PARAMETERS AFFECTING THE LOADING OF HYDROGEN ISOTOPES INTO PALLADIUM CATHODES

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Abstract

We have tested our new Degree of Loading (DoL) cell design which can be directly transferred to the SRI mass flow calorimeter. We have shown that appropriately prepared Pd cathodes can reach high loadings in this new design and that the cells can be transferred to the calorimeter without degrading the cathode's or cell's performance. In all of the experiments the cathode deloaded at higher current densities, and ostensibly identical cathodes yield significantly different D:Pd loading/current density profiles.

In the new cell design high purity Pd from IMRA Materials and Johnson Matthey have generally loaded better than recent lots of 99.9% Engelhard Pd. Pd that IMRA Materials cast in air with added CaB_6 held its loading best at higher current densities. Electrolyte additives Al, Si, Nd and Sm had no perceptible effect on loading behavior. The regular addition of Cl^- ion, similar to what might happen when topping up open cells, can increase or maintain loading. The presence of Cu is detrimental to good loading.

Electrochemical surface potential (E_{surf}) measurements made in H_2SO_4 yield potentials similar to those predicted by high pressure H_2 loading experiments. LiOH (LiOD) significantly affects E_{surf} but that effect may be deconvolved to allow an estimate of the surface loading in alkaline electrolytes.

1. Introduction

Our laboratory has been studying[1-6] the electrochemical deuterium loading characteristics of palladium for over 7 years. This is in conjunction with our program to measure for anomalous heat effects reported to occur in such experiments. We have measured these anomalous effects, excess power, several times in our mass flow calorimeters. We have found certain D:Pd loading levels and current protocol parameters necessary, but not sufficient, to yield excess power. We use a pre-calorimeter trial, which we refer to as a degree-of-loading (DoL) "farm", to ascertain which cathodes can achieve these loading/current criteria. We observe a lack of reproducibility among replicates which we ascribe to metallurgical, chemical, or physical differences presently beyond our control.

The near-surface loading of hydrogen isotopes into Pd will affect the bulk crystalline loading, $H(D):Pd_{bulk}$, as well as the Pd surface potential. Fleischmann[7] and Storms[8] have separately reported using Pd potentials as a predictor of oncoming excess power in these experiments. We report here our efforts to measure Pd surface potentials (E_{surf}) and correlate those potential with $H(D):Pd_{bulk}$.

As shown in our earlier reports we have found three necessary, but not sufficient, simultaneous conditions for production of excess power in the D/Pd electrolysis system:

- High D:Pd loading (>0.89)
- High current densities (> 300 mA-cm^2)
- Long times at loading

Most of our early successful experiments used a single lot of Pd obtained from Engelhard designated as E#l. We found our original preparation protocol yielded more reproducible, better loading, when compared to using Pd as received. These early cells also used a relatively small electrode chamber with rather uniform current distribution. The original calorimeter cell design was modified to accommodate larger cathodes, larger inventory of electrolyte, more efficient heat transfer, and special safety procedures. Loading results in this modified design were poor. We also attempted to transfer already-loaded cathodes from small DoL cells into the larger calorimeter cells, with disappointing results. New calorimeter cells were redesigned with an electrode chamber similar to that used in earlier experiments. These cells were operated thermodynamically closed with internal recombiner catalysts and capable of withstanding 5 atm. pressure for calorimetric reasons.

Based on reports[7,8] of using cell potential measurements to predict excess power production, we devised experiments to correlate cell voltage, surface potential, and bulk loading measurements. We used results of Baranowski[9] to correlate surface potential (E_{surf}) with surface loading (H(D):Pd$_{surf}$).

2. Experimental

Figure 1 shows a schematic diagram of the DoL cell used in this program. The electrode chamber and experimental protocol are similar to those described earlier. [1-3]

Electrolyte is added to the cell only after potential is applied to prevent oxidation of the pure Pd. The initial current density is chosen such that $17 \leq \bar{i} \leq 35$ mA-cm^{-2}. The cell is then flushed with 5 volumes of H$_2$(D$_2$) or N$_2$. To ascertain steady-state loading measurements, the current is stepped to high values of $\bar{i}$ in regular intervals. The length of time at each current is chosen to minimize de-loading at higher current densities. After H(D):Pd$_{max}$ is achieved in the first loading cycle the cell current is reduced to the minimum current density and an automated current step protocol is initiated. This protocol has a repeat period of 48-96 hours. Table 1 shows a typical current step protocol for a 1 mm × 30 mm cathode, where positive currents are cathodic and negative currents anodic.

Table 1. Current Step Protocol

Time (hr)	0	0.5	24	32	40	48	56	64	72	80	88	96=0
$\bar{i}$ (mA/cm^2)	-35	35	50	100	200	300	400	500	750	1000	35	-35

Sometimes the length of time at higher current densities is reduced to minimize deloading.
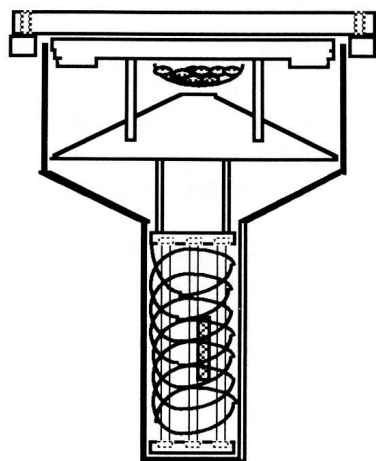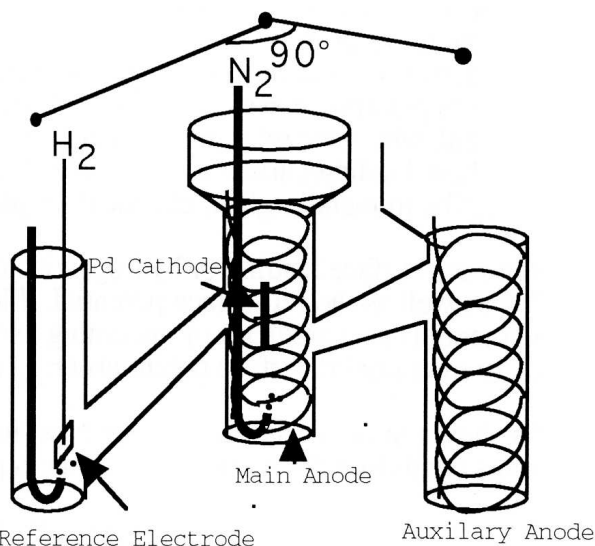
Figure 1. Degree of Loading Cell

Figure 2. Electrochemical Surface Potential Measurement Cell

The Pd cathode rods, either 1, 2, or 3 mm diameter, were 30 mm long. Engelhard 99.9% Pd was machined from either 3.2 mm diameter to 3.0 mm or from 3.0 mm dia. to 2.8 mm diameter. No surface machining was applied to the Pd from other sources. Cathodes larger than 2 mm dia. usually had notches machined near each end to accept Pt wire contacts. The experimental data acquisition system has been described elsewhere. Cathodes were prepared from Pd supplied by Engelhard (E#n, where n is our lot number), IMRA Materials (I/M) or Johnson Matthey (J/M). DoL cells were operated in an air-cooled safety enclosure containing a quartz double-bubbler filled with D_2O connected to the cell's gas outlet tube to minimize contamination from moist air. The gas inlet tube was stoppered with a rubber septum and used to make gas or liquid additions.

Figure 2 shows the three-compartment cell used for electrochemical surface potential measurements. Two quartz cylindrical cells, 25 mm dia. $\times$ 70 mm tall were connected together with a quartz tube. The reference electrode compartment is a quartz tube, 10 mm dia. $\times$ 70 mm tall attached at right angle to the central electrolysis chamber. The connecting tubes have vertical slopes as shown in the figure to minimize O_2 contamination in the reference compartment and the main electrolysis chamber during the surface potential measurement. The cell was sealed with two H_2O-filled double bubblers. H_2 was continually bubbled over the Pt reference electrode ($5 \times 5 \times 0.1$ mm), which had been platinized for 20 seconds at 50 mA in a 2% H_2PtCl_6 solution. N_2 continually flushed O_2 out of the central electrolysis chamber. This cell design was chosen as analogous to the method for reference potential measurement used in the DoL cells which cannot accommodate a Luggin capillary.

Johnson Matthey (J/M) special lot "Z" (low Pt-group metal) 1 mm wire was cut to 10 mm long and solvent cleaned for this experiment. The cathode was annealed, Pt lead wires attached and acid etched as described in earlier reports.[1-3] A 24-hour repeating automatic current protocol similar to that described for the DoL cell was employed. Every hour the cell was set to open circuit for 2 seconds and the potential between the hydrogen electrode and the Pd cathode was recorded at ~ 25 ms intervals. Fifteen minutes before each open circuit decay the power supply anode connection was moved from the central anode to the auxiliary anode using a computer

controlled 40 A mechanical relay. This was done to allow the N_2 to purge the O_2 from the main electrolysis chamber. The data acquisition system was similar to that used for the DoL cells.

A DoL cell used for empirical E_{surf} measurements had D_2 bubbled over a platinized Pt hydrogen reference placed directly below the Pd cathode. The potential was measured without the use of an auxiliary anode.

3. Results

Since we are unable to design experiments which are guaranteed to yield high loading we perform replicates of those experiments which we feel are most likely to do so. From these replicates we choose the cells which best meet our three criteria and transfer them to the calorimeter. This requires us to load Pd cathodes in the DoL farm using the identical cell used in the calorimeter. We therefore tested different Pd sources for cathodes that can load well in a closed cell, with a recombiner catalyst at room temperature.

There are three criteria which must be met to assure the viability of the DoL farm concept: (1) The cathode must survive extended periods, up to 120 minutes, of open-circuit without degrading subsequent loading performance. (2) Cathodes must load well at room temperature in a closed cell with a recombiner catalyst. (3) The cell must survive the physical transfer from the DoL farm into the calorimeter without degrading its performance.

Testing the first criterion, Figure 3 shows a typical loading curve (R/R_0 vs time) for a 3 mm diameter cathode under three different current protocols designed to test a cathode's sensitivity to open-circuit. The three current protocols used are (1) a 5 hour open circuit step; (2) a 4.5 hour open circuit step immediately before a 0.5 hour anodic strip; and (3) a 0.5 hour anodic strip. The open-circuit step does not degrade and probably enhances the cathode's subsequent loading, at least for the next few cycles.

Although this experiment used E#5 Pd, 3 mm diameter × 30 mm long annealed before use, we have found this result to hold true for all of the Pd that we have tested. This protocol may allow surface impurities to desorb slowly without disturbing the Pd near-surface structure. Alternatively, absorbed D may relax slowly until $D:Pd_{bulk}$ and $D:Pd_{surf}$ are equal, minimizing stress on the Pd grain structure. We are not yet able to distinguish the effects of these and any other possible mechanism initiated by an open-circuit step.

Figure 4 shows the results of our attempts to load a cathode of I/M#1 Pd (cast in air with CaB_6 added), 1 mm diameter × 30 mm long, with D to D:Pd > 0.95 ($R/R_0 < 1.6$). This experiment verifies that we can load a Pd cathode to high loading in the new DoL cell for transfer into the calorimeter. However, the cathode deloads at extended times and at higher current densities. It is encouraging that the loading of ~ 0.95 is maintained at ~ 400 mA-cm^{-2}, which implies that other cathodes from this lot should be able to sustain high loading at moderate current densities for extended periods.
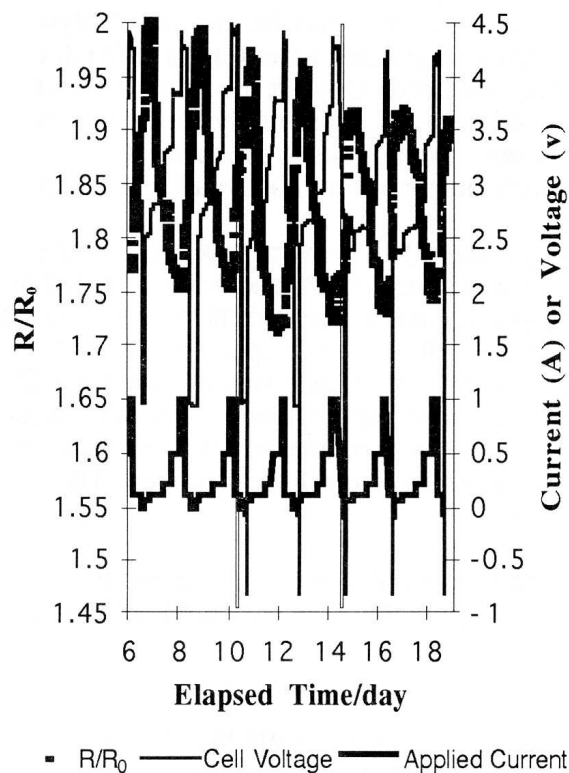
Figure 3. Effect of open-circuit and anodic strip protocols on loading
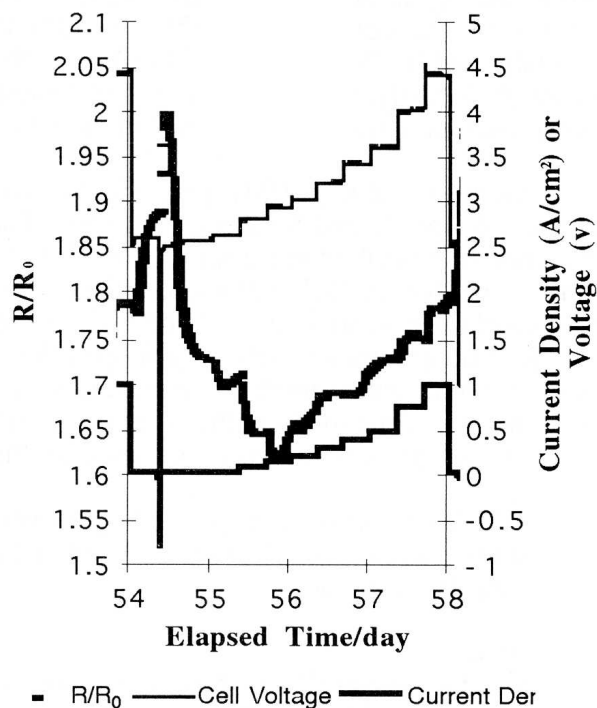

Figure 4. Typical loading curve for a well loaded Pd cathode

In another experiment, cathodes identical to those used for the experiment shown in Figure 4 with a 1 M LiOD electrolyte with no additives, yielded significantly different $D:Pd_{max}$ results. Occasionally the loading for the poorly-loaded Pd increases with current such that cathodes which had significantly different loading at lower current densities have the same mediocre, but stable loading, at some higher current. Loading performance is quite reproducible over several cycles within the same experiment. The good individual reproducibility allows us to draw conclusions about different parameters by comparing the best loading performance from each set of replicates or about different additives by making additions during experiments.

Next, we studied Pd cathodes of a different source and treatment, all performed in 1M LiOD without electrolyte additives. The results are shown in Table 2. Obviously in this cell design, I/M #1,1/M #2 and J/M "Z" are better than E#5 for initial loading. However I/M #1 holds its loading best at higher current densities. Also we found earlier that annealing and etching the Engelhard Pd cathodes in our laboratory was necessary for good loading but similar processing by IMRA Materials at the time of manufacture made further processing at SRI unnecessary and, in some cases undesirable.

Having established the baseline performance of different cathodes in pure LiOD we compared this to the performance found using electrolytes containing 200 ppm Al, shown in Table 3. This Al in LiOD electrolytes shows no beneficial effect on any of the cathodes tested in the new cell design when compared with LiOD. Also shown is a comparison of loading results in the old cell designs using Engelhard cathodes with LiOD and Al, where the E#3 cathode loaded very well. Dissolved Al usually improved and never diminished the loading in the old cell design.

Table 2. Different Pd Sources, No Additives

Sample	Pd	D:Pd$_{max}$/$\bar{i}$ mA-cm^{-2}	D:Pd @ 300 mA-cm^{-2}
AA5	E#5, 3 × 30 m, anneal, etch.	0.93/300	0.93
V4	I/M#1*, 1 × 30 mm, etch	> 0.95/100	0.93
X3	I/M#2*, 1 × 30 mm	> 0.95/200	0.9
Y6	J/M ("Z") 1 × 30 mm, etch	0.95/150	0.94

* Annealed and etched by manufacturer

Table 3. Effect of Al in Electrolyte

Sample	Pd Source	Additive	D:Pd$_{max}$/$\bar{i}$ mA-cm^{-2}	D:Pd @ 300 mA cm^{-2}
AA5	Eng. #5	--	0.93/300	0.93
U5	Eng. #5	Al	0.92/100	0.88
V4	I/M#1	--	> 0.95/100	0.93
U3	I/M#1	Al	0.95/100	<0.88
V2	J/M "Z"	--	0.95/150	0.93
V3	J/M "Z"	Al	0.92/100	0.8
S2†	Eng. #3	Al	0.97/160	0.93
S4	Eng. #5	Al	0.93/80	0.91

† Old Cell Design

   Table 4 summarizes the effect of some dissolved species and some *in-situ* additions on cathode loading. The Rare Earth elements Sm and Nd were added at the suggestion of Professor Hagelstein of MIT in hopes of depositing them onto the Pd to yield anomalous radiation or thermal effects. The presence of these metals, attached to the Pt anode, had no significant effect on loading performance. Experiments U3 and U2 had ~ 200 ppm Al dissolved in the electrolyte at the outset and both cathodes had loaded to D:Pd$_{max}$ = 0.95. On day 21 of the experiment ~ 1000 ppm Si and ~ 2000 ppm Cu were added to cells U3 and U2, respectively. The Si addition had no significant effect on the loading performance of the U3 experiment while the Cu addition reduced D:Pd$_{max}$ = 0.91.

   Open cells may yield higher loading than those in closed cells due to Cl^{-} and other ion additions during the D$_2$O top-up which may contain impurities leached from the storage bottle. Experiment XI had run with no electrolyte additives until day 50 when 1 ppm LiCl was added, whereafter the maximum loading increased from D:Pd = 0.9 to ~ 0.93 after the Cl^{-} addition, but diminished back to 0.9 after 3 current-step cycles.

Table 4. Effect of Various Additives

Sample	Pd	Additive	D:Pd$_{max}$/$\bar{i}$ mA-cm^{-2}	D:Pd @ 500 mA cm^{-2}
Z2	J/M "Z", anneal, etch	--	0.91/500	0.91
Z4	J/M "Z", anneal, etch	Sm	0.9/500	0.9
Z5	J/M "Z", anneal, etch	Nd	0.9/500	0.9
U3	I/M#1*	Al, Si[†]	0.95/100	<0.88
U2	I/M#1*	Al, Cu[†]	0.91/100	<0.85
X3	I/M#2*	--	> 0.95/200	0.9
XI	I/M#2*	Cl^{-}[†]	0.93/200	0.88

* Annealed and etched by manufacturer
[†] Added during experiment

Thermodynamically relevant electrochemical surface potentials (E$_{surf}$) can be used to estimate surface loading (H:Pd$_{surf}$) in this system. A good estimate of H:Pd$_{surf}$ can be used to estimate HPd$_{bulk}$ at steady state cathode loading without intrusive axial resistance measurement. We designed a cell (see Figure 2) to simultaneously measure E$_{surf}$ and H:Pd$_{bulk}$. The overpotentials affecting the measurement have been mathematically eliminated using the current interruption method. We used H$_2$SO$_4$ electrolyte, with no dissolved cations or metals, to minimize interfering reactions on the Pd surface that could change E$_{surf}$ and to assure the attainment of high loading in H$_2$O.

The electrochemical surface potential of the Pd cathode, E$_{surf}$, is reported relative to the standard hydrogen electrode (SHE). E$_{surf}$ is positive when H:Pd < 0.7 and negative when H:Pd > 0.8 as shown by Lewis.[10] For ease of presentation -E$_{surf}$ is plotted since only the region where H:Pd > 0.8 is shown. Figure 5 shows -E$_{surf}$, D:Pd$_{bulk}$, and $\bar{i}$ measured on a J/M "Z" 1 mm diameter $\times$ 10 mm long, cathode in 0.1M H$_2$SO$_4$. The relatively reproducible H:Pd$_{bulk}$ reaches a maximum of ~ 0.93 at ~ 0.9 A cm^{-2}. The most negative potential obtained at H.Pd$_{max}$ (0.93) was E$_{surf}$ = -0.12V vs. standard hydrogen electrode (SHE). After 5 cm^3 of electrolyte was removed and replaced with 5^3 cm of 0.1 M Li$_2$SO$_4$, no effect attributed to the Li+ ion, including simple Li adsorption, was seen during the 36 hour remainder of this experiment. However, the addition caused the cathode to load more poorly during the remaining two current step cycles. Figure 5 shows -E$_{surf}$ tracking H:Pd$_{bulk}$ at this lower value.
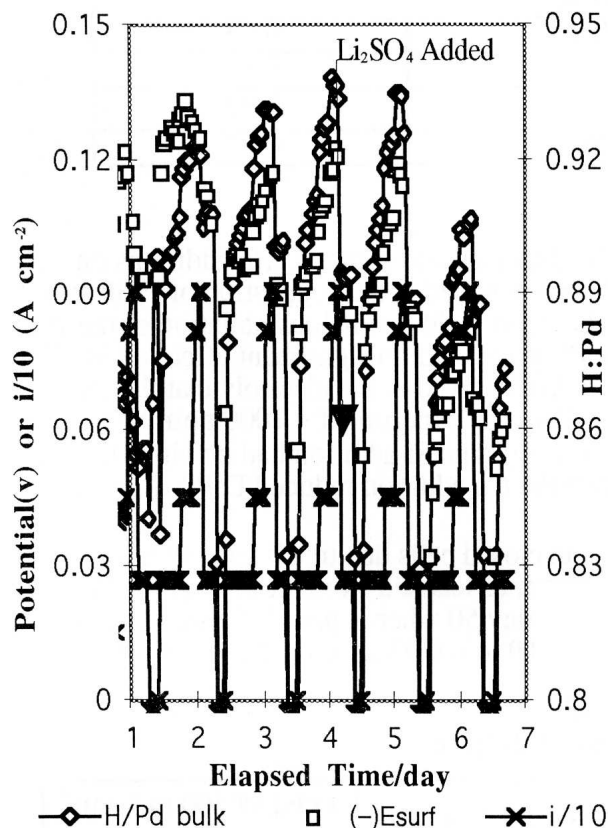
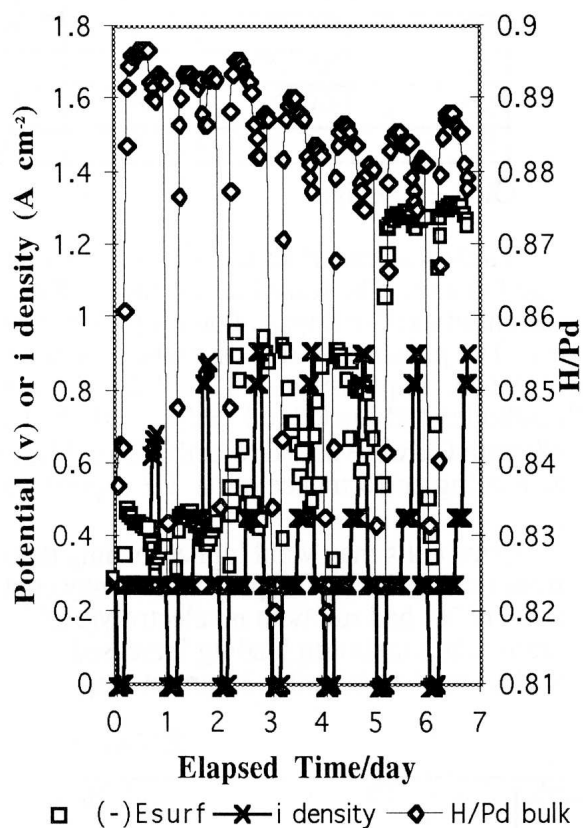**Figure 5. Correlation of surface potential with H:Pd in 0.1 M H₂SO₄**

Figure 6. Correlation of surface potential with H:Pd in 0.2 M LiOH

At the experiment's termination the electrolyte was replaced with 0.2 M LiOH. The results of this new experiment are shown in Figure 6. Using the same current-step cycles the maximum cathode loading is ~ 0.9. The largest negative value of E_{surf} obtained was -0.4V for the first two current cycles then alternated between -0.4V and -0.9V, and reached a stable value of -1.3 V when H:Pd_{bulk} = 0.89. E_{surf} varied from -1.15 V to -1.3V tracking H:Pd_{bulk} as it varied from ~0.85 to ~0.89 after cycle 4. These results suggest a surface film formed during the electrolyte replacement when the cathode was exposed to air, probably oxide and/or hydroxides of surface lithium. Another surface film formed gradually, or replaced the first, starting with the third current cycle. This latter "film" may be Li absorption into the Pd cathode.

A technically simpler experiment was performed in a modified cell, where *in-situ* E_{surf} measurements were made in 1 M LiOD. Measuring the potential at the end of each current step to assure the attainment of the D:Pd_{bulk} steady state, the maximum loading obtained was ~ 0.91 and most negative E_{surf} = -1.02 V. These raw values of E_{surf} can be empirically modified to approximate the potentials predicted for E_{surf} versus D:Pd (see below).

4.   Conclusions

We have designed, constructed, and run on the bench several cells to measure D:Pd loading and have successfully transferred these cells to our mass-flow calorimeter system. We have met the criteria necessary to assure the viability of the DoL farm concept. While testing the effect of

open-circuit we have shown that a combination of open-circuit and anodic strip steps generally yields improved cathode loading.

We have verified that different types of Pd have different loading characteristics in our new cell design and that Pd from specific sources load differently in the new cell design when compared to performance in the original cell design. I/M #1, which was cast in air with CaB_6 added to the melt, held its loading to higher current densities than did I/M #2, which was cast in *vacua* with no additives although both were processed from the same high-purity Pd powder. Although vacuum processing may introduce deleterious impurities, it is more likely that air processing was beneficial. High temperature air processing may form volatile oxides of deleterious impurities which volatilize. A more subtle explanation may involve CaB_6 particles acting as inter-granular or intra-granular stress-relief facilitators at high D flux (large $\bar{i}$).

We have also shown that high purity Pd (I/M #1, I/M #2 and J/M "Z") loads better than 99.9% pure Pd from Engelhard. Loading performance for the high purity Pd is not enhanced by further annealing immediately before use. Poor replicability among ostensibly identical experiments remains an important problem. This may be due to irreproducible metallurgy and/or random surface contamination along the length of Pd rods or imperceptible differences in cell preparation procedures.

In the series of experiments described here, loading performance in 1 M LiOD electrolyte with 200 ppm (molar) Al was no better and sometimes worse when compared to those performed in pure LiOD. Of the electrolyte additives tested, either present at the experiment's commencement or added *in situ,* only Cl^- ion was found to be beneficial, yielding a temporary loading increase. This Cl^- ion addition may unintentionally take place during top-up of open cells. The addition of Cu ions was detrimental to loading while Nd, Sm, and Si had no observed effect on performance.

We have measured the electrochemical surface potential (E_{surf}) and $H:Pd_{bulk}$ (using axial resistance measurement) of a Pd cathode electrolyzed in H_2SO_4 and LiOH. At loadings of H:Pd < 0.8 the potential versus loading curve reproduces that reported by Lewis.[10] Using recent data from Baranowski[9] for H:Pd vs $[H_2]$, hydrogen fugacity (f(H)) versus H:Pd curves have been generated. Using the Nernst equation the $H:Pd/E_{surf}$ relationship can be estimated and fit to a third order equation:

$$H:Pd_{surf} = 0.727 - 1.78 * E_{surf} - 0.29 (E_{surf})^2 + 9.814 (E_{surf})^3$$

We found $H:Pd_{surf} > H:Pd_{bulk}$ during increasing loading and at high loading, but at steady state loadings of D:Pd < 0.94 the bulk and surface loadings were found to be sensibly the same in the absence of reducible cations.

The addition of Li^+ ions to an acid electrolyte yielded poorer cathode hydrogen loading, possibly due to disruption of a beneficial film already formed on the Pd surface, but did not otherwise affect E_{surf}. Exposing the cathode to air during electrolyte transfer caused a significant change (-300 mV) to the Pd surface potential, possibly due to the formation of a stable oxide or hydroxide of lithium. Continued cathodic electrolysis yields the slow (72-hour) formation of a new surface state which changed the potential by -1.2V relative to that measured in acid. Assuming that Li has diffused in the Pd cathode this new potential may be due to a Pd Lix/H surface reaction or a mixed potential of the Pd/H and Li/H reactions in OH^-. We hope to identify the species and/or surface states which correspond to this measured E_{surf} in future studies.

We have also measured E_{surf} in 1 M LiOD in a modified version of our DoL cell. The stable measured potential E_{meas} (-1V @ D:Pd = 0.91) after several loading cycles was 900 mV more negative than the E_{surf} predicted in the absence of reducing cations. Also, since at high current densities the D_2 bubbling does not completely flush the O_2 from the cathodes electrolyte environment, E_{meas} contains a reproducible current-dependent voltage offset. The equation

$$E_{surf} = E_{meas} + 0.89 + 0.05 \ (i) \ (D:Pd_{bulk} > 0.88)$$

where i is the positive cathodic current in A, yields values of E_{surf} comparable to those measured in H_2SO_4. These can be used to compare $D:Pd_{surf}$ to $D:Pd_{bulk}$ in order to predict which Pd cathodes are capable of achieving high bulk loading with a chemically clean surface. We hope to also identify the reactions and/or surface states from which these surface potential arise. In sum, we have been able to correlate measured electrochemical surface potentials with bulk loading in the Pd electrolysis system in H_2SO_4, LiOH and LiOD electrolytes.

Acknowledgments

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