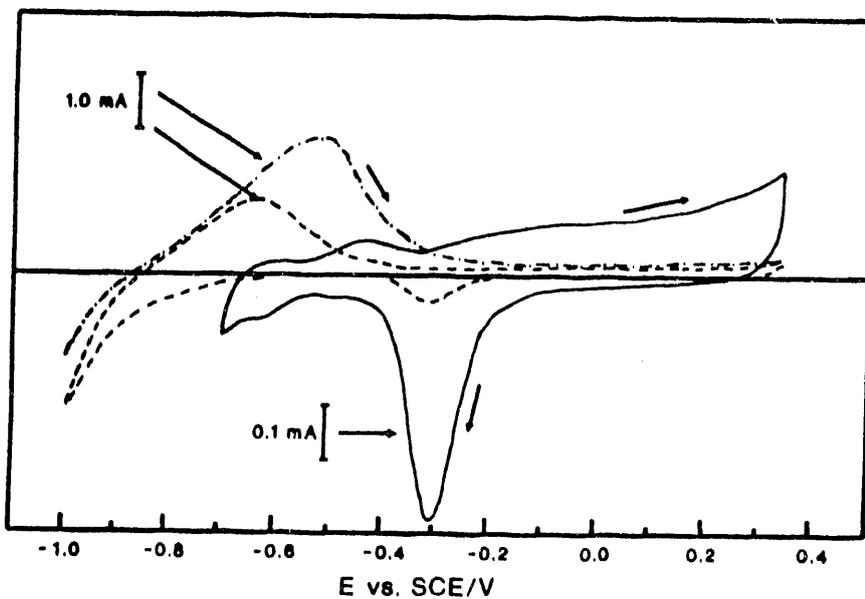


Fig. 2. Cyclic voltammograms on Pd in 0.1 M NaOH; voltammogram in oxide region (—), after extension to hydrogen absorption region (- - -) and anodic sweep after a potential arrest of 5 s at -1.0 V (-·-·-). Sweep rate 50 mV/s. Electrode area 2 cm².

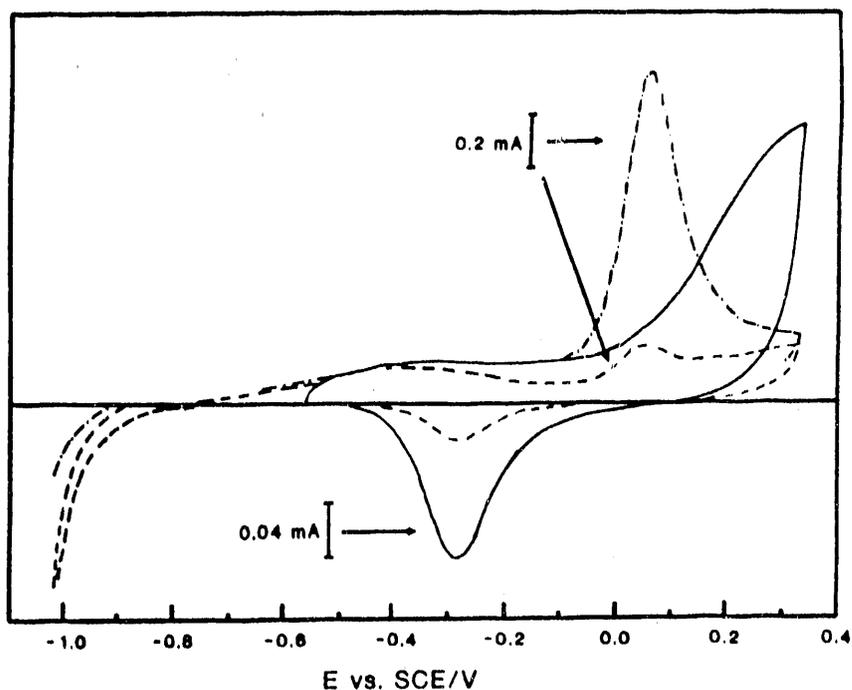


Fig. 3. Cyclic voltammograms on Pd in 0.1 M NaOH + 10^{-3} M NaCN; voltammogram in oxide region (—), after extension to hydrogen absorption region (---), and anodic sweep after potential arrest at -1.0 V for 5 s (-·-·-). Sweep rate 50 mV/s. Electrode area 2 cm².

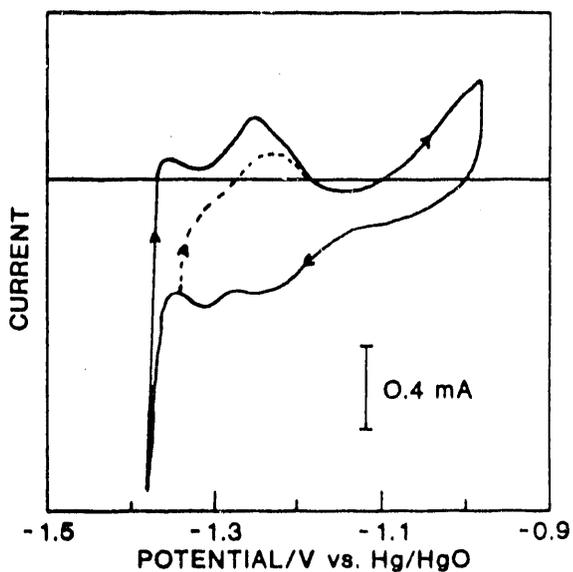


Fig. 4 Cyclic voltammogram for an iron electrode in 8.4 M KOH + 0.74 M ZnO, electrode area = 2 cm², sweep rate = 50 mV/s.

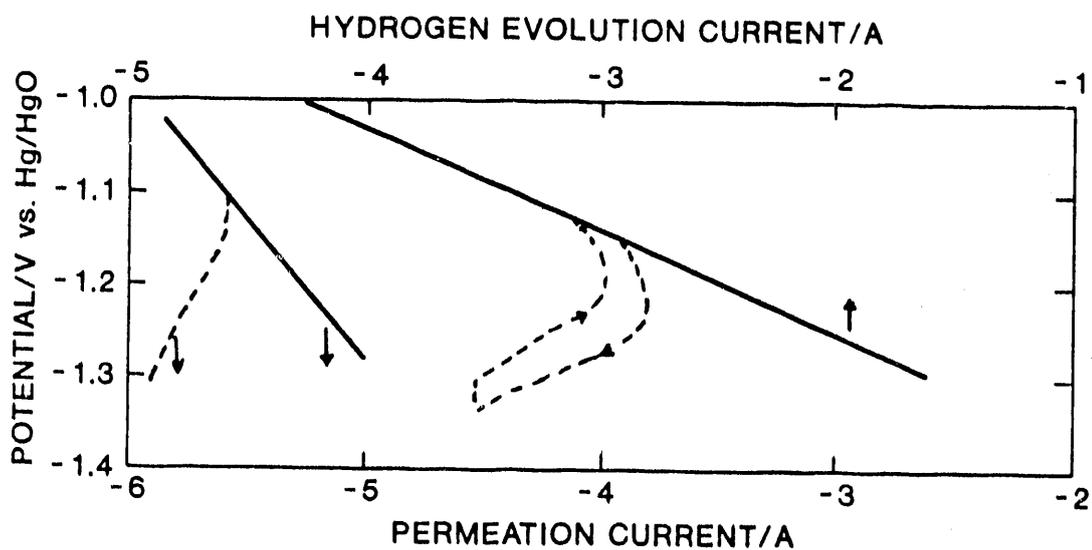


Fig. 5 Tafel and permeation current plots for an iron membrane. Solid lines shows data for 8.4 M KOH, broken lines show data for 8.4 M KOH + 0.74 M ZnO. Electrode area = 1.26 cm².

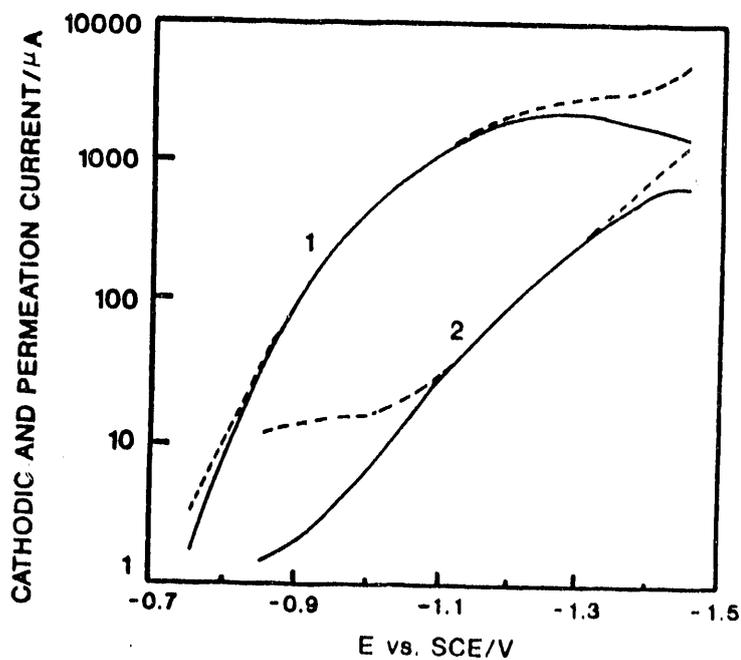


Fig. 6. A comparison of the cathodic current (---) and the permeation current (—) for various potential steps in (1) 0.1 M NaOH and (2) 0.1 M NaOH + 10⁻³ M NaCN. Working electrode area was 1.26 cm². Membrane thickness = 0.025 mm.

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