J. Condensed Matter Nucl. Sci. 19 (2016) 1–9

Research Article

Effect of Cathode Pretreatment and Chemical Additives on H/D Absorption into Palladium via Electrochemical Permeation

Orchideh Azizi*, Jinghao He, Dan T. Paterson, Arik El-Boher, Dennis Pease and Graham Hubler†

The Sidney Kimmel Institute for Nuclear Renaissance (SKINR), Department of Physics and Astronomy, University of Missouri, Columbia, Missouri, MO 65211, USA

Abstract

In this study, we applied a variety of palladium pretreatment methods, including nitric acid etching, Aqua regia etching and electrochemical oxidation/reduction to determine the effect of cathode initial condition on hydrogen absorption into palladium during the loading process. The electrochemical behavior of palladium was characterized using electrochemical permeation, electrochemical desorption, and electrochemical impedance spectroscopy (EIS). The hydrogen diffusion coefficient in palladium membrane was obtained using the time-lag method. The lattice diffusivity of hydrogen as well as the amounts and distribution of the diffused and trapped hydrogen were analyzed using the desorption rate of hydrogen. We also investigated the effect of pyridine, a permeation promoter on hydrogen absorption in palladium membranes. Electrochemical parameters of double layer capacitance, charge transfer resistance and surface roughness were characterized using electrochemical impedance spectroscopy for both treated and untreated cathodes. This study shows that the ability to load Pd with hydrogen is only mildly affected by surface pretreatment and the chemical additives, and therefore, we consider the pretreatments a second order effect regarding the ability to load.

Keywords: Absorption, Deuterium, Impedance spectroscopy, Palladium, Permeation

1. Introduction

Palladium hydrogen system has been intensively investigated due to the exceptional ability of palladium to adsorb and absorb hydrogen. Achieving consistent high loading of Hydrogen (H) and Deuterium (D) in Palladium (Pd) is one of the most challenging issues in the field of Anomalous Heat Effect (AHE). Numerous researchers have suggested that the concentration of deuterium loaded into palladium may have to exceed a critical value before the generation of excess heat [1–3]. Studies show that the hydrogen permeation and loading behavior is sensitive to the surface treatment of the sample [4,5] and chemical impurities [6–8]. The Sidney Kimmel Institute for Nuclear Renaissance (SKINR) has

---

*Corresponding author. E-mail: oazizi@missouri.edu

†E-mail: hublerg@missouri.edu

conducted loading studies of 50 μm thick Pd foils in an attempt to enhance the electrochemical activity of palladium and increase loading by using various pretreatment methods and chemical additives. The objectives of this work is to study hydrogen absorption and loading in palladium affected by various surface treatment and chemical additives as permeation promoters using an electrochemical permeation technique.

2. Experimental

The electrochemical permeation measurements of hydrogen were performed in a two-compartment electrochemical cell [9]. In each glass half-cell a platinum plate and Ag–AgCl electrode were used as a counter and reference electrode, respectively. The electrolyte solution was 0.1 M LiOH made using 18.2 MΩ-cm Millipore water.

Palladium foils of 50 μm thickness were prepared using cold rolling of a 1 mm thick palladium (Holland Moran) followed by thermal annealing at 850°C for 60 min in a protocol to ensure all samples having the same initial conditions. Such a Pd foil with surface area of 3.14 cm^2 was used as a membrane (working electrode). To study the effect of initial conditions on hydrogen permeation and hydrogen loading into palladium, four types of palladium samples were used as a membrane. They are Pd foil etched in concentrated nitric acid for three minutes (type 1), Pd foil etched in Aqua regia for 3 min (type 2), pretreated Pd by electrochemical oxidation/reduction (type 3), and un-etched palladium (type 4).

In the electrochemical permeation cell the palladium surface at which water molecules were reduced is referred to as the entry surface and the corresponding surface at which the diffusing hydrogen was oxidized is labeled the exit surface.

During the permeation measurements, the entry side of the membrane was subjected to galvanostatic cathodic charging. The exit side of the membrane was continuously polarized at a constant potential close to open circuit potential. Under this potential, hydrogen atoms escaping from the membrane were oxidized. The current measured at the exit side corresponds to the permeation rate of hydrogen through the membrane. Figure 1 shows schematic of the electrochemical permeation cell.

3. Results and Discussion

3.1. Effect of chemical etching on hydrogen permeation and loading

Figure 2 shows the hydrogen permeation currents measured at the exit side for different charging currents at the entry side and for un-etched Pd and Pd foils etched in nitric acid and in Aqua regia. After 10 min of permeation, the hydrogen charging current from the entry side was interrupted and the entry side of the membrane was polarized immediately at the same potential of the exit side. At charging currents less than 7 mA, after few seconds, the permeation rate reaches the steady-state value and remains constant with time. At charging currents higher than 7 mA, the permeation current after reaching the maximum value decreases with increasing of time. Figure 2(d) shows that permeation current of palladium etched in Aqua regia decreased slightly faster than those of Pd etched in nitric acid and un-etched palladium.

Figure 3(a) shows the permeation efficiency (steady-state permeation current/charging current) vs. charging current for palladium membranes without etching and etched in nitric acid and Aqua regia. At charging currents less than 7 mA, the permeation efficiency for all three electrodes was close to 90%. At charging current higher than 7 mA the permeation efficiency dropped to 60% and decreased further to 20% by increasing the charging current up to 40 mA. These results show that the permeation efficiency on Pd etched in Aqua regia at charging current less than 7 mA is slightly lower than those of other two electrodes. To pinpoint the underlying mechanism, we plotted the steady-state permeation current as a function of the square root of the charging current in Fig. 3(b), and found that permeation current is linearly dependent upon the square root of the charging current at charging currents lower than 7 mA. Furthermore, this linear relationship is independent on the surfaces of un-etched or etched Pd, suggesting the

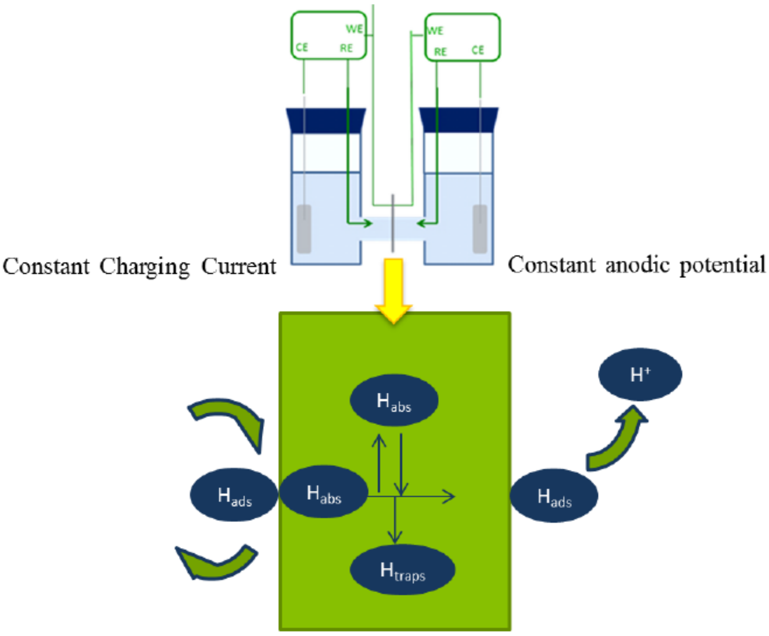

Figure 1. Schematic of electrochemical permeation test.

permeation process is fairly well determined by hydrogen diffusion rate [10]. In other words, water discharge and hydrogen absorption in Pd are controlled processes at low charging currents and pretreatment of palladium has no effect on the surface kinetics. However, at charging current larger than 7 mA the steady-state permeation current no longer follows the linear relationship and appears to be not affected by charging current much, especially for strongly etched Pd (in Aqua regia). In this case, hydrogen recombination flux increase and absorption flux decreases.

For hydrogen permeation measurements under galvanostatic charging, the diffusion coefficient through palladium membrane is conventionally calculated from the lag time of current transient [11] according to $D = L^2/2t_1$, where L is the thickness of the palladium membrane, and t_1 is the time at which the permeation current reaches 0.63 of the steady-state value. Using the results of permeation current versus time in Fig. 1, we determined the diffusion coefficient of hydrogen in both etched and un-etched palladium is about $3.5 \times 10^{-7}\mathrm{cm}^2\mathrm{s}^{-1}$, which is in good agreement with the literature [12,13].

Figure 4(a) presents the steady-state polarization behavior of palladium in 0.1 M LiOH obtained by sweeping the potential at a sweep rate of 0.16 mV/s. The steady-state polarization curve reveals that at low over-potentials the Tafel slope is about –0.18, but it changes to –0.25 at over-potentials higher than –1.1 V.

The entry potential versus hydrogen permeation current in Fig. 4(b) show particularly sharp changes at a potential of –1.2 (V) above which the permeation current is independent of potential. Steady-state polarization data in conjunction with permeation current data reveals that the mechanism of hydrogen evolution from Pd in alkaline solution at low charging current starts with water discharge and the formation of adsorbed hydrogen followed by hydrogen absorption into Pd. At higher charging current when the concentration of hydrogen increases near the surface of palladium entry side the mechanism changes to a coupled discharge and desorption reactions, in which the rate of hydrogen desorption increases significantly and the absorption flux decreases [14].

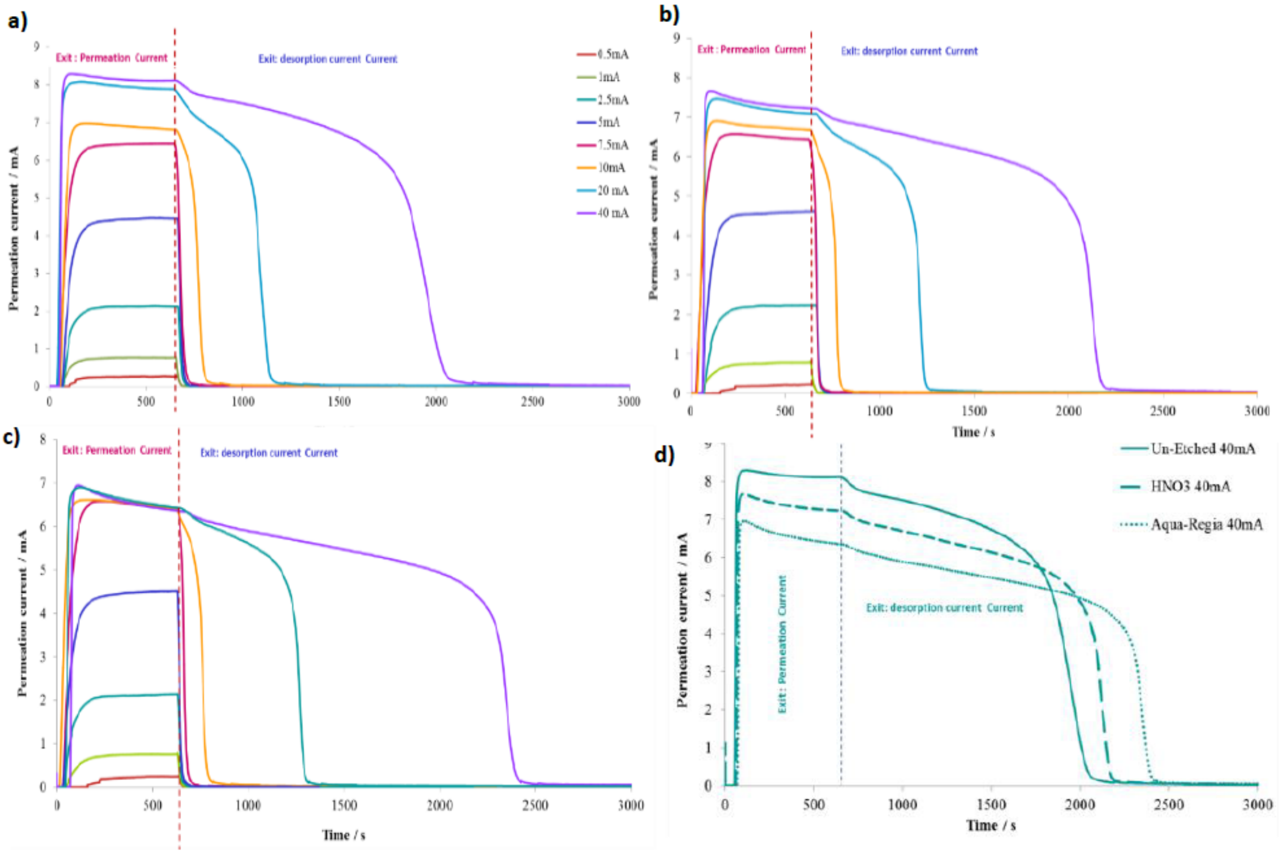

Figure 2. Permeation currents on the exit side of palladium membrane during applying different cathodic currents from the entry side for 10 min in 0.1 M LiOH solution. (a) un-etched palladium; (b) Pd foil etched in concentrated nitric acid for 3 min; (c) Pd foil etched in Aqua regia for 3 min and (d) comparing the permeation current vs. time for all three electrodes at 40 mA charging current. Data after vertical dashed line represents hydrogen discharge process under no charging current from the entry side of the membrane.

To study the hydrogen loading into Pd membrane the electrochemical desorption method was used. As shown in Fig. 1, after 10 min, the cathodic current was switched off and entry side was polarized immediately at the same potential of the exit side. From this moment the anodic currents were recorded at the both sides of the membrane and they correspond to hydrogen desorption rate from the Pd membrane. Integration of the desorption current – time curves at both sides of the membrane leads to the total amounts of diffusible and absorbed hydrogen in the palladium membrane (see inset of Fig. 5).

The results show that for all palladium membranes, etched and un-etched, the hydrogen concentration at the entry side is higher than that at the exit side.

The H/Pd loading ratio, calculated using hydrogen desorption data for un-etched and etched palladium, is presented in Fig. 5. The results reveal that the hydrogen loading increases with increasing charging current as expected, and H/Pd loading ratio is slightly higher for palladium etched in Aqua regia in comparison to Pd etched in nitric acid and un-etched palladium.

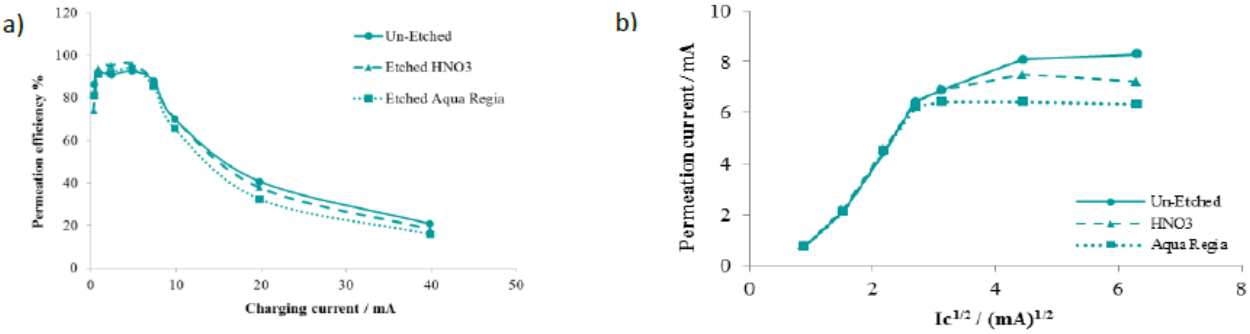

Figure 3. (a) Permeation efficiency as a function of charging current; (b) Permeation current as a function of the square root of the charging current (I_c) for un-etched Pd, etched Pd in nitric acid and etched Pd in Aqua regia.

Figure 6 shows the electrochemical impedance spectroscopy data (Nyquest plots) obtained at different potentials on etched and un-etched palladium membranes in 0.1 M LiOH solution. The data shows that the charge transfer resistance deceased by increasing the potentials which is in good agreement with steady-state polarization data.

Also fitted data showed that the double layer capacitance is slightly higher for etched Pd in Aqua regia probably due to higher surface area on roughed surfaces.

3.2. Effect of high current

Figure 7 shows the discharge current vs. time at entry side (Fig. 7(a)), the permeation current vs. time at exit sides after hydrogen charging for 10, 20 and 40 min at 40 mA charging current (Fig. 7(b)). The atomic ratio of H/Pd vs. charging time obtained from electrochemical desorption technique at both sides of the membrane (Fig. 7(c)) reveals that hydrogen loading into Pd increased linearly with time for the first 40 minutes and hydrogen loading reaches close to 25%. For longer charging time at 40 mA the hydrogen loading increased to about 89% and remained almost constant for charging times higher than 3 h.

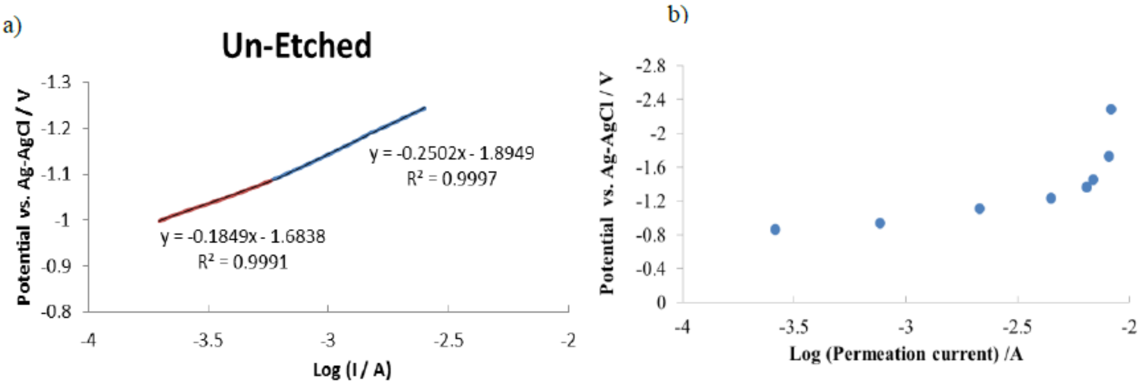

Figure 4. (a) Steady-state polarization curve of un-etched palladium in 0.1 M LiOH solution; (b) Dependence of the log of hydrogen permeation current on potential for un-etched 50 μm thick Pd in 0.1 M LiOH solution.

3.3. Electrochemical pretreatment

The effect of specific electrochemical oxidation reduction procedure was studied in attempt to improve the electrochemical activity of palladium and increase the hydrogen loading into palladium. In this procedure a symmetric square-wave potential ±1.5 V was applied to the Pd electrode for about 20–30 s, with frequency of 800 Hz. Figure 8(a) shows the cyclic voltammetry (CV) obtained from untreated and electrochemically treated palladium. The treated electrode presents almost the same features as the untreated electrode, but the treated cathode gives higher currents during the whole potential sweep, suggesting the cathode is more active after electrochemical treatment.

Figure 8(b) shows the permeation current vs. time at several different charging currents at the entry side for unetched, Aqua regia etched, and electrochemically treated palladium membranes, among which the electrochemically treated membrane has the highest permeation current.

3.4. Chemical impurities

Alternative to chemical etching and electrochemical pretreatment, we also studied the effect of Pyridine, a permeation promotor on hydrogen permeation current and loading behavior of palladium. As shown in Fig. 9(a), pyridine improves the hydrogen permeation after adding 1 mM pyridine to the entry side at a 10 mA charging current. The permeation current increased during the initial 10 min charging, but it soon reached the steady-state value. Adding pyridine to the both sides of the permeation cell results in a decrease of the steady-state permeation current in comparison to adding pyridine at only one side. However the permeation current is still higher than that in pure electrolyte.

The desorption data from both sides of the membrane shows less hydrogen loading into the palladium membrane in the presence of pyridine. In the presence of pyridine the hydrogen coverage on the entry side is less than in pure electrolyte. As a result the permeation efficiency is slightly higher than that in pure electrolyte under the same condition.

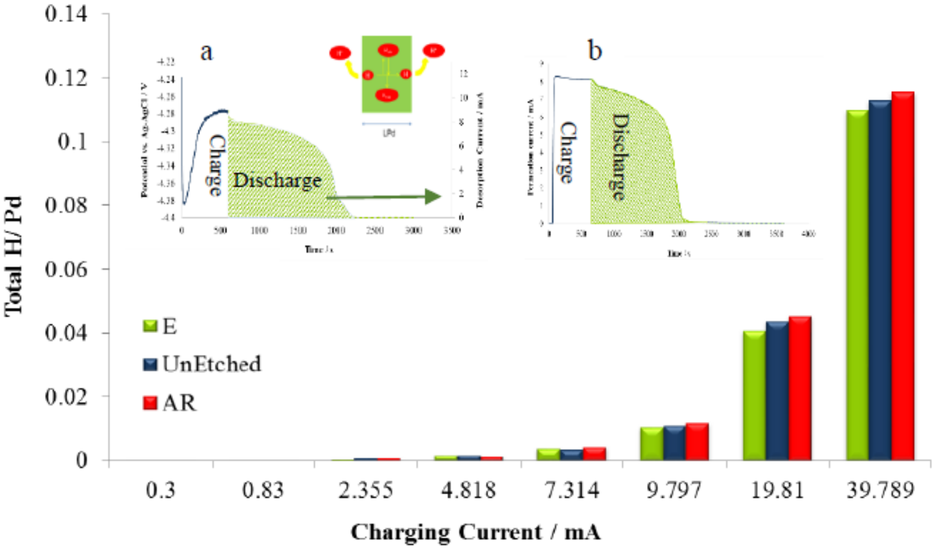

Figure 5. Total atomic ratio of H/Pd calculated using hydrogen discharge data as a function of charging current, in 0.1 M LiOH solution. Inset: Desorption rate of hydrogen from palladium membrane after 10 min charging at 10 mA current; (a) entry side and (b) exit side .

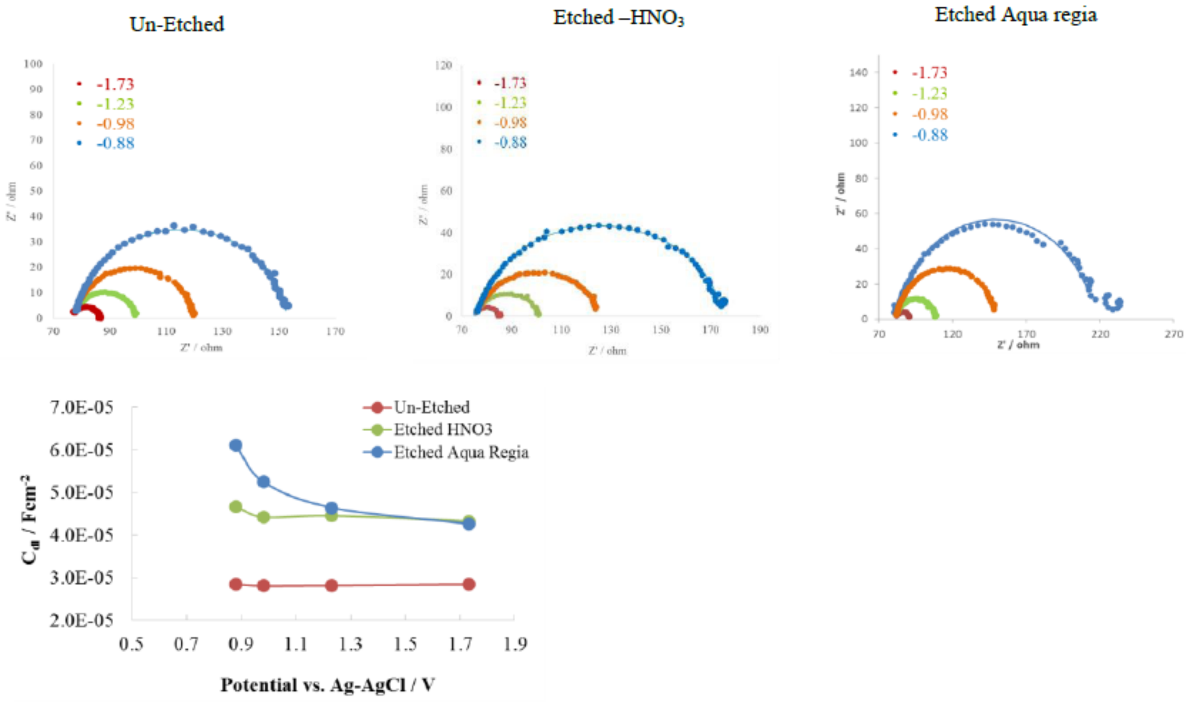

Figure 6. Potential vs. Ag–AgCl/V.

Figure 9(b) shows the effect of pyridine concentrations on hydrogen permeation current. For the concentration up to 5 mM the increasing pyridine concentrations resulted in a high permeation current. But for higher pyridine concentration, the permeation current decreased but it was still higher than that in pure electrolyte as pyridine may block the active sites for water reduction at the entry side.

4. Conclusion

At low charging currents, the permeation efficiency for all un-etched and etched palladium was close to 90% and they are determined by hydrogen diffusion in Pd membranes. Hydrogen diffusion coefficient around $3.5 \times 10^{-7}\mathrm{cm}^2/\mathrm{s}$ was obtained using the time-lag method. The kinetics of hydrogen is controlled by water discharge followed by, hydrogen absorption into Pd. At intermediate charging currents the permeation efficiency was about 60%. At high charging currents, it further decreased to 20%, suggesting the hydrogen recombination flux increases significantly and the absorption flux decreases.

Hydrogen loading in Pd etched in Aqua regia is slightly higher than that of un-etched Pd mainly due to higher surface area and more available active sites. Square-wave electrochemical oxidation reduction pretreatment of palladium appears to improve H loading in palladium. Presence of pyridine affects the mechanism of hydrogen reactions and slightly enhances the permeation current, but it does not have significant effects on improving H loading in palladium. Our study shows that the ability to load Pd with hydrogen is only mildly affected by surface pretreatment and the chemical additives studied, and therefore, we consider the pretreatments a second order effect regarding the ability

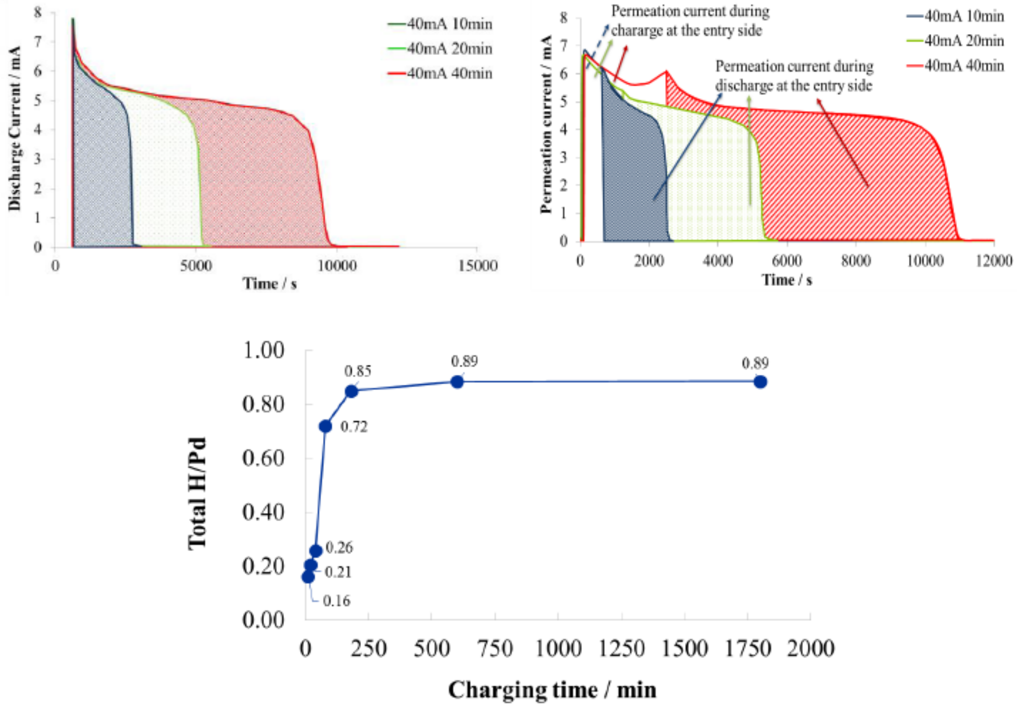

Figure 7. (a) Hydrogen discharge current vs. time at 50 mV at the entry side of the Pd foil; (b) Hydrogen permeation vs. time at the exit side. All data obtained at charging current of 40 mA for 10, 20 and 40 min; (c) Atomic ratio of H/Pd loading as a function of time at charging current of 40 mA.

to load which suggests that subtle alterations of the kinetics of surface processes like Tafel recombination, probably caused by surface impurities, govern the de-loading.

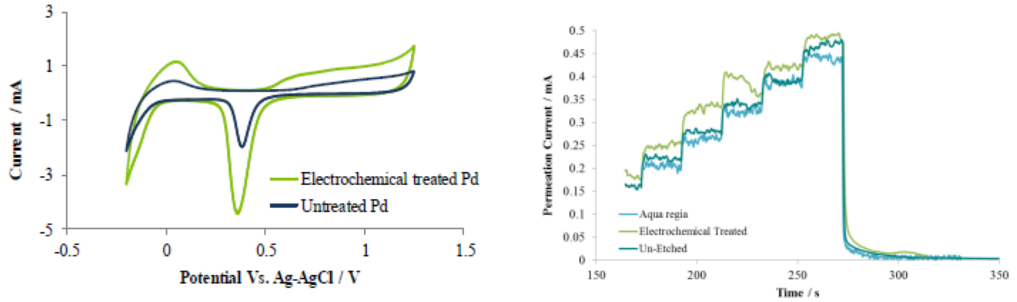

Figure 8. (a) Cyclic voltammograms of untreated palladium and electrochemically treated palladium in 0.1 M LiOH, scan rate of 100 mV/s. (b) Permeation current as a function time for electrochemically treated and untreated palladium in 0.1 M LiOH solution.

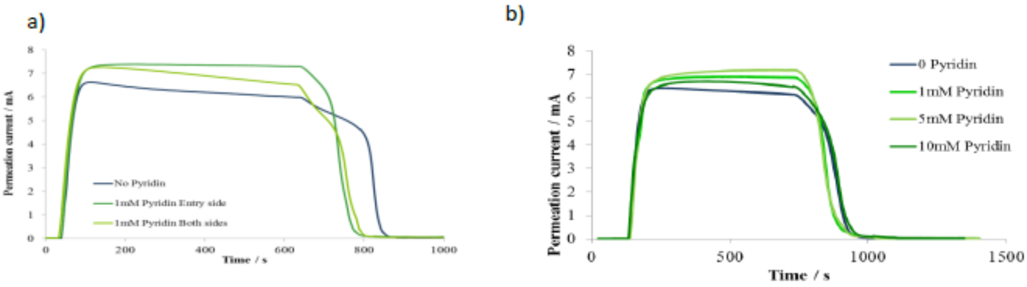

Figure 9. (a) Permeation current versus time obtained in the absence and presence of pyridin; (b) Permeation current versus time obtained in the absence and presence of 1, 5 and 10 mM pyridin.

Result of loading at high charging current is somewhat surprising in that a loading ratio of 0.89 was readily achieved in 3 h in a 50 μm thick foil, and, that the fact that hydrogen was constantly being removed at the exit side. For foils loaded from both sides, it generally takes much longer than 3 h to reach H/Pd of 0.89 and often, such high loading cannot be reached at all. This may indicate that internal stresses caused by the large volume change with increasing H/Pd ratio are more easily accommodated by the foil in one-side charging

Acknowledgment

This work is fully supported by Mr. Sidney Kimmel

References

[1] G.K. Hubler, U.S. Surface and Coatings Technology **201** (2007) 8568.
[2] M.C.H. McKubre et al., *Fifth Int. Conf. on Cold Fusion*, IMRA Europe, Sophia Antipolis Cedex, France, Monte-Carlo, Monaco, 1995.
[3] R.A. Oriani, *Fourth Int. Conf. on Cold Fusion*, Electric Power Research Institute, Lahaina, Maui, 1993, 312 Hillview Ave., Palo Alto, CA, USA.
[4] T. Harris and R.M. Latanislon, *Int. J. Hydrogen Energy* **14** (1989) 623.
[5] T.A. Green and T.I. Quickenden, *J. Electroanaly. Chem.* **368** (1994) 121.
[6] T. Maoka and M. Enyo*, Surface Technol.* **9** (1979) 147.
[7] L. Birry and A. Lasia, *Electrochim. Acta* **51** (2006) 3356.
[8] J.-N. Han, S.-I. Pyun and T.-H. Yang, *J. Electrochem. Soc.* **144** (1997) 4266.
[9] M.A.V. Devanathan and Z. Stachurski, *Proc. Roy. Soc. A: Mathematical, Physical and Eng. Sci.* **270** (1962) 90.
[10] M. Zamanzadeh, A. Allam, H.W. Pickering and G.K. Hubler, *J. Electrochem. Soc.* **127** (1980) 1688.
[11] S. Schuldiner and J.P. Hoare, *J. Electrochem. Soc.* **103** (1956) 178.
[12] J.G. Early, *Acta Metall.* **26** (1978) 1215.
[13] J. Bowker and G.R. Piercy, *Metall. Trans.* **16A** (1985) 715.
[14] J. O'M Bockris, R. Sundaresan, Z. Minevski and D. Letts, *Fourth Int. Conf. on Cold Fusion*, Electric Power Research Institute, Lahaina, Maui, 1993, 312 Hillview Ave., Palo Alto, CA, USA.