

IN-SITU CHARACTERIZATION OF SPUTTERED PD THIN-FILMS UNDERGOING ELECTROLYSIS

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ABSTRACT

In-situ measurements on the resistance and temperature variations of Pd thin films are carried out during electrolysis. The measurement is made possible by covering parts of the Pd films with a protective layer of thermal and electric insulators. Electrical contacts are made by using either silver epoxy or indium soldering. The resistance-loading curve deviates somewhat from the typical curve for a bulk Pd/H(D) system. The initial resistance increase shows a much faster hydrogen diffusion rate along the film axis than that observed in bulk systems. The characteristic resistance-loading curve is explained by the electronic band structures of Pd loaded with different H(D) fractions. An excess heat of 30% during the electrolysis process was detected using an open calorimeter and a novel circuit switching methodology. The corresponding excess power density reaches 100 W/cm^3 .

1. INTRODUCTION

There have been recent reports of nuclear transmutation and excess heat phenomena [1] in light water electrolysis carried out through cathodes made of hydrogen absorbing metals. Reproducibility of such experiments is required in order to accomplish a clear understanding of such phenomena. Because a high H/PD ratio is regarded as the necessary condition for all of these phenomena to occur. Therefore an in-situ determination of the H loading with metal cathodes' undergoing electrolysis is essential to understand the phenomena. The measurement of a resistance change in Pd is the most used method to determine the loading factor. Thin film Pd electrodes sputtered on various substrate surfaces have also been a focus of the University of Illinois research. These films have several advantages: more reaction area for the same amount of metal, and the potential to borrow ideas from the semiconductor industry for the manufacturing process. However, there are also some disadvantages, one of the main questions being the maximum loading ratio that can be achieved. The Pd matrix needs to expand up to 3.4 % in order to accommodate H at an 1:1 ratio. Such an expansion is limited by a rigid substrate on which Pd is often sputtered, hindering the loading ratio that can be obtained without any physical damage to the film. This may account for unsatisfactory reproducibility of experiments where a large amount of excess heat (about 500%) has been reported. Therefore the present work is intended to determine thin-film loading using a resistance technique for the measurement.

2. EXPERIMENTAL

The electrodes are made by sputtering Pd thin films of 8000 \AA on alumina or glass substrates. An AJA International ATC-2000 sputtering machine was used. The background vacuum was kept as low as 2×10^{-7} Torr and the sputter films were of good surface morphology under metallurgical microscopes. The film adhesion is suitable for alumina substrates.

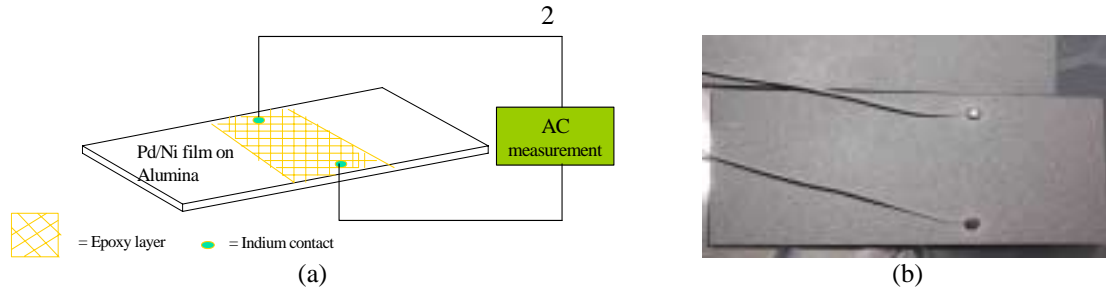


Figure 1. (a) Schematic for the resistance measurement.
(b) A Pd/Ni electrode with electrical leads attached through indium contacts

The immediate problem encountered in measuring resistance during electrolysis is the bypass (short-circuit) effect of electrolyte. For a wire experiment [2], this is not a critical issue, because the conductance of metal wire dominates in that geometry. However for thin films in our electrolytic cell configuration, the conductance of electrolyte and Pd films are comparable. Therefore the electrolyte must be isolated from the part of films where the actual resistance measurement is carried out: the electrolysis happens in the non-covered part, and hydrogen diffuses to the measurement area by density gradient [3]. Fig. 1(a) is the basic geometry for resistance measurement. AC is used to de-couple from the DC electrolysis current. The standard AC frequency used is 10 KHz. The AC frequency is varied from 10 to 100 KHz, or over 4 decades to determine any frequency dependence of the experiments. The resistance change measured was within 2%. A typical half-finished (i.e., “uncovered”) electrode with indium contacts is shown in Fig. 1(b). The electrolysis is carried out at currents around 1 A, with the corresponding voltage drop in the order of 4 V. The resistance-time curve is shown in Fig. 2.

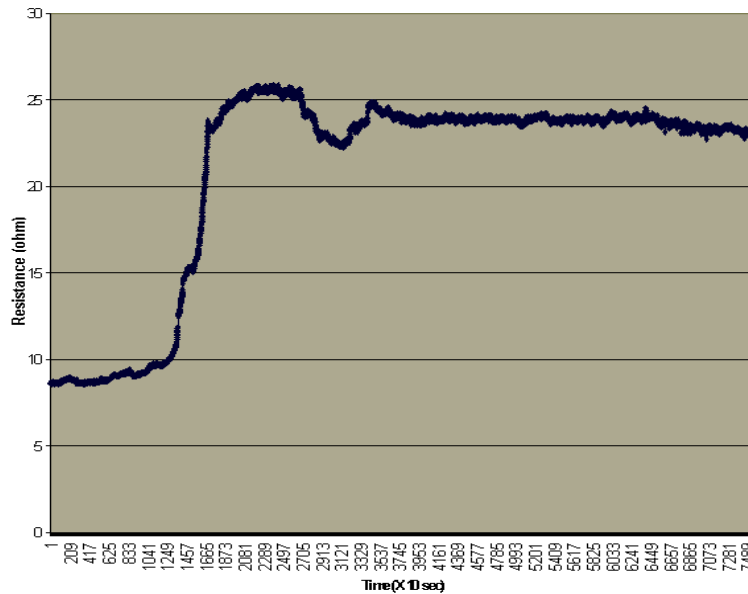


Figure 2. Resistance of Pd thin-film versus time. Note that the time axis is in unit of 10 seconds.

The data are similar to the typical loading curve of bulk electrodes or wires but with some significant differences. First the initial loading rate is much faster. Ordinary experiments take weeks or even months to load, but here the resistance reached maxima in a matter of half an hour. There are possibly two contributing factors. The first factor is due to the fast H diffusion through grain boundaries that are abundant in sputtered films. Sputtered metal films tend to have much smaller grain size compared to a bulk metal made of ordinary metallurgical methods. As a result, the films are rich in grain boundaries. This helps the diffusion of the hydrogen all over the film. The second factor is associated with a higher current density often used with the film configuration. The conducting cross-section of a typical sputtered electrode is measured $2.5\text{cm} \times 0.8 \mu\text{m} = 2 \times 10^{-4} \text{cm}^2$. The resulting current density is at least 2 orders of magnitude higher than those for wire experiments. A higher current density brings about a higher electric field, resulting in a higher drift velocity for H ions.

A preliminary calorimetry study was prepared to probe the excess heat generated in the electrolysis process. A new “switch” scheme is used in order to better investigate whether any excess heat is generated. As shown in Fig. 3(a), a double-blade double-throw switch is used. A certain amount of calibration power P_c was first applied to the resistor to create temperature rise ΔT_c for calibration purposes. Then electrolysis was initiated by switching the power from the resistor to the electrodes. The electrolysis power P_e applied now is fine-tuned so that $P_e = (V_e - V_d) \times I_e = P_c$, where V_d is the dissociation voltage with V_e , I_e the electrolysis voltage and current, respectively. By observing the new temperature rise ΔT_e as opposed to the previous ΔT_c , a clear-cut determination of excess heat is then possible. This procedure is repeated periodically to insure the stability of the calibration point.

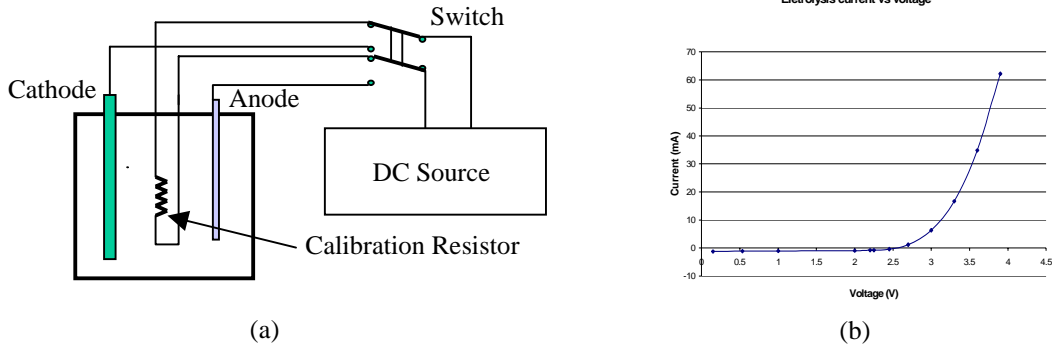


Figure 3. (a) Schematic of the “switch” calorimetry.
 (b) The I-V characteristic of our electrolytic cell used to determine the dissociation voltage V_d .

The determination of dissociation voltage V_d is important. The often quoted 1.48V is actually for Pd-black electrode only and does not apply to different surface [4] and pH conditions [5]. Therefore V_d has to be determined from experiment. The I-V curve of the electrolytic cell was measured and from Fig. 3(b) V_d is seen to be 2.2 V. The recombination in an open-cell calorimeter such as this one is often a concern. Willis however has shown that it is safely limited to 5% for a typical cell [6]. Assuming that this condition holds, and with all other possible error sources considered, the excess heat calculated using the measured dissociation voltage is around $30\% \pm 10\%$. A detailed error breakdown is summarized in Table 1.

Error Source	Error Percentage, %
Temperature in-homogeneity	1
Temperature measurement	1
Evaporation loss	2
Recombination	5
Power measurement	1.2
Total	10.2

Table 1. The error budget of the “switch” calorimetry.

In order to check if there are some “hot-spots” on the Pd surface causing erroneous results, some 10K thermistors was attached across the Pd surface. To improve the thermal conductivity, a thin layer of heat-conducting silver epoxy was applied. The thermistors on the surface detected sizeable temperature increase as compared to the electrolyte, but the temperature and spatial resolution of this technique have not been optimized so as to detect individual hot spots on the film. At a typical current of 0.5 A, the temperature rise at the electrode surface is only about 0.2°C, far less than what we expected for “hot-spots.” One of the problems is associated with the high thermal conductivity of the alumina substrate. This difficulty may be solved in the future by different substrates with better thermal insulation.

3. THEORETICAL

The resistance-loading curve is potentially explained by our band structure calculations [7]. At very low loading, one hydrogen faces a number of Pd atoms. Then the hydrogen tends to lose its electron to

the host Pd metal because its electron affinity, 0.702 eV, is much less than that of bulk Pd, 5.12 eV, which is also often termed the “work-function” for a bulk metal. The H then tends to be fully ionized. The ionized hydrogen acts as a strong scattering center and gives rise to an increase in resistivity. At higher loading, say near Pd/H=1, the situation is different, because the affinity of a single Pd atom, 0.518 eV, is comparable to and actually a little less than that of H. Therefore the H is now neutral or more likely, slightly negatively charged. The scattering caused by this H state is therefore reduced. As a result the resistance will show a decrease. The band-structure calculation shown in Fig. 4 further supports such an argument.

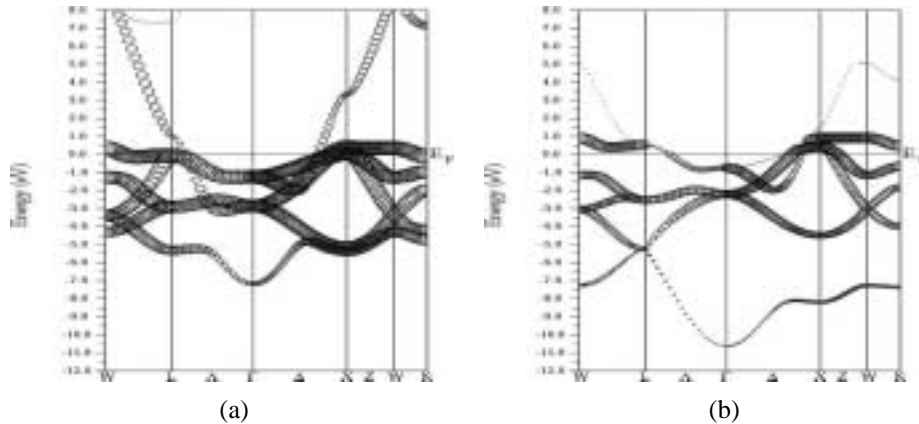


Figure 4. (a) The Band structure of Pd and, (b) that of PdH, showing charge transfer from Pd to H. The size of circles signifies the amount of contribution from Pd atomic states. Observe that: 1) Circles in PdH are smaller: charge is transferred out of Pd. 2) H introduces new s-like states at the bottom of Pd d-bands.

4. CONCLUSION

Resistance measurements of Pd thin films were carried out under electrolysis. The results show that the film was loaded slightly over 0.80. Higher loading are generally desired. One possible reason that they were not obtained here is the large strain from the Pd lattice expansion incurred during H loading. Resulting micro-cracks may have caused H leakage. An approach to resolve this dilemma could be to investigate is to adding an additional surface barrier layer.

ACKNOWLEDGEMENT

The authors are grateful to support from Lattice Energy, LLC. We gratefully acknowledge Dee Staley and Prajakti Joshi for their editorial support.

REFERENCES

- [1] G. H. Miley et al., *Proc. ICCF-6*, Toya, Japan, October (1996), p679.
- [2] G. H. Miley et al., *Proc. ICCF-8*, Lercici, Italy, May (2000), p169.
- [3] N. Luo et al., Resistance Measurement of Sputtered Pd Thin-Films During Electrolysis, *Bult. APS, APS Spring Mtg.*, Indianapolis, IN, March (2002).
- [4] A. G. Lipson, private communication.
- [5] P. Atkins, *Physical Chemistry*, 5th Ed., (Freeman & Company, New York, 1994) p. 344.
- [6] F. G. Wills, *J. Electroanalytical Chemistry*, **426**, 177 (1997).
- [7] G. H. Miley et al., Transport in Thin-film Pd-Ni Cathodes, *Bult. APS, APS Spring Mtg.*, Indianapolis, IN, March (2002).