

Some Observations Related to the Presence of Hydrogen and Deuterium in Palladium

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ABSTRACT

Surface and bulk analytical work carried out on palladium rod samples returned to Johnson Matthey by Fleischmann and Pons indicates that a number of elements, including platinum and lithium were deposited on the surface during electrolysis in D_2O . Surface analysis via time of flight SIMS indicates that the Li^6/Li^7 isotope ratio is unusually low but no original reference is available.

One electrolysed rod exhibited recovery of part of the wrought microstructure which would ordinarily require a temperature of $> ca. 200^\circ C$, and another rod showed recrystallisation of a portion of its length and this would normally require a temperature of $> ca 300^\circ C$. These effects, which were observed at the ends of the rods away from the spot welds, cannot readily be explained by known processing history, and could not be reproduced by filing or sawing.

Temperature programmed hydrogen absorption/desorption profile measurements on a range of palladium samples indicate wide differences in properties; for example a rod electrolysed in aqueous LiOH solution absorbed hydrogen more readily than a similar rod electrolysed in aqueous NaOH. This technique would therefore seem to be of value in characterising the palladium electrode.

Electrochemical measurements conducted in H_2O show that there are significant differences between the behaviour of Pd in LiOH, and in NaOH and KOH solutions.

1 Analysis of Palladium Rods Returned to JMTC by Fleischmann and Pons

Three of the rods, which had been loaned by JM, were returned from Utah and analysed:

Rod 1: 4mm diameter, 10cm long, as received condition.

Rod 2: 2mm diameter, 9cm long, used as cathode at $64\text{mA}/\text{cm}^2$

Rod 3: 2mm diameter, 1.2cm long, used as cathode at $512\text{mA}/\text{cm}^2$

1.1 Surface Analysis

SEM analysis using a Cambridge Stereoscan 250 Mark II fitted with Princeton Gamma Tech (PGT) System 4 energy dispersive X-ray analyser indicated cracks and scratches on the surface, with the intensity of features increasing from Rod 1 to Rod 3. There was no significant surface contamination on Rod 1 but iron, copper, platinum and zinc were detected on the used rods. SEM EDAX analysis profile plots for percentages of these four elements for various positions along the rod for a penetration depth of one micron indicated platinum concentrations of up to 9% for Rod 3 and up to 2% Pt for Rod 2. The other elements were present in lower percentages (usually <1%).

XPS analysis was undertaken with a Kratos XSAM 800 surface analyser using a beam of argon ions at 4keV to etch back the surface until the bulk metal was reached. Elements found were oxygen, nitrogen, sodium, chlorine and palladium on Rod 1; oxygen, sodium, silicon and platinum on Rod 2; and oxygen, silicon, iron, sodium, platinum, zinc and copper on Rod 3. Spectral line overlaps interfered with the detection and measurement of lithium in the presence of iron. Instead of a sharp demarcation at the palladium surface the impurities showed a gradual fall off. This is interpreted as an effect of the roughness of the surface with a surface film of variable thickness within the analysis area.

Time of flight SIMS analysis has been carried out on the two palladium Rods 1 and 2. A Cambridge Mass Spectrometry TOF SIMS instrument was used, and it was operated so that not more than one monolayer of metal

was ablated in a twenty minute period during spectrum collection, so that isotope ratio measurements were not confused by depth profiling effects. The surface of the sample was ablated by a gallium ion beam. This has the advantage that oxide species are not present to complicate the mass spectrum as is normally the case when an oxygen ion beam is used. The palladium isotope values measured for the two rods are closely similar, but differ somewhat from values quoted in the literature.

ISOTOPE	VIRGIN ROD No.1	USED ROD No.2	LITERATURE VALUES	ISOTOPE	REPLICATE MEASUREMENTS			LITERATURE VALUES
102	1.28	1.31	0.92					
104	11.58	11.50	10.43					
105	22.96	23.77	22.33	6	4.0	4.8	4.7	7.5
106	28.00	28.39	27.23					
108	25.25	23.90	26.70	7	96.0	95.3	95.3	92.5
110	1091	11.10	12.36					

Figure 1. TOF SIMS Pd isotope ratios(%)

Figure 2. TOF SIMS Li isotope ratios(%)

No lithium was detected at the centre of the rod. Lithium was detected at a very low level on Rod 1 after the removal of four monolayers and only as the isotope of mass 7; this was considered to be a trace contaminant. After the removal of four monolayers on Rod 2 a larger amount of lithium was detected with both isotopes being found. The measured values for isotope 6 seem to be consistently different from the expected values. So far as can be ascertained from an inspection of the mass spectra there is no possibility of a significant interference with isotope 7 so that the effect is considered to be real. There was no opportunity to measure the ratio on the lithium used in the electrolysis cell.

Overall conclusions from the surface analysis results were that platinum was detected on the electrolysed rods by all the methods used, and O, Si, Fe, Na, Zn, Cu, Li, Cl were also detected. The Pt, Cu, Fe, and Zn were present as metals.

1.2 Bulk Analysis

Spectrographic analysis for trace impurities is normally made on pure metals produced by JM. The batch analysis for the materials supplied to Fleischmann and Pons is given in Figure 3. Samples for ICP were dissolved in aqua regia in closed containers (to minimise loss of Ru). Rods 1 and 2 were analysed in quadruplicate and Rod 3 in duplicate. Results are given in Figure 4. Li and Pt show increases from Rod 1 to Rod 3. B, Al, Cu and Au values are substantially constant, low levels of Rh and Ru were found in all these analyses.

Element	Ingot 1 ppm	Ingot 2 ppm
Al	5	10
B	20	20
Ca	30	30
Cr	2	3
Cu	10	10
Fe	10	10
Ni	1	1
Ag	1	1
Pt	10	10
Au	30	30

Mg and Si were detected at levels below 1 ppm.

Figure 3 Spectrographic bulk analysis

INSTRUMENT USED - VG Plasma Quad PQ2.

Element	ROD 1 ppm	ROD 2 ppm	ROD 3 ppm
Li	6	9	12
B	25	25	31
Al	7	8	9
Cu	13	14	15
Zn	< 1	< 1	6
Rh	1	1	2
Ru	0.6	0.4	0.3
Au	13	13	13
Pt	6	16	27
Pb	0.2	0.3	0.6

Elements not detected:
 < 0.1 ppm Bi, Th, U, Ta, Re, Hf, In.
 < 0.2 ppm Hg, Tl, Os, Ir, Cs, Ba, Sb, Nb, Mo, Y, Sr, Rb, Mn, Co and all lanthanides.
 < 1 ppm W, Te, Zr, Ga.
 < 2 ppm Ni, Mg, Tl.
 < 5 ppm Ge.
 < 10 ppm Cr.

Not determined:- Cd, Ag, V, Na, Ca, Si, P, K, As, Fe, Se and halogens.

Figure 4 ICP-Mass Spec bulk analysis

1.3 Metallography

The end of Rod 2 furthest from the spot weld exhibited microstructural variation from the norm, i.e. recovered grain structure, which would be consistent for instance with temperatures of greater than 200°C having been generated for a short period. Rod 3 showed complete recrystallisation over a distance of approximately 4mm from the non-spot welded end, consistent with a temperature of greater than 300°C having been generated. However we do not know the total history of the rods after they passed out of our hands so we cannot independently draw definite conclusions.

Vigorous filing and sawing of virgin and hydrogenated rods did not produce this recrystallisation phenomenon.

2. Temperature Programmed Hydrogen Absorption/Desorption on Various Palladium Samples

2.1 Temperature Programmed Absorption/Desorption Technique

Hydrogen absorption and desorption is measured by monitoring changes in the exit hydrogen concentration of a 10% hydrogen in nitrogen stream passing over the sample at a slow rate (25ml per minute). The sample itself can be heated or cooled at a linear rate. The method allows for the measurement of very small amounts of hydrogen and the temperature at which it is absorbed (or reacted) and desorbed. Typically the temperature is cycled between ambient and 400°C at 5°C per minute, one complete cycle therefore lasting some three hours. For samples which have been electrolytically charged the total hydrogen content, usually expressed as H/Pd atomic ratio, and the temperature at which the hydrogen is desorbed can both be measured. The latter reflects the combined effects of changes in hydride structure, changes in the cleanliness and catalytic effectiveness of the surface, and the effects of changes in surface to volume ratio reflecting changes in physical dimensions. Changes in the results between successive cycles can reflect changes in the surface, i.e. reactivation, which can occur during the high temperature part of the desorption cycle.

Our rationale for making such measurements lies in our belief that the differences which seem to occur amongst different palladium samples should be related to their ability to trap hydrogen or deuterium under non-equilibrium conditions, particularly under conditions of incipient temperature increases.

2.2 Measurement of Palladium Hydride/Deuteride Decomposition/Formation

Figure 5 shows typical literature data for the decomposition and formation of palladium deuteride and palladium hydride at one atmosphere pressure as the temperature is changed. As the temperature of a loaded sample is increased, one might expect a rather sharp evolution of hydrogen or deuterium at a relatively low temperature, say below 100°C, as the beta-hydride decomposes, followed by a small loss as the temperature increases and the alpha-hydride decomposes. Cooling the sample should incur a hysteresis effect, absorption taking place at a lower temperature than the

corresponding desorption. These temperatures should be lower for a deuterided sample than one which has been hydrided. Figure 6 gives the Pd-H phase diagram.

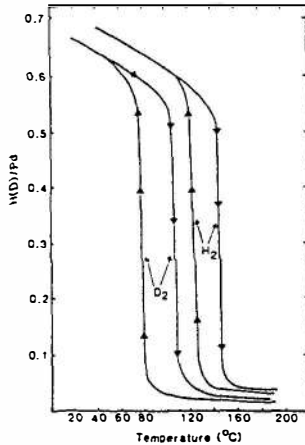


Figure 5. Absorption/Desorption of H or D at 1 atm vs temperature (Sieverts)

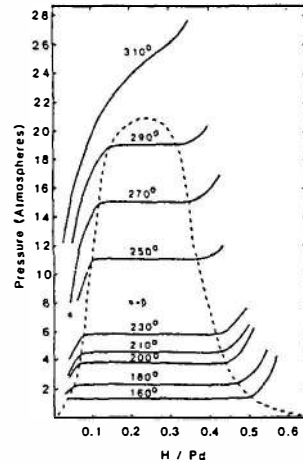


Figure 6. Pd-H Phase Diagram

Since the samples available were very different in geometry and surface condition, the magnitude of the peaks cannot be compared, but this technique does give an indication of the absorption/desorption characteristics of the samples.

The palladium hydride decomposition within these massive electrode samples can be very difficult and in some cases the temperature rises close to the critical temperature (ca 300°C) before decomposition occurs. Figure 7 shows the qualitative results for decomposition of six different samples of various surface to volume ratios. From this figure it is seen that for the palladium sponge and the palladium wire the results are very much what we might have expected from information on hydride formation shown in Figure 5, i e a sharp decomposition at around 100°C. With the 2mm rod, however, there is a marked shift in decomposition temperature with no evidence of significant gas evolution at 100°C. One might expect that the difficulty that the gas would have in permeating to the surface might explain this observation, at least in

part. The results for the 4mm, 6.3mm, and 8mm rods do not however seem to fit this simple explanation so some other factor(s) would seem to be involved. Since the 2 and 4mm rods are from the original experiments in which excess heat was observed, and the 8mm rod was tested at the same time and apparently failed to generate excess heat, we would like to identify these factors. There would seem to be a possible connection between the hydride stability as determined in this way and the heat generation under electrolytic conditions, in line with our original rationale.

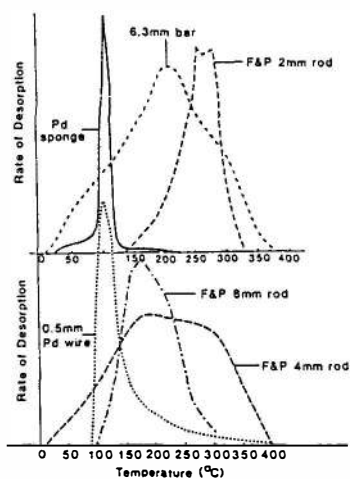


Figure 7. TPD curves for Pd hydride samples

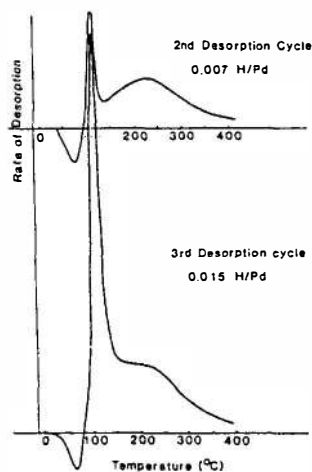


Figure 8. Sequential TPD on hydrided Rod 1

An indication of the effect of surface poisoning can be obtained by repeating the absorption/desorption cycles as indicated in Figure 8 for the same 4mm rod as used previously. When re-hydriding in the absorption apparatus with 10% hydrogen for a relatively short time the hydrogen uptakes are much less, as shown. What is most striking is that a significant desorption spike is now seen at 100°C and this increases substantially for the third cycle. In both cases a second desorption peak is recorded above 200°C which seems to correspond with the peak observed after electrolytic charging.

2.3 Comparison Between Rehydriding Characteristics of Pd Electrolysed in 0.1M LiOH and 0.1M NaOH

One other interesting observation, another part of the mystery and possibly another part of the solution is shown in Figure 9. This concerns part re-hydriding in the hydrogen absorption apparatus of two similar 6.3mm bar samples hydrided electrolytically in 0.1M LiOH and 0.1M NaOH electrolytes respectively. The initial desorption results were identical, giving broad peaks with maxima at 200°C (see Figure 7). Upon cooling the samples in hydrogen the results shown in Figure 9 were obtained:

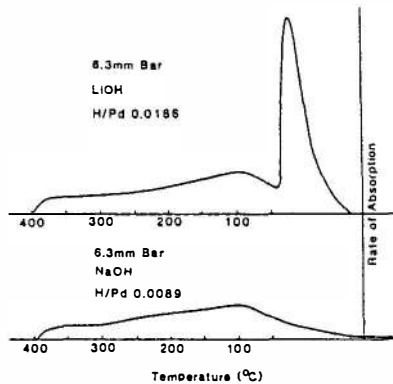


Figure 9. Rehydriding of 6.3mm Pd bar samples electrolysed in 0.1M LiOH and 0.1M NaOH

These results indicate that similar hydrogen re-absorptions occur at elevated temperatures, but there is a marked difference at the lower temperature, where the sample treated in LiOH absorbed hydrogen readily, but that treated in NaOH did not: in fact the pattern of the NaOH case was similar to that of an untreated rod. The low temperature absorption obtained in the LiOH experiment was matched by a corresponding low temperature desorption peak on the next desorption cycle.

Clearly the temperature programmed absorption/desorption measurements described above are indicating large sample differences. Interpreting how these differences arise and how they can be manipulated to an advantage is very much an open question.

The conclusions from the temperature programmed absorption/desorption results are that Pd sponge and Pd wire behaved as expected, but Pd rods gave a range of results probably dependent to some extent on the surface condition of the Pd. The rod electrolysed in LiOH absorbed hydrogen more readily than the similar rod electrolysed in NaOH.

3. Electrochemical Measurements in H₂O

3.1 Galvanostatic Charging of Pd Electrodes

In order to establish whether there are major differences between 'Pd hydride' formed by electrolysis in LiOH and other alkali metal hydroxides, a series of galvanostatic charge/discharge experiments have been carried out on Pd foil and rod electrodes in LiOH, NaOH, and KOH solutions. The charging process is highly sensitive to surface conditions in all of the electrolytes examined. In one experiment (LiOH, 60°C), which as yet we have been unable to reproduce, the overpotential during charging reached a maximum and then steadily declined and the electrode subsequently acted as an efficient hydrogen evolver (Figure 10):

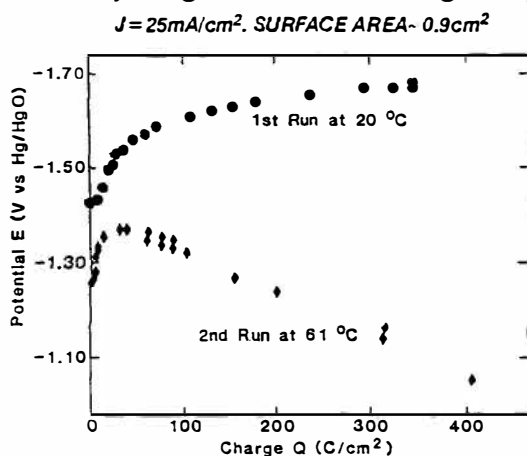


Figure 10. Galvanostatic charging curves for 0.05cm thick Pd foil in 0.1M LiOH at 20 and 61°C

The result obtained with LiOH electrolyte at 60°C could possibly be explained by the surface of the Pd electrode becoming progressively covered with Pt from the anode. The galvanostatic charging experiments carried out to date give (with one exception) similar results in the

three electrolytes tested. However there is some tentative evidence to suggest that galvanostatic discharge is somewhat inhibited in the case of LiOH.

The 'steady state' voltammograms given in Figure 11 show that palladium electrochemistry is sensitive to the nature of the alkali metal cation present. The comparatively diminished re-oxidation wave in the LiOH system is consistent with the galvanostatic discharge behaviour, i.e. some form of inhibition for the hydride dissolution reaction is present. However, the possibility that a surface Pd-Li alloy is involved cannot be ruled out.

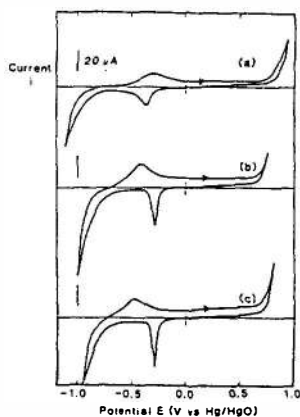


Figure 11. Steady state voltammograms for a Pd disc electrode (surface area $3.1 \times 10^{-2} \text{ cm}^2$) in (a) 0.1M LiOH, (b) 0.1M NaOH, and (c) 0.1M KOH. 20°C, sweep rate 30mV/sec

Our conclusions from the electrochemical measurements in light water are that palladium electrochemistry is sensitive to the nature of the alkali metal cation and there are significant differences in the results obtained for LiOH, compared with those for NaOH and KOH solutions.

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