

THE PERMEABILITY OF HYDROGEN IN NOVEL MEMBRANES AT ELEVATED TEMPERATURES AND PRESSURES

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Considerable interest in hydrogen separation and membrane reactors has motivated the research and development of hydrogen permeable materials. One particular interest in membrane technology is the application to processes that can benefit from operation at elevated temperatures (up to 1173 K) and pressures (up to 2.75 MPa). Although high cost, poor mechanical characteristics and low flux have prevented palladium from being a practical bulk membrane material, its catalytic surface and infinite selectivity have not diminished its applicability in reduced amounts. Therefore, the permeability of bulk palladium was determined at elevated conditions in efforts to better understand its bulk characteristics for application in reduced amounts.

1. Introduction

As we embark on the 21st century, the scientific community seeks viable technologies with the potential to increase overall process efficiency and to help resolve the diminishing fossil fuel resources that future generations will face. As a result, considerable interest has arisen in the research area of high performance hydrogen membranes under the severe conditions typical of gasification to fuels reforming.

Viable membrane candidates have identified with compositions ranging from metals, ceramics, and polymers to any combination thereof. Although many compositions and methods have been proposed for hydrogen separation membranes, palladium has been a popular and constant material in most of the viable hydrogen membrane concepts.

Palladium was initially identified as a hydrogen membrane material in the mid-1800's [1-3], and since has been a material involved in extensive hydrogen transport research at primarily low to moderate temperatures and pressures. Palladium has been such an advantageous membrane material as a result of its relatively high permeability and catalytic surface, which is thought to rapidly dissociate molecular hydrogen. However, due to its high cost and poor mechanical characteristics (i.e. α - β -phase transition) [4], research has focused on methods of reducing the amount of palladium needed (i.e. Pd-coated substrates), decreasing the effect of hydrogen embrittlement (i.e. Pd alloys), and/or eliminating palladium as a membrane component (i.e. porous membranes).

Attempts to reduce the amount of palladium used in membrane development have focused primarily on coated substrates. Applying palladium (0.1 to 100 μm) can have the ability of obtaining the advantageous surface characteristics of bulk palladium, without the high cost and poor mechanical characteristics. However, for this technology to succeed, the substrate must exhibit a minimum overall hydrogen transport resistance with

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respect to that of palladium. Thus, a successful composite membrane may be achieved by the application of a thin palladium coating to a dense, highly permeable metal (i.e. Ta, Nb, Zr) or a porous substrate (i.e. stainless steel, alumina, etc.).

Although an extensive amount of palladium data has accumulated in the literature, a systematic study on the effect of pressure on the permeability of palladium over a wide temperature range has not been previously conducted. Therefore, the objective of this study was to characterize the permeability of palladium at high temperatures (623 to 1173 K) and pressures (0.1 to 2.75 MPa) which are associated with gasifier effluent streams.

Expressions for Hydrogen Flux and Permeability

A detailed derivation of the governing equations for hydrogen transport through dense membranes is described elsewhere [5,6], however a generalized description is given here.

Hydrogen transport through the membrane can be described by “flux”, which is defined as the rate of hydrogen passing through the membrane per unit area. Assuming that the rate-limiting step in the hydrogen transport mechanism is diffusion and that transport is uni-directional, the hydrogen flux can be described by Equation 1.

$$N_{H_2} = -k \frac{(P_{H_2,ret}^{0.5} - P_{H_2,perm}^{0.5})}{X_M} \quad (1)$$

Where N_{H_2} is the hydrogen flux, k is the membrane permeability, X_M is the membrane thickness and $P_{H_2,Ret}$ and $P_{H_2,Per}$ are the partial pressure of hydrogen on the retentate and permeate sides of the membrane, respectively.

However, studies have shown [5] that the assumption of diffusion as the rate-limiting step in the membrane mechanism may not be the most accurate representation of the process. Therefore, by relaxing the assumption that the rate of adsorption/dissociation on the membrane surface is much greater than diffusion, a more generalized expression for hydrogen transport can be obtained, Equation 2.

$$N_{H_2} = -k \frac{(P_{H_2,ret}^n - P_{H_2,perm}^n)}{X_M} \quad (2)$$

Moreover, the permeability, k , of a membrane can also be represented in Arrhenius form and is illustrated in Equation 3.

$$k = k_o \exp \left[\frac{E_p}{RT} \right] \quad (3)$$

Where k_o is the pre-exponential factor, E_p is the activation energy of permeation, R is the universal gas constant and T is the temperature in absolute units.

2. Experimental

Membrane Preparation

Three membranes were fabricated by punching 16 mm diameter disks out of a 1 mm thick palladium sheet (Alfa Aesar, 99.9%). The palladium disks were polished using 800 grit silicon carbide paper prior to mounting into an Inconel 600-alloy holder using a brazing technique developed at the National Energy Technology Laboratory (NETL). The brazing material was composed of high-purity gold powder with a boric acid flux which promoted braze flow and surface oxide removal in the contact area. The palladium membranes, positioned in the Inconel 600-alloy holders, were heated to approximately 1473 K under an argon blanket for five minutes to form the seal, and then cooled to ambient temperature.

The mounted membranes were then cleaned of flux contamination by boiling in deionized water for a minimum of 30 minutes. The mounted membrane, in its holder, was welded to predetermined lengths of 19.05 mm O.D. Inconel 600 tubing on both sides of the membrane holder assembly. These tubes acted as “extension tubes” and served to contain pressure and house components carrying feed gas and permeate gas both to and from the membrane. The mounting configurations illustrated in Figure 1.

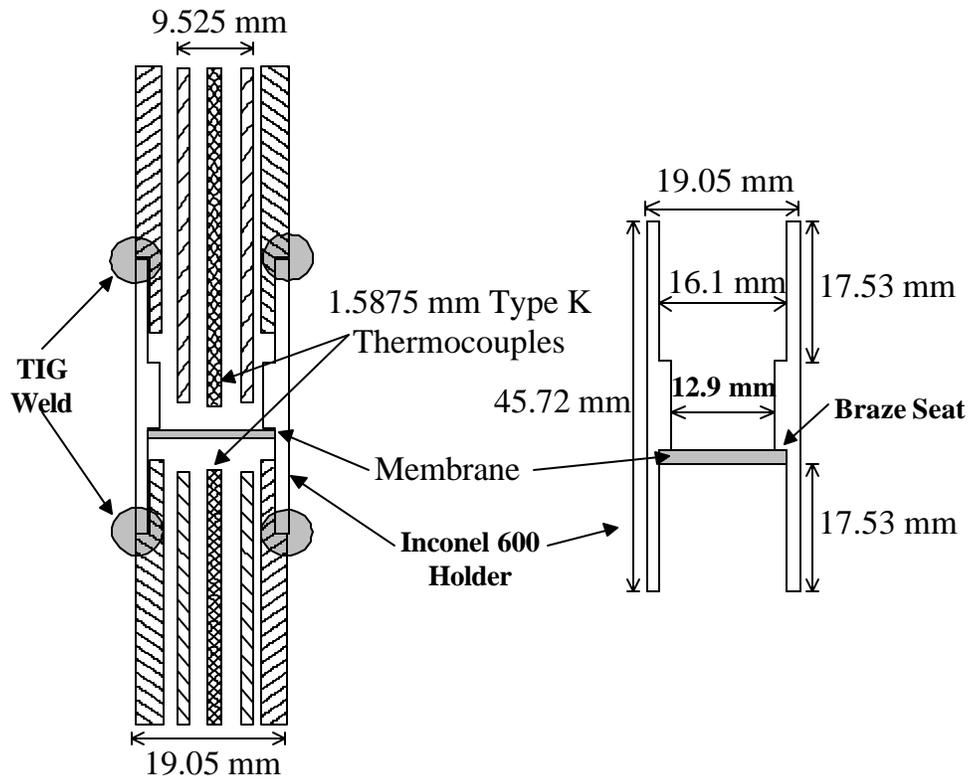


Figure 1: Schematic of the palladium membrane set-up.

Permeability Test Unit

The hydrogen membrane testing (HMT) unit was designed and constructed at NETL [5-7]. The apparatus was designed to allow testing of hydrogen separation membranes at high temperatures and pressures, up to 1173 K, and 3.1 MPa respectively. A simplified schematic of the HMT unit is illustrated elsewhere [5-7].

The membrane unit feed gas consisted of a mixture of 10 percent helium in hydrogen. Helium was used as an internal check for membrane leaks. Since helium does not have the ability to permeate palladium, its detection in the permeate stream would indicate a leak in the membrane or membrane-to-holder seal. The hydrogen-helium feed stream flow was controlled from 190 to 250 sccm. An argon sweep gas was passed over the permeate side of the membrane at a rate that maintained the concentration of hydrogen in the permeate at less than 6.0 mol-%. The hydrogen-containing permeate stream was directed to a Hewlett Packard 5890 Series II gas chromatograph equipped with a packed zeolite column, and thermal conductivity detector for hydrogen quantification.

3. Results and Discussion

Hydrogen flux through three palladium membranes was measured at a temperature range of 623 K to 1173 K and retentate pressures between 0.1×10^6 to 2.76×10^6 Pa. The hydrogen flux results shown in Figure 3 correspond to a pressure exponent value that was constrained to 0.5. Linear regression analysis of the five isotherms yielded R^2 values ranging between 0.940 and 0.991, with an average value of 0.971.

The permeability of palladium was determined at each temperature from the slope of these isotherms (Equation 5). The temperature dependence of the permeability values was then fit with an Arrhenius-type expression for the permeability of palladium, assuming a constrained hydrogen partial pressure exponent value of 0.5, equation 4.

$$k \left[\frac{\text{mol H}_2}{\text{m s Pa}^{0.5}} \right] = 3.30 \times 10^{-7} \exp \left\{ \frac{-17130 \left[\frac{\text{J}}{\text{mol}} \right]}{8.314 \left[\frac{\text{J}}{\text{mol K}} \right] * T[\text{K}]} \right\} \quad (4)$$

An improved fit of the data was obtained by determining the optimal value of the hydrogen partial pressure exponent, 'n'. Figure 4 illustrates the results for $n=0.63$, the exponent value that optimized the average R^2 value of the linear regression to 0.990.

The expression for hydrogen flux under this condition is:

$$N_{\text{H}_2} \left[\frac{\text{mol H}_2}{\text{s m}^2} \right] = \frac{k (P_{\text{H}_2, \text{retentate}}^{0.63} - P_{\text{H}_2, \text{permeate}}^{0.63}) [\text{Pa}^{0.63}]}{X_{\text{M}} [\text{m}]} \quad (5)$$

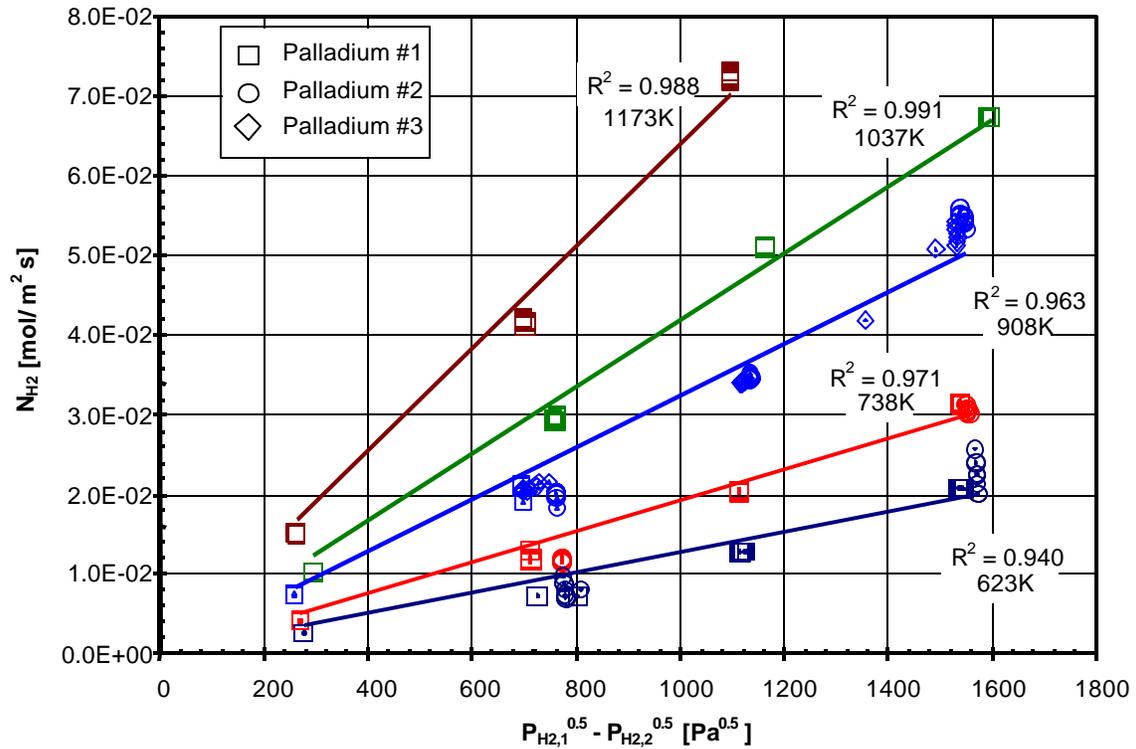


Figure 3: Hydrogen permeability results with the partial pressure driving force exponent, 'n', constrained to 0.50.

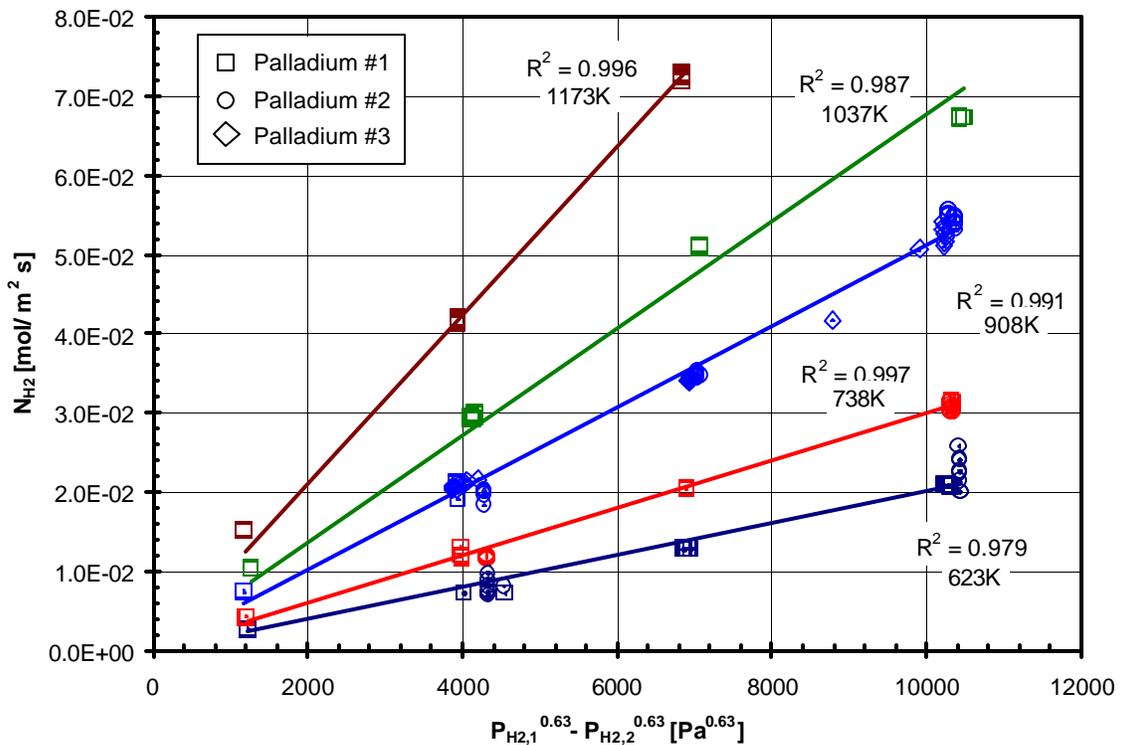


Figure 4: Hydrogen permeability results with the best partial pressure representation ($n=0.63$) for the membranes and experimental conditions of this study.

Permeability values were determined from the slopes of best-fit isotherms in Figure 4. The Arrhenius expression that correlates these results is given in Equation 6:

$$k \left[\frac{\text{mol H}_2}{\text{m s Pa}^{0.63}} \right] = 5.70 \times 10^{-8} \exp \left\{ \frac{-17710 \left[\frac{\text{J}}{\text{mol}} \right]}{8.314 \left[\frac{\text{J}}{\text{mol K}} \right] * T[\text{K}]} \right\} \quad (6)$$

Prior investigators, with a single exception, employed high-vacuum test apparatus operating at sub-atmospheric hydrogen test pressures. These investigations reported a pressure exponent of 0.5 in the flux expression, Equation 1, as would be expected for bulk-diffusion controlled transport.

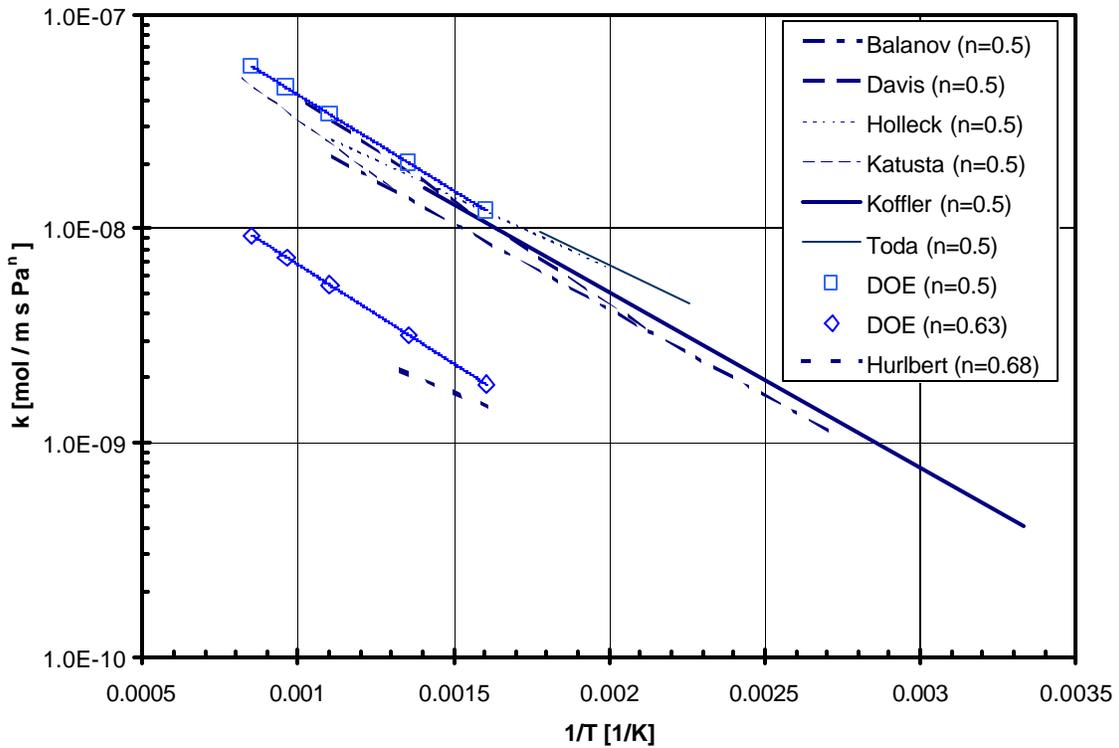


Figure 5: Arrhenius comparison of literature palladium permeability values as a function of temperature and the results obtained in this study with the best representation ($n=0.63$) and constrained partial pressure exponent ($n=0.5$).

The temperature dependence of both the literature and NETL permeability values with similar membrane thicknesses (100 to 12000 μm) is shown in Figure 5. This figure also illustrates how differences in the partial pressure driving force exponent, n , affect the reported permeability. The NETL expression for permeability is in good agreement with prior literature, provided that ‘ n ’ is constrained to a value of 0.5. The activation energy, 17.13 kJ/mol, and the pre-exponential factor, $3.30 \times 10^{-7} \text{ mol H}_2 / (\text{m s Pa}^{0.5})$ fall well within the range of previously reported values [5]. However, when the partial pressure exponent (n) is optimized to a value of 0.63, the effect of the partial pressure exponent on the apparent permeability is realized, Figure 5. Additionally, the only prior high-pressure

permeability results [8] illustrate similar effects to the partial pressure exponent as those reported in this high pressure study.

Values of ‘n’ greater than 0.5 are commonly reported in ultra-thin, supported palladium membrane studies [6,9], with the decreased thickness of the membrane enhancing the influence of various surface effects. However, the experiments described here were conducted with thick “bulk” membranes. Therefore, an attempt was made to establish that the partial pressure exponent was a function of the increased hydrogen pressure associated with high-pressure conditions of this study.

The optimal value of ‘n’ was determined as a function of the maximum pressure of the NETL data set used in the analysis. Optimal values of ‘n’ were determined for the 0-700 kPa, 0-1400 kPa and 0-2800 kPa pressure ranges. Figure 6 illustrates that as the maximum pressure value decreased, the pressure effects were diminished and the optimized partial pressure exponent decreased. An extrapolation of these results to zero pressure indicated that the exponent approaches the appropriate limiting value of 0.5 for bulk-diffusion controlled transport in bulk membranes at low-pressure.

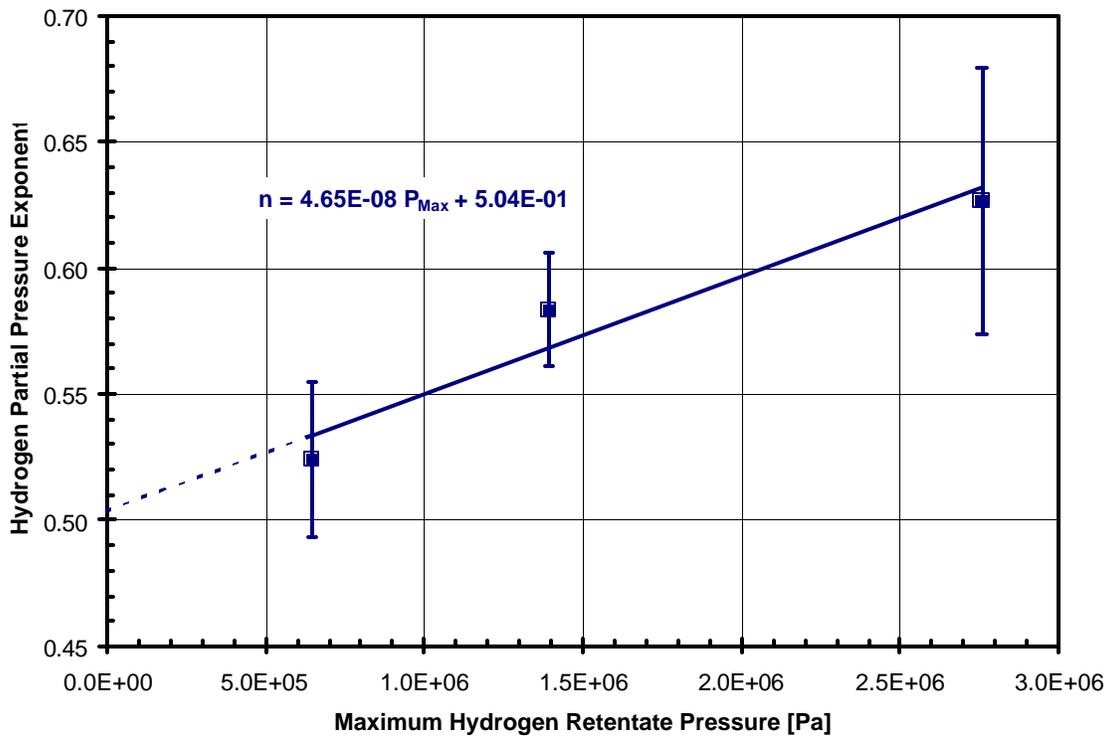


Figure 6: The effect of the hydrogen feed pressure on partial pressure exponent, ‘n’. Error bars indicate range of ‘n’ values obtained from individual membrane tests, while points indicate average ‘n’ value from all membranes.

4. Conclusion

The permeability of bulk palladium was determined for the first time at the elevated temperature and pressure conditions associated with gasifier and/or other process streams that are being considered as candidate feeds for membrane applications. The permeability

results were comparable to those reported at lower pressures when the hydrogen partial pressure exponent of the hydrogen flux was constrained to a value of 0.5. A much better fit of the data was realized when the hydrogen partial pressure exponent value was optimized to a value of 0.63. This result was similar to a previously reported value of 0.68 at 623 K [8]. This deviation of the exponent value from 0.50 to 0.63 for bulk membranes may be attributable to the increased resistances associated with increasing hydrogen pressure, possibly due to significant surface coverage.

5. References

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