

SOME OBSERVATIONS RELATED TO THE PRESENCE OF HYDROGEN AND DEUTERIUM IN PALLADIUM

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SUMMARY

Surface and bulk analytical work carried out on Pd rod samples returned to JM by Fleischmann and Pons indicate that a number of elements, including Pt and Li were deposited on the surface during electrolysis in D₂O.

One electrolysed rod exhibited recovery of part of the wrought microstructure which would ordinarily require a temperature of > ca. 200°C, and another rod showed recrystallisation of a portion of its length and this would normally require a temperature of > ca. 300°C. These effects cannot be readily 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 Pd samples indicates wide differences in properties; for example a rod electrolysed in LiOH absorbed hydrogen more readily than a similar rod electrolysed in NaOH. This technique would therefore seem to be of value in characterising the Pd electrode.

Electrochemical measurements conducted in H₂O 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

SLIDE 2

Three rods were returned. The dimensions are given on this slide.

1.1 Surface Analysis

SLIDE 3

There were two principal objectives here. Firstly, an assessment of the surface texture of the rods; and secondly, analysis of the surface to detect the presence of gross contaminants or a layer of electro-deposited material formed during use.

SLIDES 4 - 7

SEM EDX analysis profile plots for Cu, Fe, Zn and Pt percentages for various positions along the rod are given on these four slides. Penetration depth is ca 1μ.

SLIDE 8

XPS analysis using the Kratos XSAM 800 surface analyser showed that the immediate surface of all the rods showed a very high signal for carbon - probably from the plastic bags used for transport.

The surface was etched back, over an area greater than the analysis area, using a beam of argon ions at 4keV and the analysis repeated. It was proposed to repeat this procedure with each specimen until signals indicated that bulk metal had been reached.

Elements found were as follows:

Rod 1 - oxygen, nitrogen, sodium, chlorine and palladium.

Apart from Pd, these elements presumably represent handling contamination, although the levels of chlorine are too low compared to the sodium found for normal handling residues.

Rod 2 - oxygen, sodium, silicon and platinum.

Rod 3 - oxygen, silicon, iron, sodium, platinum, zinc and copper.

The composition profiles for the surface layer showed that sodium and silicon were removed fairly rapidly during the etching process; for Rod 2 after 100Å, and for Rod 3 after 600Å.

After removal of the Na and Si the other metallic contaminants, Pt, Cu, Fe and Zn became detectable and achieved maximum values which declined again as the bulk metal was approached. Pt, Cu, Fe and Zn were present as metals.

Spectral line overlaps interfered with the detection and measurement of Li in the presence of Fe and the measurement of O in the presence of bulk Pd.

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.

SLIDE 9

Time of flight SIMS analysis has been carried out on two palladium rod samples recovered from the experiments carried out by Professors Fleischmann and Pons. The samples examined were the as received 4mm Rod 1 and the 2mm Rod 2, which was electrolysed at 64mA/cm^{-2} . The equipment used was a Cambridge Mass Spectrometry TOF/SIMS. It was operated so that not more than 1 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 values measured for the two rods are closely similar. The values differ somewhat from values quoted in the literature; no explanation is currently offered for this in terms of instrumental parameters.

SLIDE 10

No lithium was detected at the centre of either rod.

Lithium was detected at a very low level on Rod 1 after the removal of 4 monolayers and only as the isotope of mass 7. This was considered to be a trace contaminant.

After removal of 4 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.

This work is regarded as preliminary in that better information might be expected to be gained from a rod electrolysed at a higher current density. A continuation of the profiling which was not attempted in this case would show how deeply the lithium has penetrated into the rod.

Before the analysis the rods were washed in water, hot arklone and ultra-pure hexane to remove any lithium not chemically bound to the surface.

SLIDE 11

Conclusions from surface analyses.

1.2 Bulk Analysis

SLIDE 12

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 here.

SLIDE 13

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.

Li, and Pt show increases from Rod 1 to Rod 3.

B, Al, Cu, Au values are substantially constant, low levels of Rh and Ru were found in all these analyses.

1.3 Metallography

SLIDES 14-16

The end of Rod 2 furthest from the spot weld exhibited microstructural variation from the norm, i.e. recovered grain structure, 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 $>300^{\circ}\text{C}$ 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 PD SAMPLES

2.1 Temperature Programmed Absorption/Desorption Technique

SLIDE 17

Hydrogen absorption and desorption is measured by monitoring changes in the exit hydrogen concentration of a 10% H_2 in N_2 stream passing over the sample at a slow rate (25ml/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 a 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 among 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

SLIDE 18

What then would one normally expect from such temperature programmed desorption and absorption measurements? SLIDE 18 shows typical literature data for the decomposition and formation of palladium deuteride and hydride at one atmosphere pressure as the temperature is changed. At the risk of belabouring the point, 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 β -hydride decomposes followed by a small loss as the temperature increases and the α -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 for one which has been hydrided. SLIDE 19 gives the Pd-H phase diagram.

SLIDE 20

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 adsorption/desorption characteristics of the samples.

In fact the hydride decomposition of 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. SLIDE 20 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 the previous figure, that is a sharp decomposition around 100°C. As we pass to the 2mm rod there is this marked shift in decomposition temperature with no evidence of any 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.

You can imagine how very much we would like to find out what these are when I point out that the 2 and 4mm rods are from the original experiments in which excess heat was observed and that the 8mm rod sample was tested at the same time and apparently failed to generate excess heat. In other words 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.

SLIDE 21

One can get some indication of the effect of surface poisoning by repeating the absorption/desorption cycles as shown in SLIDE 21 for the same 4mm rod which we have just seen. Of course when re-hydriding in the absorption apparatus with the 10% H₂ 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 that this increases substantially for the third cycle. The total amount desorbed also increases along with this increase in low temperature desorption but in both cases a second desorption peak at around 200°C is seen which seems to agree with the peak observed after electrolytic charging. This second peak seems to remain about the same size. It would seem to be significant that a sample of the same rod when processed in the hydrogen absorption apparatus and never exposed to an electrolyte or polarising current showed only a trace of a low temperature desorption spike, most of the desorption occurring in a broad peak centred on 225°C.

2.3 Comparison Between Re-hydriding Characteristics of Pd Electrolysed in 0.1M LiOH and 0.1M NaOH

SLIDE 22

One other interesting observation, another part of the mystery and possibly part of the solution is shown in SLIDE 22. 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, one of which is shown in the previous slide, were identical as a broad peak with a maximum at 200°C. Upon cooling the samples in hydrogen the results shown in SLIDE 22 were obtained. These show similar hydrogen re-absorptions at elevated temperatures but a marked difference at the lower temperature at which 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 was matched by a corresponding low temperature desorption peak on the next desorption cycle.

Clearly the temperature programmed absorption measurements are showing large sample differences. Interpreting how these differences arise and in what way they can be manipulated to advantage is still very much an open question.

SLIDE 23

Conclusions for temperature programmed absorption/desorption.

3. ELECTROCHEMICAL MEASUREMENTS IN H₂O

3.1 Galvanostatic Charging of Pd electrodes

SLIDE 24

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.

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.

SLIDE 25

The "steady-state" voltammetry shows that Pd electrochemistry is sensitive to the nature of the alkali-metal cation present. The comparatively diminished reoxidation 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.

SLIDE 26

Pd electrochemistry is sensitive to the nature of the alkali-metal cation, Li shows comparatively anomalous behaviour.

SLIDE 27

Conclusions.

ACKNOWLEDGEMENTS

The authors thank members of the Analytical Department (JMTC) for the SEM EDAX, XPS, TOF SIMS and bulk analysis measurements. These include Drs P Whitehead, D R Hepburn, J A Busby and Mr M J Lovell.



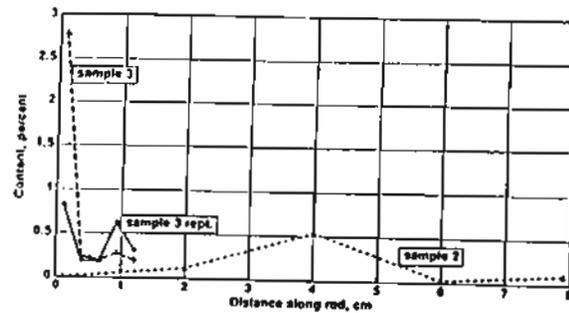
SOME OBSERVATIONS RELATED TO THE PRESENCE OF HYDROGEN AND DEUTERIUM IN PALLADIUM

1. ANALYSIS OF FLEISCHMANN AND PONS RODS RETURNED FROM D₂O EXPERIMENTS.
2. TEMPERATURE PROGRAMMED HYDROGEN ABSORPTION/DESORPTION ON VARIOUS PALLADIUM SAMPLES.
3. ELECTROCHEMICAL EXPERIMENTS IN H₂O.

SLIDE 1



SEM EDX ANALYSIS OF PALLADIUM RODS
Analysis for Copper



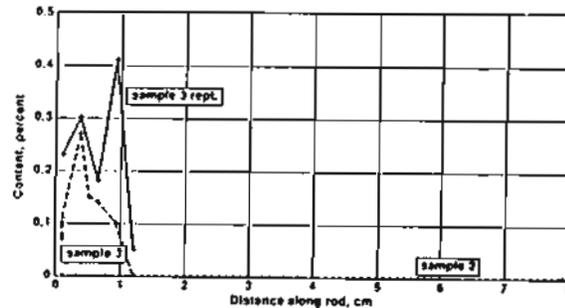
SLIDE 4

FLEISCHMANN AND PONS RODS ANALYSED AT JMTC

- ROD 1
4 MM DIAMETER, 10CM LONG
AS RECEIVED CONDITION.
- ROD 2
2 MM DIAMETER, 9CM LONG
USED AS CATHODE AT 64 MA/CM².
- ROD 3
2 MM DIAMETER, 1.2CM LONG
USED AS CATHODE AT 512 MA/CM².

SLIDE 2

SEM EDX ANALYSIS OF PALLADIUM RODS
Analysis for Iron



SLIDE 5

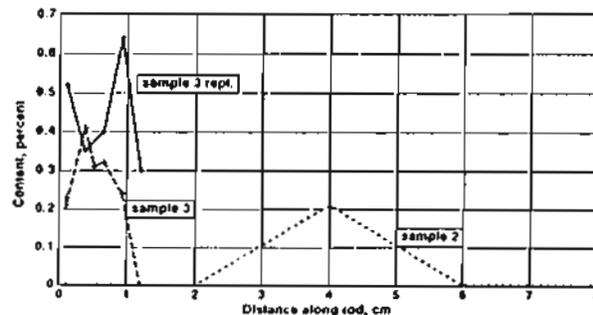
SURFACE ANALYSIS - SEM

INSTRUMENT USED - Cambridge Stereoscan 250 Mark II fitted with Princeton Gamma Tech (PGT) System 4 energy dispersive X-ray analyser. Instrument is capable of producing clear images up to a magnification of about x20,000 and can detect X-rays from sodium and elements with greater atomic number.

1. SURFACE FEATURES INCLUDE CRACKS AND SCRATCHES
- INTENSITY OF FEATURES INCREASES FROM ROD 1 TO ROD 3.
2. NO SIGNIFICANT SURFACE CONTAMINATION IN ROD 1.
3. Fe, Cu, Pt, Zn DETECTED ON USED RODS.

SLIDE 3

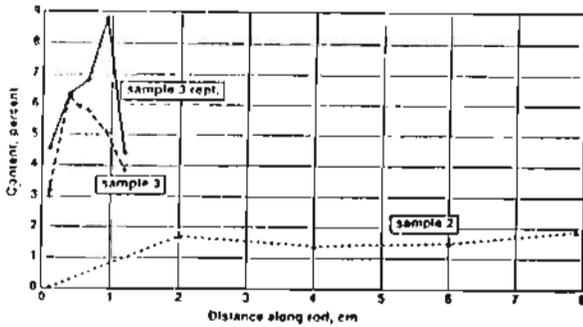
SEM EDX ANALYSIS OF PALLADIUM RODS
Analysis for Zinc



SLIDE 6



SEM EDX ANALYSIS OF PALLADIUM RODS
Analysis for Platinum



SLIDE 7

SURFACE ANALYSIS - XPS

INSTRUMENT USED - Kratos XSAM 800 surface analyzer using Mg K alpha radiation at 15kV and 10mA. The area analysed was 1.5mm square.

ROD 1 - Oxygen, nitrogen, chlorine, palladium
(Etching --> 100Å depth).

ROD 2 - Oxygen, sodium, silicon, platinum
(Etching --> 300Å depth).

ROD 3 - Oxygen, silicon, iron, sodium, platinum, zinc, copper
(Etching --> 1800Å depth).

SLIDE 8

SURFACE ANALYSIS - TOF SIMS

INSTRUMENT USED - CAMBRIDGE MASS SPECTROMETRY TOF/SIMS

LITHIUM ISOTOPE RATIOS (%)

ISOTOPE	REPLICATE MEASUREMENTS			LITERATURE VALUES
6	4.0	4.8	4.7	7.5
7	96.0	95.3	95.3	92.5

SLIDE 10

SURFACE ANALYSIS - CONCLUSIONS

1. Pt DETECTED ON ELECTROLYSED RODS BY ALL TECHNIQUES USED.
2. O, Si, Fe, Na, Zn, Cu, Li, Cl ALSO DETECTED.
3. Pt, Cu, Fe AND Zn PRESENT AS METALS.

SLIDE 11

SURFACE ANALYSIS - TOF SIMS

INSTRUMENT USED - CAMBRIDGE MASS SPECTROMETRY TOF/SIMS

PALLADIUM ISOTOPE RATIOS (%)

ISOTOPE	VIRGIN ROD No 1	USED ROD No 2	LITERATURE VALUES
102	1.28	1.31	0.92
104	11.58	11.50	10.43
105	22.96	23.77	22.33
106	28.00	28.39	27.23
108	25.25	23.90	26.70
110	10.91	11.10	12.36

SLIDE 9

BULK ANALYSIS - SPECTROGRAPHIC

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.

SLIDE 12



BULK ANALYSIS - ICP MASS SPECTROMETRY

INSTRUMENT USED - VG Plasma Quad PQ2.

Element	ROD 1 ppm	ROD 2 ppm	ROD 3 ppm
Li	6	9	12
R	25	25	31
Al	7	8	9
Cu	13	14	15
Zn	<1	<1	8
Pb	1	1	2
Pu	0.5	0.4	0.3
Au	13	12	13
Pt	8	16	27
Pb	8.2	0.3	0.8

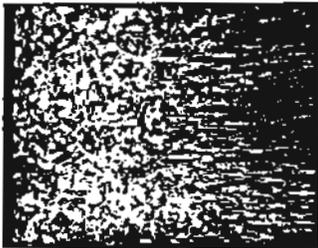
Elements not detected:

- < 0.1 ppm Bi, Th, U, Ta, Re, Hf, In.
- < 0.2 ppm Hg, Tl, Os, Ir, Cs, Ba, Sb, Mo, Y, Sr, Rb, Mn, Co and all lanthanides.
- < 1 ppm W, Te, Zr, Ga.
- < 2 ppm Ni, Mg, Il.
- < 5 ppm Ge.
- < 10 ppm Cr.

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

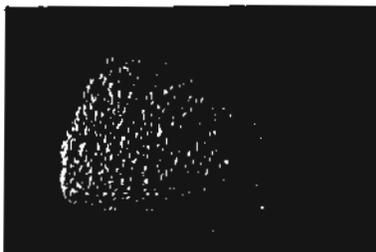
SLIDE 13

LONGITUDINAL SECTION FROM ROD 3 SHOWING AN ABRUPT CHANGE IN MICROSTRUCTURE INDICATIVE OF RECRYSTALLATION



SLIDE 14

LONGITUDINAL SECTION OF END (BOTTOM) OF ROD 2 SHOWING A RECRYSTALLISED MICROSTRUCTURE



SLIDE 15



METALLOGRAPHY

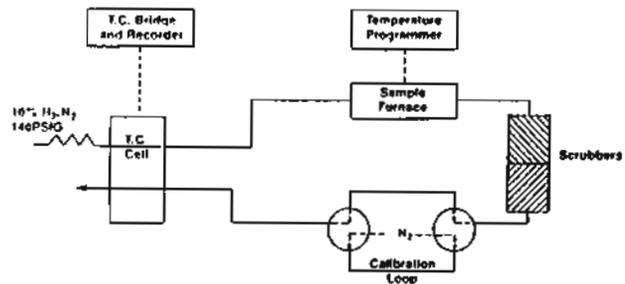
RECOVERY AND RECRYSTALLATION OF THE ENDS ONLY OF RODS 2 AND 3 INDICATE LOCAL TEMPERATURES OF > 200°C AND > 350°C RESPECTIVELY.

NOTES

- 1 THIS PHENOMENON OBSERVED AT ENDS AWAY FROM SPOT WELD.
- 2 FILING OR SAWING DID NOT PRODUCE THIS KIND OF RECRYSTALLISATION IN HYDROGENATED OR UNHYDROGENATED RODS.

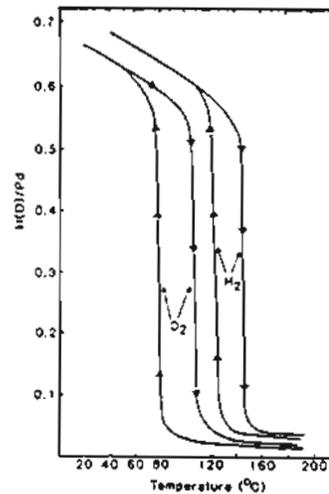
SLIDE 16

TEMPERATURE PROGRAMMED HYDROGEN ABSORPTION/DESORPTION APPARATUS



SLIDE 17

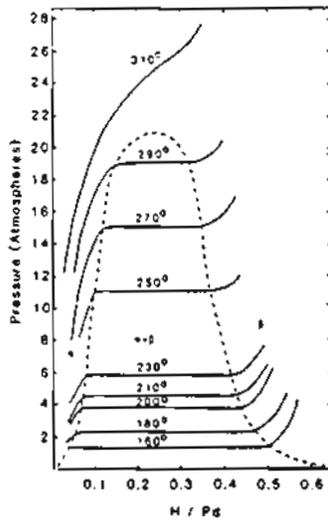
ABSORPTION/DESORPTION OF HYDROGEN OR DEUTERIUM AT ONE ATMOSPHERIC PRESSURE vs TEMPERATURE (SIEVERTS)



SLIDE 18



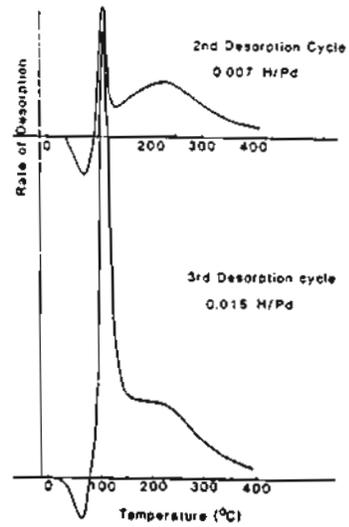
Pd - H PHASE DIAGRAM



SLIDE 19

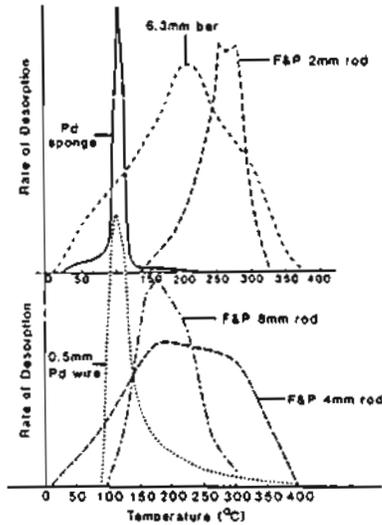


SEQUENTIAL TEMPERATURE PROGRAMMED DESORPTION ON HYDRIDED ROD 1



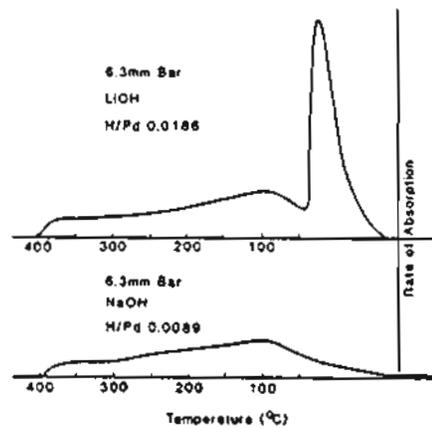
SLIDE 21

TEMPERATURE PROGRAMMED DESORPTION CURVES FOR VARIOUS Pd HYDRIDE/DEUTERIDE SAMPLES



SLIDE 20

REHYDRIDING OF 6.3mm Pd BAR ELECTROLYSED IN 0.1M LiOH and 0.1M NaOH



SLIDE 22



TEMPERATURE PROGRAMMED ABSORPTION/DESORPTION
- CONCLUSIONS

- 1 Pd SPOJGE AND Pd WIRE BEHAVE AS EXPECTED
- 2 Pd RODS GIVE RANGE OF RESULTS PROBABLY DEPENDANT TO SOME EXTENT ON SURFACE CONDITION OF Pd
- 3 ROD ELECTROLYSED IN LiOH ABSORBED HYDROGEN MORE READILY THAN SIMILAR ROD ELECTROLYSED IN NaOH.

SLIDE 25



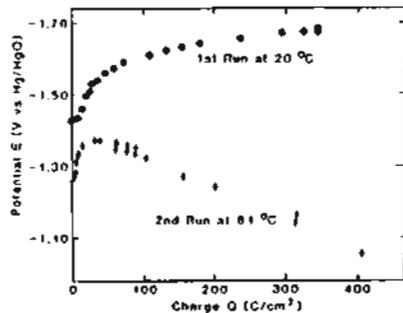
MEASUREMENTS IN H₂O - CONCLUSIONS

- 1 HYDROGEN EVOLUTION/DISSOLUTION IS SUBJECT TO SURFACE CONDITIONS ON Pd
- 2 SIMPLE EXPERIMENTS IN LIGHT WATER INDICATE THAT THERE ARE SIGNIFICANT DIFFERENCES IN THE ELECTROCHEMISTRY OF PALLADIUM IN LITHIUM HYDROXIDE COMPARED TO SODIUM AND POTASSIUM HYDROXIDE SOLUTIONS.

SLIDE 26

GALVANOSTATIC CHARGING CURVES FOR 0.05cm THICK Pd
FOIL in 0.1M LiOH AT 20° & 61°C.

$J = 25 \text{ mA/cm}^2$, SURFACE AREA - 0.9 cm^2



SLIDE 24

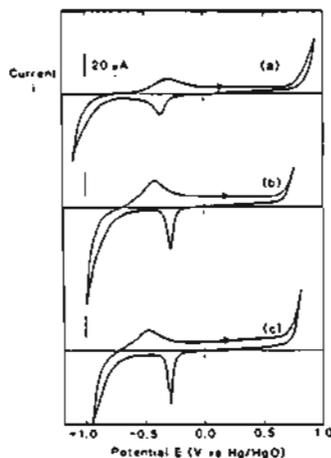
GENERAL CONCLUSIONS

1. A NUMBER OF ELEMENTS INCLUDING Pt AND Li ARE DEPOSITED ON Pd-CATHODE SURFACE DURING ELECTROLYSIS IN D₂O.
2. ⁶⁷Zn ISOTOPE RATIO SEEMS TO BE UNUSUALLY LOW BUT NO ORIGINAL REFERENCE IS CURRENTLY AVAILABLE.
3. RECOVERY AND RECRYSTALLISATION HAS BEEN OBSERVED IN RETURNED Pd RODS.
4. TEMPERATURE PROGRAMMED HYDROGEN ABSORPTION/DESORPTION SEEMS TO BE A USEFUL TECHNIQUE FOR CHARACTERISING THE Pd ELECTRODES.
5. ELECTROCHEMICAL BEHAVIOUR OF A Pd ELECTRODE IN LiOH DIFFERS SIGNIFICANTLY FROM ITS PERFORMANCE IN NaOH AND KOH.

SLIDE 27

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, c) 0.1M KOH, 20°C,
SWEEP RATE 30mV/s



SLIDE 25