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Non-ideal absorption effects on hydrogen permeation through palladium–silver alloy membranes

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ABSTRACT

Current theoretical models for the permeation behavior of hydrogen through palladium and palladium alloys predict that low temperature operation of thin membranes will result in permeation which is no longer controlled by the diffusion of hydrogen through the metal lattice. Specifically, the process of desorption from the downstream surface is predicted to become the dominant resistance to mass transfer. However, these models neglect the non-ideal absorption behavior of hydrogen in palladium which typically occurs at temperatures below 300 °C. In this work a model is developed which accounts for the non-ideal behavior of hydrogen in palladium–silver alloys (25% silver by weight) which are typically used for hydrogen purification. This model predicts that the diffusion-limited regime should be characterized by an increase in the activation energy to ∼32 kJ/mol at temperatures below 200 °C. This prediction is supported by data available in the literature for thick (>125 μm) palladium–silver alloy membranes.

1. Introduction

Energy efficient purification of hydrogen is an important technological challenge with broad applications in the chemical, petrochemical, metallurgical, pharmaceutical, textile and energy industries. Palladium-alloy membranes are particularly suited to this problem due to their high hydrogen permeability, thermal stability, and virtually infinite selectivity. In current systems hydrogen flux is observed to be inversely proportional to membrane thickness which indicates that hydrogen diffusion through the metal lattice is the rate-controlling process. This observation, along with the high cost of palladium, has motivated continuous efforts to fabricate palladium-alloy membranes of decreasing thickness. Recently, application of microfabrication techniques has enabled repeatable fabrication of free-standing palladium-alloy membranes with a thickness on the order of one micrometer [1–9]. As the thickness of palladium-alloy membranes continues to decrease, a natural question which must be addressed is whether there is a fundamental upper limit to the hydrogen permeation rate.

It is widely accepted that the process of hydrogen permeation though metallic membranes proceeds through a series of five distinct steps, any of which could potentially limit the permeation process under certain conditions. These steps include dissociative adsorption onto the metal surface, transition from a surface site into an unoccupied sub-surface (bulk) site, diffusion through the bulk metal toward the downstream surface, transition from the bulk to the downstream surface, and finally desorption into the permeate environment. Numerous experimental investigations have shown that under sufficiently low upstream pressures, or if the membrane surface is contaminated, the adsorption process will dominate mass transport resistance [10–15]. While important information about the permeation process can be gleaned from these studies, the operating pressures at which the adsorption process becomes relevant for a clean membrane are too low to have much relevance in a system designed to purify hydrogen. For example, in the study by Serra et al. [14] the pressure at which adsorption began to impact the overall permeation rate was 10^{-4} to 10^{-3} atm, depending on temperature.

Theoretical modeling has been utilized to predict conditions under which other transport processes will limit the hydrogen permeation rate through palladium. A detailed model for hydrogen permeation through metals was developed by Pick and Sonnenberg [15] and this model was later refined and applied specifically to the H–Pd system by Ward and Dao [16]. Recently, Caravella et al. [17] have added a new level of complexity by including the effects of hydrogen transport through a porous support layer and describing the diffusion transport rate as a function of chemical potential gradient rather than concentration gradient. In these models a mechanistic approach is taken to describe each of the transport steps using an appropriate rate constant and the hydrogen concentration immediately upstream and downstream of that process. Using such a system of equations the model predicts that low temperature operation of a thin free-standing membrane will

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become limited by the desorption process. The transition in rate-limiting transport mechanism should manifest itself as an increase in activation energy of permeation from a value of 5–10 kJ/mol in the diffusion-limited regime to a value of 80–100 kJ/mol at lower temperatures as the desorption process becomes dominant. The permeation activation energy in the diffusion-limited regime is dictated by a combination of the heat of absorption and activation energy for diffusion while in the desorption-limited regime the activation energy is indicative of the energy required to overcome the surface potential, which is estimated as the negative of the heat of adsorption.

If verified, existence of a desorption limitation to the hydrogen permeation rate has important ramifications for the future of palladium membrane research. In a desorption-limited regime neither decreasing membrane thickness nor increasing the upstream hydrogen pressure will enhance hydrogen permeation. As such, the desorption rate represents a fundamental upper limit to the attainable hydrogen flux at a given temperature. However, any model predictions rest on the ability of the model to capture the relevant physical processes under consideration. In this work it is demonstrated that the non-ideal absorption behavior of hydrogen in palladium can drastically impact the expected diffusion-limited behavior. Non-ideal effects have not been considered in existing models. To this end, an improved model is developed to capture the non-ideal behavior and this model is utilized to predict the diffusion-limited behavior of palladium–silver alloy membranes.

2. Non-ideal absorption behavior and Sieverts' law

One significant problem with the existing models is the lack of information available to describe the surface-to-bulk transition rate. Due to the additional freedom for motion of the surface state, the vibrational frequency of the adsorbed atom cannot be directly linked to an attempt frequency to enter the bulk. To overcome this difficulty, Ward and Dao [16] used a thermodynamic reciprocity relationship to estimate the rate of this transition. When the hydrogen in the gas phase and in the bulk are in equilibrium the rates of adsorption and desorption are equivalent, as are the surface-to-bulk and bulk-to-surface transition rates. In addition, the thermodynamic equilibrium pressure-composition behavior of hydrogen absorbed by palladium is well-characterized. Using this fact, Ward and Dao calculated the surface-to-bulk transition rate which is required to ensure that their model would reproduce the known equilibrium behavior in the limit that the surface equilibrium is achieved. By itself this approximation is a valid approach and should produce accurate predictions of membrane performance. The problem arises when Ward and Dao choose to describe the equilibrium behavior of hydrogen in palladium using Sieverts' law

$$K_s\chi = \left(\frac{P}{P_0}\right)^{0.5} \tag{1}$$

where K_s is the temperature-dependent Sieverts' coefficient, P is the hydrogen partial pressure in the gas phase, P_0 is standard pressure (1 atm) in the relevant units, and χ is the atomic ratio of hydrogen to palladium absorbed in the metal. As defined in Eq. (1), the Sieverts' coefficient is the reciprocal of the equilibrium constant for the absorption process (Eq. (2)) and the temperature dependence can therefore be described using Eq. (3).

$$0.5\mathrm{H}_2^{\mathrm{gas}} \rightleftharpoons \mathrm{H}^{\mathrm{absorbed}} \tag{2}$$

$$\ln\ K_s = \frac{\Delta\bar{H}_{\mathrm{H}}^{\mathrm{o}}}{RT} - \frac{\Delta\bar{S}_{\mathrm{H}}^{\mathrm{o}}}{R} \tag{3}$$

The quantities $\Delta\bar{H}_{\mathrm{H}}^{\mathrm{o}}$ and $\Delta\bar{S}_{\mathrm{H}}^{\mathrm{o}}$ are the standard molar heat of absorption and molar entropy of absorption at infinite dilution, respectively, and R and T are the ideal gas constant and temperature. The utility of Sieverts' law lies in the fact that it defines a simple and concise relationship between the hydrogen pressure, temperature, and equilibrium concentration of absorbed hydrogen: the absorption isotherms using Sieverts' law are of the form $\chi \propto P^{0.5}$. Unfortunately, Sieverts' law is only valid over a specific range of temperature and pressure. Strictly speaking, Sieverts' law describes the ideal behavior of hydrogen in the metal lattice which occurs only at infinite dilution. As long as there is negligible interaction between absorbed hydrogen atoms, Sieverts' law should adequately predict hydrogen absorption behavior. Fig. 1 shows three isotherms for the Pd–H system as measured by Frieske and Wicke [18] and the same isotherms as predicted using the Sieverts' law expression from the work of Holleck [19] with values of $\Delta\bar{H}_{\mathrm{H}}^{\mathrm{o}} = -8.4$ kJ/mol and $\Delta\bar{S}_{\mathrm{H}}^{\mathrm{o}} = -48.7$ J/mol K; these are also the values used by Ward and Dao in making their predictions.

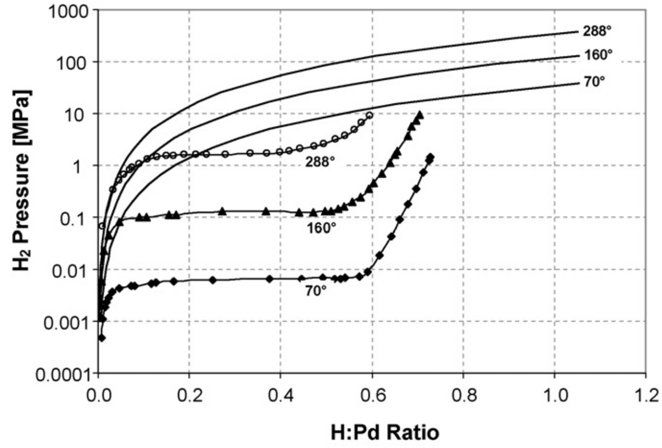

Fig. 1. Pressure–composition equilibrium diagram for the hydrogen–palladium system. Solid lines calculated using the Sieverts' law expression from Holleck [19] and measured data points taken from Frieske and Wicke [18] (lines are included only to connect data points measured at a common temperature). Temperature (°C).

It is clearly seen that starting at a fairly low H:Pd ratio, below 0.05, there is significant deviation between the ideal case (Sieverts' law) and the actual measured values from Frieske and Wicke. At low hydrogen pressure and/or elevated temperature, when the absorbed concentration is low relative to its saturation value, the absorption behavior is adequately described by Sieverts' law. The initial deviation is a marked decrease in the pressure required to attain a given increase in hydrogen absorption. In fact, in each isotherm there is a plateau region where there is no increase in hydrogen pressure required to substantially increase the amount of hydrogen absorbed by the metal. This feature of the Pd–H system has been extensively studied, and it is known that this is caused by the precipitation of the β-phase palladium hydride induced by attractive interactions between the absorbed hydrogen atoms [20]. Across these plateaus the α-phase, with low hydrogen content, and the β-phase, with high hydrogen content, coexist. Once the entire sample is converted to the β-phase, there is once again an increase in hydrogen pressure required to further increase the hydrogen content. The H:Pd atomic ratio in the β-phase is roughly 0.6, rather than a fully saturated value of 1. This is attributed to an electronic contribution to the excess potential of absorbed hydrogen as the 4*d* conduction band of Pd is filled and additional electrons must enter its 5*s* band which has a lower density of states [21–23]. As can be seen in Fig. 1, neither of these phenomena are captured by the use of Sieverts' law which is only valid in the α-phase hydride where the hydrogen content is well below the solvus line.

To illustrate the importance of these non-ideal effects, consider one operation point included both in the modeling predictions