

THE METAL HYDROGEN SYSTEM: INTERPHASE PARTICIPATION IN H-TRANSPORT

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ABSTRACT

The metal/hydrogen system is a key element in the construction of ecologically preferred energy conversion/storage devices. Although reduced to practice decades ago, its effectiveness requires further examination of a number of issues, among them the role that the electrode/electrolyte interphase plays during the charging/discharging processes. In this communication the following topics are considered: Thermodynamics and kinetics of the structure of the interphase, the identity and components of the driving force(s) for the absorption/desorption of hydrogen, and the discussion of the applicable transport equation. Agreement between theoretical results and observed behavior is illustrated and selected design approaches affecting cell performance are explored.

INTRODUCTION

With an increased awareness of the environment and how human activities impact the ecosystem, current trends in the development of energy storage systems are to employ more environmentally compatible materials. In particular, recent years have witnessed increased interest and activity in the development of a hydrogen economy, with particular emphasis on using hydrogen as the fuel in energy generating devices, eg, hydrogen/oxygen fuel cells or, more pertinent to this communication, as a component in the negative electrode of the metal/hydrogen (Me/H) rechargeable battery systems.

Although the first intermetallic hydride was developed 30 years ago and despite construction of the first prototype metal hydrogen electrode 20 years ago, Me/H electrodes experience many shortcomings, viz., high cost of alloys, poor hydrogen storage capabilities, difficult activation, pyrophoricity, problems of impurities, thermodynamic instabilities and corrosion in alkaline media. Recent results derived from efforts to address these shortcomings have led to the conclusion that an interphase is an important factor maximizing the cell performance. (Ohnishi et al, 1993; Ciureanu et al, 1993).

In this communication we examine the dynamics of the interphase region as it relates to the performance of Me/H cells. To accomplish this goal, we review the concepts and characteristic features of the Me/H system under nonequilibrium conditions using the Pd/H system as a model.

ME/H SYSTEM: STRUCTURE OF THE INTERPHASE

An interphase region is formed whenever an electrode is in contact with an electrolyte. In the simplest case, the interphase region takes the form of the electrical double layer. In reality, whenever an electrode is in contact with electrolyte, a multilayer interphase region is formed (Defay et al. 1951). This is a non-autonomous region, ie, a region whose properties are affected by the contacting phases. A further important feature of the structure of the interphase is that it is modified by participating processes (van Rysselberghe, 1966).

The origin of surface tension on metals is attributed to auto-diffusion of atoms from the surface to the bulk resulting in lattice contraction of the surface atoms, changes in spacing between atomic layers and polarization effects (Defay et al, 1951). The simplest model of the Pd/H interphase is illustrated in Fig. 1a (Schlapbach, 1991). Here, the Pd surface is in contact with gaseous hydrogen. Following the dissociative adsorption, the Pd surface undergoes a reconstruction process to accommodate adsorbed hydrogen and a redistribution of adsorption sites (Protopopoff and Marcus, 1991). As the concentration of adsorbed hydrogen increases, the physically adsorbed hydrogen penetrates the surface and occupies sites underneath the first atomic layer. This chemisorbed hydrogen promotes a strong surface reconstruction.

When the Pd electrode is in contact with an aqueous electrolyte, a new situation arises. The inclusion of electrolyte modifies the interphase by adding a complex structure on the solution side. In this new situation, hydrogen is brought to the surface by charge transfer reaction and split into two streams: one entering the metal lattice, the other escaping as gaseous hydrogen. The resulting interphase structure is illustrated in Fig. 1b. According to this model, cathodic polarization produces weakly adsorbed hydrogen which is transferred into the Pd lattice by a twostep process: (i) hydrogen entering the interphase $H(a) \rightarrow H(\lambda^*)$ and (ii) transiting into the bulk electrode, $H(\lambda^*) \rightarrow H(b)$. Briefly, in this model, a palladium/electrolyte interphase consists of two sharply defined regions with discontinuous physico-chemical properties (Bucur and Bota, 1983). However, there exists a common adsorption surface in contact with, and affected by, homogeneous solid and liquid phases. This concept was further extended by emphasizing its non-autonomous character (Szpak et al. 1992). In particular, they defined a transfer zone $\lambda^* = \lambda_s + \lambda_e$, where λ_s and λ_e denote those segments of the solid and electrolyte phase that actively participate in, and/or dominate, the transport of hydrogen between the latter, Fig. 1c (Szpak et al. 1994). By splitting the interphase into several distinct layers, it is possible to identify processes that control the transport of hydrogen during the potential sweep and to examine the effect of electrolyte composition and electrode surface morphology on that transport. These observations lead to tentative conclusions that the structure and properties of the λ^* part of the interphase are potential dependent. Also, it is apparent from the behavior of the current/potential (j/η) curves generated by slow scan voltammetry that the interphase region contains positively charged species, perhaps the $[H...H]^+$ complex proposed by Horiuti and subject of a spirited discussion between Horiuti and Bockris (Horiuti, 1961). Curiously, there is a degree of similarity with the solid/gas system where three energetically different states of hydrogen exist (Auer and Grabke, 1974).

DYNAMICS OF THE INTERPHASE

The question that arises naturally: Is the interphase an active element in the course of hydrogen transport across it? The answer is yes. Furthermore, if an analogy to the behavior of a thoroughly investigated liquid/liquid interphase can be invoked, then the review of the latter would be helpful in guiding the discussion concerning the dynamics of hydrogen transport. The use of this analogy seems natural inasmuch as the solid/liquid interphase is also a system under tension as indicated by, eg, the lattice contraction/extension following adsorption (Lennard-Jones and Dent, 1928). The evidence indicates that, in all systems the dynamic character of the interphase is driven by the energetics associated with the transport itself.

Taking as a common starting point that a surface separating two phases can be visualized as a membrane in tension or compression, we can examine its behavior under any prescribed set of events. For example, at low concentration of transported species, the rate of transport in liquid/liquid systems varies with time in a manner resembling a pumping action of the interphase (Szpak, 1961). This action clearly identifies the interfacial region as a separate phase and indicates that time-dependent driving forces act upon the transported species. As the concentration of the material at the interphase

increases, the pumping action is often transformed into violent eruptions (Nassenstein and Kraus, 1956). Violent eruptions are associated with rapid release of stored energy, again identifying the interphase as a kind of interfacial engine, a term coined by Sternling and Scriven (1959) while discussing instabilities arising from small temperature or concentration fluctuations accompanying the transport of a substance between two immiscible phases. Clearly, the interphase region constitutes an active element whose activity can be modified by a number of factors, all being the manifestation of changes in the energy content of the interphase.

HYDROGEN SORPTION IN ELECTROCHEMICAL SYSTEMS

The examination of the role of the interphase is facilitated by an experimental arrangement where the surface to volume ratio is maximized, as illustrated in Fig. 2, and where the effect of surface morphology is clearly displayed. This requirement can be satisfied by employing palladium black (Chevillot et al. 1975) or by a codeposition process whereby palladium is electroplated from aqueous solution in the presence of evolving hydrogen (Szpak et al. 1992).

The interphase dynamics is particularly well displayed by slow scan voltammetry of the codeposition process. During the charge transfer the interphase region is an open system in which a number of consecutive processes takes place. These processes include transport of the reactants from the bulk to the electrode surface by diffusion, adsorption on the electrode surface, charge transfer and desorption of the reaction products followed by transport of reaction products away from the electrode surface. In a discharging battery, the same processes occur; however, in a battery the electrons ultimately flow into an external circuit where the electrical work is delivered. The dynamics of the codeposition process is best discussed by considering Fig. 3 which is the schematic representation of the superposition of the j_n/η ; $n = 1, 2$ relation of partial currents upon a portion of a Pourbaix diagram indicating thermodynamic stability of water. The driving force for each partial charge transfer reaction is given by $(\Delta\Phi - \Delta\Phi_{0,n})$ where $\Delta\Phi$ is the Galvani potential difference and $\Delta\Phi_{0,n}$'s are the respective equilibrium potentials. Here, we assume independent charge transfer reactions and ignore the small shift in the Galvani potential difference associated with the alloy formation (Gorbunova and Polukarov, 1967).

A detailed picture of the dynamics of the interphase during the codeposition is presented in Fig. 4, where the dominant fluxes consistent with the voltammogram shape are indicated. At equilibrium, the composition of the interphase is such as to maintain equality of chemical potentials resulting in no net flux across all segments of the interphase. However, as soon as the electrode is polarized, the composition of the interphase changes, as indicated by the magnitude and direction of transported species, solid arrows for the $\text{Pd}^{2+} + 2e^- \rightarrow \text{Pd}$ reaction, and open arrows for the hydrogen flux. The electrodeposition of metallic palladium at the diffusion limited rate occurs throughout the potential span investigated, cf. Fig. 3. In particular, upon initiation of the cathodic sweep, Fig. 4 segment 1, only the reduction of Pd^{2+} ions occurs. Within this potential range, only the hydrogen present in the bulk electrode can enter the interphase region, specifically the λ_s part of the interphase. The situation changes abruptly at point D where the hydrogen sorption is rapid. At this point a significant increase in cathodic current is observed which is attributed to the high activity of the freshly prepared Pd layer arising, most likely, from surface restructuring and the creation of new adsorption sites. At more negative potentials, Fig. 4, segment 3, sorption into the freshly formed palladium layer is fast while slower transport by diffusion into the bulk initiates the formation of a resistive (supercharged) layer, I^* . A direct consequence of the simultaneous rapid accumulation of sorbed hydrogen in the λ_s -layer and the deposition of metallic Pd is the formation of thin layer, I^* , having a high H/Pd ratio. This layer becomes part of the bulk electrode and represents a barrier for H transport due to the strong dependence of the diffusion coefficient on the H/Pd atomic ratio. As the cathodic polarization is

increased, the resistive layer increases the hydrogen concentration in the interphase to the point where the Tafel recombination is the dominant reaction, Fig.4, segment 4.

Upon scan reversal the interphase behaves as follows: Immediately after scan reversal, Fig. 4 segment 5, the partial current j_2 becomes less while j_1 remains at its limiting value. This change in ratio results in thinning of the supercharged region. With further increase in the electrode potential, the cathodic current becomes less than $j_{1,lim}$ indicating reversal of j_2 due to the oxidation of the weakly adsorbed hydrogen, Fig. 4 segment 6, followed by the oxidation of strongly adsorbed hydrogen, Fig. 4 segment 7.

The slow scan voltammetry indicates that the oxidation of weakly and strongly adsorbed species is independent of each other which means that the transition between these species is slow and that hydrogen diffusion into the bulk electrode occurs after a complete saturation of the surface. Structurally, this means that the interaction of screened protons modifies the potential field near metallic ions, and the repelling action tends to dilate the crystal structure. To a first approximation, this effect is proportional to the coefficient of compressibility of the metal. The dilation of structure propagates in the whole volume of palladium beginning at the surface (Chevillot et al. 1975).

TRANSPORT IN BULK PHASES

Because of the non-autonomous character of the interphase, its activity cannot be separated from activities of the contacting phases. Here, the effect of transport in the electrolyte phase is of lesser interest for two reasons: (i) The concentration of reactant (H_2O molecules) generating hydrogen on the electrode surface is sufficiently high so that mass transport is irrelevant and (ii) the hydrogen surface coverage is controlled by charge transfer kinetics. However, the effect of surface active additives affecting the kinetics of adsorption must be included. On the other hand, transport of absorbed hydrogen as well as the components of the driving force acting within the bulk electrode, are of considerable interest. Thus, a detailed examination of the driving forces operating within the bulk electrode is essential.

To assist in the analysis of the mutual interaction between the interphase and the bulk, we first review the structural aspects of the solid phase. In general, defects in metals that affect hydrogen transport are: point defects, solute defect complexes, dislocations and internal boundaries and isolated metal clusters. The simplest point defect is the vacancy, ie, an empty lattice space. A strong interaction (attraction) exists between the interstitial hydrogen and the open-volume character of the defect, that is, the interstitial hydrogen is driven into the vacancy by the presence of the open-volume. The binding energy is similar to that of chemisorbed hydrogen.

The interaction of hydrogen with solute and solute-defect complexes is weaker than with vacancies. The strength of interaction is influenced by elastic distortion and by electronic differences in H-bonding between the host and impurity atoms. The open-volume effects produced by the lattice strain are less than those generated by vacancies thus resulting in weaker interactions. As the H atom approaches the dislocation, the binding energy changes. Mobility of interstitial H atoms is reduced by attractive interactions with dislocations. The interaction between internal boundaries and interstitial hydrogen are of special interest. In fully metallic boundaries, the binding energies are much less than for vacancy trapping. The smallness of interaction is related to the absence of open-volume defects on these boundaries. However, if the boundary contains a non-metallic phase which tends to form a covalent bond to the H atom, the situation is different; the binding energy is substantially higher. In addition, the boundary plays another role: it provides paths for accelerated diffusion. The accelerated diffusion is ascribed to a reduced vacancy formation in the excess volume of the boundary. Note that

the diffusion of interstitial H does not depend on vacancies; thus, the acceleration of diffusion may be related to the reduction of saddle-point energies at the boundaries. The acceleration of diffusion at higher concentration may be due to saturation of deep trapping. There is an indication that small metal clusters (on the order of 40 atoms) can trap as many as eight H atoms per metal atom. For clusters containing more than 40 atoms, the behavior is that of metallic phase (Cox et al. 1990).

MODELING

From a practical point of view two factors are of interest while designing a Me/H system, viz., the amount of stored hydrogen and the rate at which it can be moved between phases. In general, when modeling a charging/discharging cell, one must take into account the material balance, Faraday's law, Ohm's law and the polarization equation (Szpak, 1991). When modeling the Me/H system, we also have to include the effect of the interphase and hydrogen transport between, and within, particles making up the porous structure of the Me/H electrode. The latter effect will be described by the form of the auxiliary equations.

The development of a general model is not a trivial undertaking since charging/discharging of a metal hydride is a very complicated process. To illustrate, we consider the electrochemical charging of Pd rods, recently a topic of considerable interest. A model has been developed that incorporates the essential features of these processes and involves variables such as the electrochemical rate constants, the bulk diffusion coefficient and the charging current (Szpak et al. 1991). This simplified model predicts rather well the experimentally observed behavior of the charging of the palladium rods (Riley et al. 1992). The data show a number of characteristic features during charging, among them (i) the existence of an apparent threshold value for the cathodic current density; (ii) a slower rate for "unloading" than for "loading" the bulk electrode; and (iii) an initial charging rate that depends, for the most part, inversely on the radius of the Pd electrode. These features, in turn, imply the following: (i) cell current density controls the mode of charging/discharging; (ii) directional transport across the interphase—an unlikely situation for a passive interphase and diffusion control; and (iii) importance of geometrical considerations.

The difference in the loading and unloading rates and the incompleteness of unloading provide additional evidence for active participation of the interphase. The observed asymmetry is inconsistent with the linear-diffusion model because such a model would be analogous to ordinary diffusion with constant initial bulk concentration. Evidently, there exists a mechanism(s) that causes the adsorbed hydrogen to affect the loading and unloading rates differently. If we assign an active role to the interphase then a mechanism suggested by the slow scan voltammetry is provided. In particular, the force driving hydrogen across the interphase contains a contribution due to the electrode overpotential, affecting the λ_e layer, as well as contributions involving the electronic and mechanical interactions, influencing the λ_s part. Upon current reversal, the magnitude of the driving force is different and the asymmetry follows naturally. The transition between the diffusion and surface control, accounting for the observed difference in the mode of charging/discharging, occurs within the practical range of current densities.

Electrochemical charging of Pd electrodes involves coupling of interfacial processes with transport of interstitials in the electrode interior. Obviously, boundary conditions arise from the solution of equations governing the elementary adsorption-desorption and adsorption-absorption steps and the symmetry of the electrode. The active participation of the interphase manifests itself as inhomogeneous changes in surface morphology during prolonged exposure to evolving hydrogen. One way to demonstrate the inhomogeneity of the surface, particularly with respect to absorption, is to view the surface using Nomarski optics (Szpak et al. 1991). Such an inhomogeneity can be viewed as time

dependent boundary conditions and, if combined with the concentration dependent diffusion coefficient, may lead to the formation of space structures (metastable regions) localized near the surface (Samgin et al. 1992).

A more complete model would include: conservation of energy from which the temperature distribution is determined; and recognition that the interphase constitutes an active, non-autonomous element in the transport of hydrogen. Thus, the Me/H model will have to include the effects of a changing interphase as well as the effects of electrode matrix and grain boundaries. The electrode matrix refers to the porous electrode structure while the grain boundaries refer to the metallurgical aspects within individual particles. The appropriate equations would have to be formulated to include coupling of the electrode–electrolyte processes within a multiphase environment while the transport within the individual particles would have to consider the presence of grain boundaries (Zeschmar, 1983).

CLOSING REMARKS

Models are used both, to simulate a complex reality by simpler arrangements and to display essential features of a physical system. Often, a simple model clarifies the interpretation of ambiguous data and avoids lengthy calculations that might be irrelevant to the problem being examined. We have applied a model where the structure of the interphase, as well as the operating driving forces, are determined by participating processes occurring in both contacting phases. We have treated the interphase as a passive element by assuming that the surface is homogeneous with respect to the chemical potential. Such an assumption is not realistic although it might be justified on the basis of the existence of the supercharged layer, I^* . Even so, this relatively simple model does remarkably well in predicting a saturation of the initial charging rate as well as the time required to obtain a full charge. Although this model predicts some small asymmetry in loading and unloading, it does not predict the magnitude of the asymmetry and it cannot account for the incomplete electrode unloading. Evidently, a more comprehensive model must be formulated that would provide mechanisms for asymmetric loading/unloading and to specify conditions leading to reproducible charging/discharging.

A final remark: The fundamental characteristics of the Me/H system are (i) uniqueness in electronic structure; (ii) binding sites of H atoms and their relationship to binding energy; (iii) sensitivity of interactions to cluster size; (iv) the question whether the most active sites are in an excited state or in the ground state. The Pd/H system is a system with strong proton lattice coupling and weak H-H repulsive forces.

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FIGURE CAPTIONS

Fig. 1 - Concepts of the metal/hydrogen(water) interphase

Fig. 1a - The Pd/H₂(g) system. A simplified model of the Pd/H₂(g) interphase and associated processes: (i) dissociation of molecular hydrogen and solution of H atoms in the bulk on the interstitial sites (after Schlapbach, 1991)

Fig. 1b - The Pd/H₂O system. A model illustrating partial steps of the overall H⁺/H redox reaction and H absorption (after Bucur and Bota, 1983)

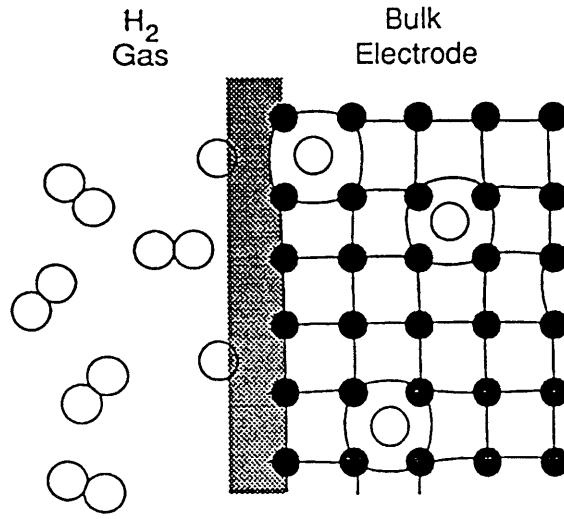
Fig. 1c - The Pd/H₂O system. A model illustrating the complexity of the interphase; a - adsorption layer; t - charge transfer layer; e - surface dividing the interphase and the bulk electrode; l - lattice; j - total cell current; H • H - Heyrovsky-Horiuti path; T - Tafel path; V - Volmer path; j₄ and j₋₄ - adsorbed/absorbed exchange fluxes; λ* - non- autonomous interphase region (after Szpak et al. 1994)

Fig. 2 - Scanning electron micrographs of palladium surface and corresponding voltammograms on smooth and palladized surfaces.

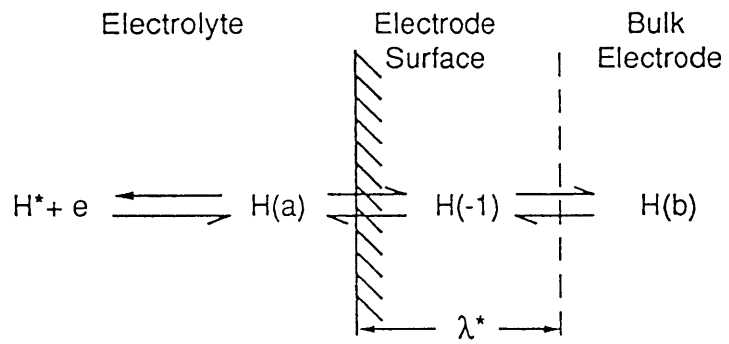
Fig. 3 - Representation of processes associated with Pd-H codeposition. Potential scan range and partial currents are superimposed on the Pourbaix diagram for the H₂O – H₂ system. (j_{1,lim} refers to the rate of Pd²⁺ ion reduction and j₂ is a measure of H₂ generation (after Szpak et al. 1994)

Fig. 4 - Dynamics of the Pd/H₂O interphase. Fluxes and their magnitude within regions defined in voltammogram.

a



b



c

