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MATERIALS ISSUES OF LOADING DEUTERIUM INTO PALLADIUM AND THE ASSOCIATION WITH EXCESS HEAT PRODUCTION

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Abstract

The ability of palladium cathodes to attain and maintain high loading levels, at high current density and for long times, is controlled by two factors: the condition of the electrochemical interface which allows the attainment of high deuterium activity; the defect density and mechanical condition of the bulk material which permits the Pd lattice to withstand and contain high bulk deuterium activities when these equilibrate to produce extreme pressures of deuterium gas inside closed incipient voids within the metal.

Examples are given from a set of 26 intentionally similar current ramps which show three distinct Modes of loading performance: Mode A - a linear decrease of Pd resistance, beyond the resistance maximum, with logarithmic increase in electrochemical current; Mode B -an initial log-linear decrease on the Mode A trajectory, followed by a rapid increase in resistance when the resistance falls below a critical value; Mode C - a shallow decrease in resistance with approximately symmetric increase as the [log] current density is increased beyond a threshold value similar to that for Mode B. Mode A is most frequently associated with the appearance of calorimetrically determined excess heat.

1. Introduction

The initial conjecture which supports the search for excess heat in the D/Pd system is that palladium is capable of achieving high concentrations or activities of deuterium, under conditions of electrochemical loading. After nine years of intensive study and consideration it is clear that factors in addition to loading are important in excess heat production. A more sophisticated, although still empirical conjecture on the circumstances which give rise to an apparently anomalous excess heat following electrochemical insertion of D into Pd, may be expressed as follows: *"High D/Pd ratios (loading or activity) must be maintained at high electrical currents and/or electrochemical current densities, in the presence of high rates of deuteron flux, for times (hundreds of hours) sufficient to produce a new state or phase which gives rise to an anomalous excess heat (and, possibly, a nuclear process or processes)".*

In previous publications[1-4] we have sought to express this conjecture in the form of an equation which attempts to correlate the rate of excess heat production with the magnitudes of the important variables (excluding time). This attempt, while quantitative, remains empirical, since the roles of the variables remain unspecified. More importantly, the elements of the empirical model are not orthogonal: the current affects the current density, the flux affects the loading, and the relationship between current density and loading evolves with time.

In the present paper we are concerned with quantifying, and specifying with greater rigor the conditions necessary for the appearance of excess heat, and the interrelationships between the (apparently) controlling variables: D/Pd loading, current, and time.

2. Experimental

Data have been analyzed from 12 calorimetric experiments selected according to the following criteria: 1) cathodes subject to slowly ramped increasing currents (25-50 mA/hour) from a well established initial condition (33 mA cm^{-2}); 2) measurements include reliable resistance ratio and high accuracy calorimetry; 3) similar electrolytes, additives and surface condition; 4) well characterized and similar Pd metals stock; 5) near ambient temperature and pressure conditions.

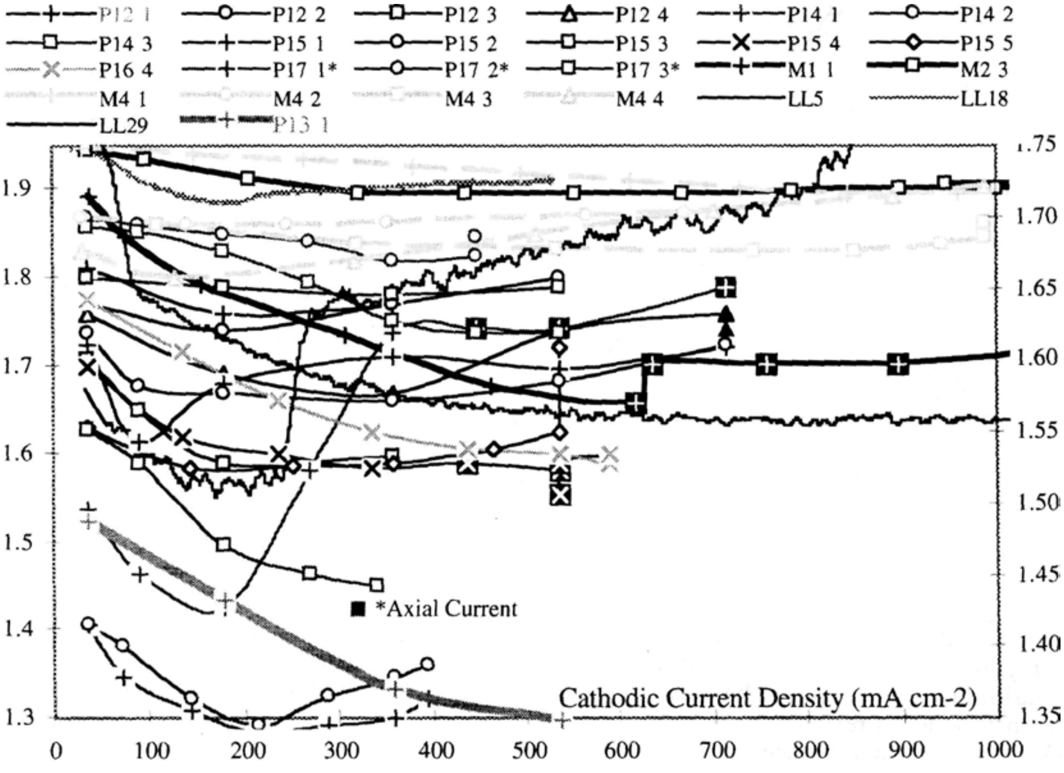
A total of 26 current ramps were performed in the 12 experiments specified in Table 1. Given the similarity of these experiments, the sometimes multiply repetitive nature of the current ramps, and the scrupulous care taken to establish and maintain procedures for electrolyte preparation, cathode fabrication and surface pretreatment, and cell assembly and operation, one would expect the results of these 26 current ramps to be closely similar.

Table 1

Experiment #	Bath Temp (°C)	Electrolyte 1.0 M	Additive	Conc. (ppm)	Electrode Source	Len. (cm) Dia. (cm)	Anneal Temp. (°C)	Time (h)	Treatment
P 12	30	LiOD	Al	200	E#l	3.0 x 0.30	800	3	1,2,4
P13	30	LiOH	Al	200	E#l	3.0 x 0.30	800	3	1,2
P 14	30	LiOD	Al	200	E#l	3.0x 0.30	800	3	1,2,3
P 15	30	LiOD	Al	200	E#l	3.0 x 0.30	800	3	1,2
P 16	30	LiOD	Al	200	E#l	3.0 x 0.30	800	3	1,2,3
P 17	30	LiOD	Si	200	E#l	3.0 x 0.30	800	3	1,2
Ml	30	LiOD	Al	200	JM "Z"	3.0 x 0.20	800	3	2
M2	30	LiOD	Al	200	E#l	3.0 x 0.28	800	3	1,2
M4	30	LiOD	Cu,Al	200	JM "Z"	10.0 x 0.10	800	3	1,1,2
LL5	30	LiOD	Al	200	E#3	3.0 x 0.28	800	3	1,2
LL 18	20	LiOD	none		IMRA	3.0 x 0.10	as rcvd.		none
LL28	22	LiOD	none		IMRA*	3.0 x 0.20	as rcvd.		2

* Air cast Surface Treatment: 1 =Surface Machined; 2=Aqua Regia rinse; 3=^{3}He implant; 4=^{4}He implant.

Figure 1 plots the measured resistance ratio corrected for temperature, versus current density, for the 26, nominally similar, current ramps. In instances where excess power was observed in the SRI mass flow calorimeter,[1-5] at levels more than 3 times the uncertainty, data are shown as solid points. The divergence of results, not only of resistance ratio which we seek to associate with D/Pd loading and excess heat production, but also in cell or cathode overvoltage and interfacial impedance (not shown), is seemingly incomprehensible. The data differ markedly in their initial values at low current densities, their initial slopes, and in their final trajectories.



R/R° Figure 1 Resistance ratio versus current density.

The initial value of i° = 33 mA cm^{-2} was selected to be sufficient to load even poor Pd specimens to the right side of the resistance maximum. Thus, a trajectory to lower resistance can be interpreted as the absorptive uptake of deuterium. There are, however, may other effects on the palladium resistance which are not directly related to deuterium uptake: (a) temperature; (b) electrosorption of light element; (c) absorption of H; (d) hydrogen chemical processing; (e) dimensional changes and cracking.

For the reasons outlined above, and others, it is very difficult to ascertain the relevant value of R° to be used in calculating the resistance ratio for experiments that last sometimes weeks or months. A significant factor in the dispersion of data in Figure 1 is the incorrect assignment of R° as it changes by a variety of mechanisms during the course of prolonged electrolysis. We have adopted a new normalization of data, intended to remove this effect from consideration, in order to eliminate R°, we divide the resistance ratio by its value at a reference electrochemical condition at the beginning of each current ramp:

$$\frac{R}{R^{\circ\circ}} = \frac{R / R^{\circ}}{\left[R / R^{\circ}\right]_{i=i^{\circ\circ}}}$$

Since the value of i°° (= 33 mA cm^{-2}) was chosen to be sufficient to drive loading to the right side of the resistance maximum, all resistance reduction during the course of a current ramp can be attributed to deuterium uptake. We consider the rapid effects (such as protium uptake) to have fully equilibrated before the start of the current ramp, and the slow effects (absorption and release of light elements and dimension change) not to occur significantly on the ramp time scale.

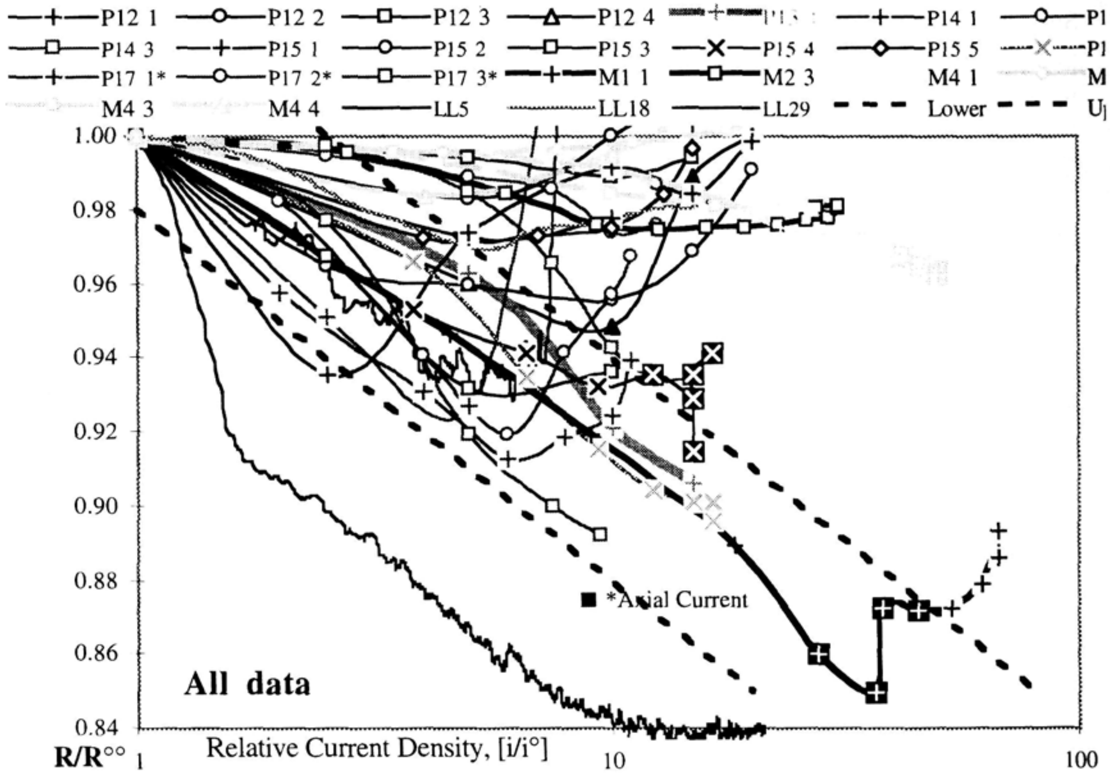


Figure 2 Renormalized resistance ratio versus current density.

Figure 2 shows a plot of relative resistance ratio versus relative current density, constructed from the data in Figure 1. Before rendering judgment it should be noted that the data in Figure 2 are constrained to go through the point [1, 1], and that the ordinate scale is logarithmic. Nevertheless, the data in Figure 2 can be grouped with modest precision into three distinct modes of response: **Mode A;** an approximately linear decrease in resistance with logarithmic increase in current density (see Figure 2A). This trajectory is followed by the light water cell, P13. When followed to a sufficient degree in heavy water cells, the Mode A response results most often in excess heat.

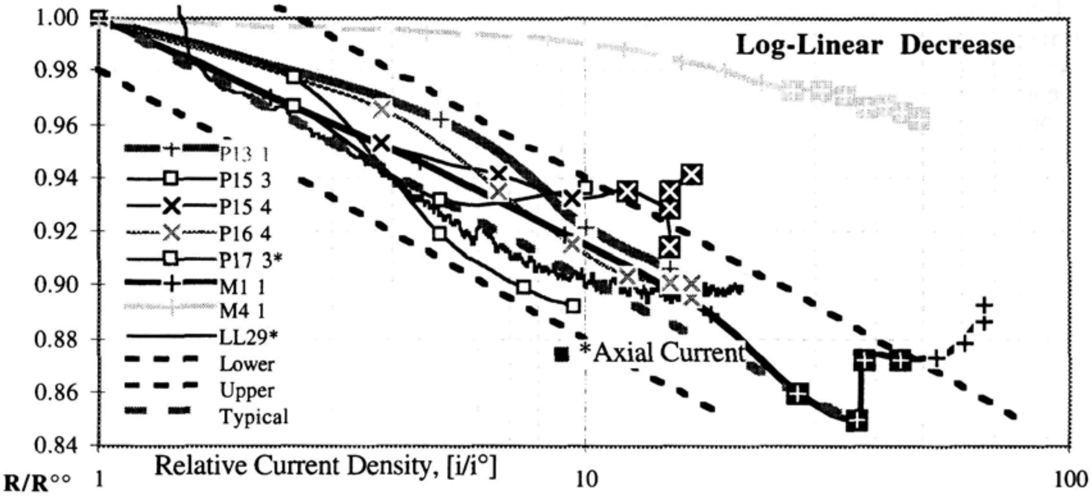


Figure 2A Mode A Resistance response.

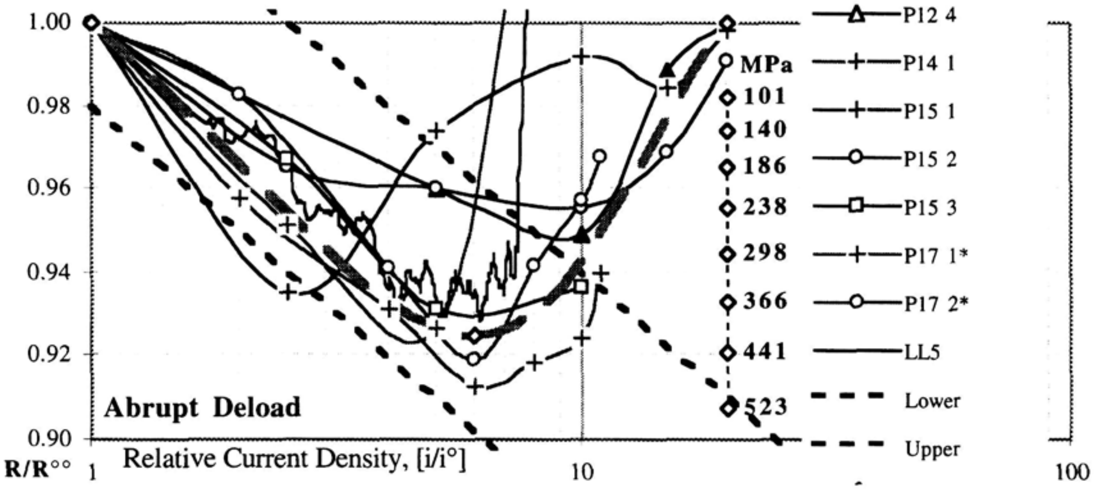


Figure 2B Mode B Resistance response.

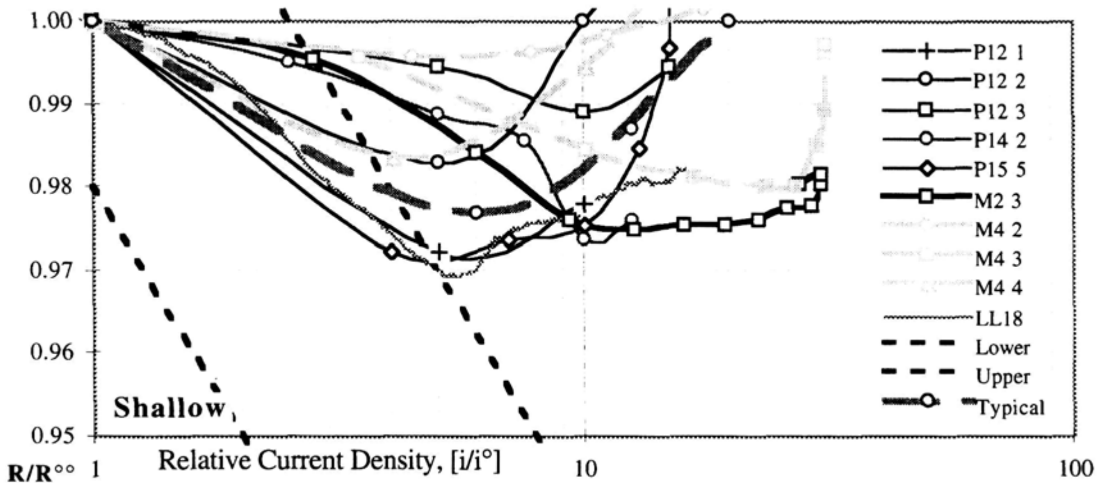


Figure 2C Mode C Resistance response.

Mode B. an initial log-linear decrease on the Mode A trajectory, followed by a rapid increase in resistance when the current density exceeds a critical value (or the resistance falls below a critical value - see Figure 2B). In one instance (P12-4) excess heat was observed at high currents during the abrupt de-load process.

Mode C; a shallow decrease in resistance with approximately symmetric increase as the [log] current density is increased beyond a threshold value similar to that for Mode B (see Figure 2C).

3. Discussion

We have postulated the need for high loading at high current densities to increase our probability of observing excess heat. This criterion is compatible only with Mode A behavior, and it is important that we understand the circumstances that give rise to this behavior or cause a departure from it. In answering the latter question we need to explain two effects: (i) What precipitates the abrupt de-load which transforms Mode A behavior into Mode B? (ii) What factors cause the poor loading characterised by of Mode C?

Here we explore the hypothesis that the rapid de-loading behavior of Mode B is a consequence of mechanical disruption of the palladium lattice caused by cracks which nucleate by internal pressure. Incipient closed voids within the cathode will attain a pressure of D_2 gas to equilibrate their activity with that of the atomic D within the Pd lattice. If we ignore the surface free energy considerations important for very small voids, the pressure achieved under equilibrium conditions in such voids is that required to attain the measured value of resistivity in gas loading experiments. When this pressure exceeds the yield strength of the palladium host material, cracks will form, ultimately connecting to the surface and providing a conduit for molecular deuterium to leave the cathode. The dimensions of these cracks are such that electrochemical processes cannot precede effectively within them, and molecular D_2 thus leaves the cathode with no effective means of replacement, resulting in rapid de-loading.

The vertical scale superimposed on Figure 2B shows the equilibrium D_2 pressure calculated from the data of Baranowski[6] assuming that at the reference current condition ($i^{\circ\circ} = 33$ mA cm^{-2}) the resistance ratio $R/R^{\circ\circ} = 1.96$ (the maximum value). The units of pressure are megapascals. The break towards higher resistance in Figure 2B clearly occurs within a narrow range of equilibrium pressures; $300 < P_{max} < 500$ MPa. This range conforms with that expected for the yield strength of palladium deuteride (although this number is undetermined, experimentally). We conclude tentatively, therefore, that the failure in Mode B is mechanical.

The resistance minimum occurs at approximately the same current density in Modes B and C. As shown in Figure 2c, however, Mode C behavior is characterized by a much diminished deuterium absorption. The failure here appears to be at the interface, either due to blockage and restricted diffusion, or to electrochemical conditions which are not conducive to the attainment of high surface activity.

It is clear, therefore, that at least two factors must be controlled in order to obtain Mode A behavior which leads to high loading at high current densities (and, potentially, to the observation of excess heat:

(i) the electrochemical condition of the surface;

(ii) the mechanical properties of the bulk.

Because of the high permeability of D in Pd, in order to obtain the desired Mode A behavior, the surface must be everywhere in the desired electrochemical condition and the bulk metal must be homogeneously sound. We might imagine a two dimensional matrix reflecting the soundness of the surface and bulk conditions.

Table 2

Sound Bulk Condition	Sound Surface Condition	
	Homogeneous	Heterogeneous
Homogeneous	**Mode A**	**M4-1**
Heterogeneous	**Mode B**	**Mode C**

Most of our results clearly fall into three quadrants of this matrix. Current ramp M4-1 exhibited a log-linear decrease of resistance, with slope much less than Mode A, and showed evidence of excess heat. We interpret this to mean that only a small section (calculated to be ~20%) of the cathode had both surface condition and bulk properties sufficient to sustain high loading.

4. Conclusions

We are able to interpret, systematically, apparently disparate results of intentionally similar loading experiments, by a new normalization procedure intended to eliminate the effects on palladium resistance that are unrelated to deuterium uptake. The variability which remains can be accounted for satisfactorily in terms of two essentially orthogonal variables:

(i) the condition of the electrochemical interface which allows the attainment of high deuterium surface activity;

(ii) the defect density and mechanical condition of the bulk material which permits the Pd lattice to withstand and contain high bulk deuterium activities.

Only cathodes which are homogeneously sound in both dimensions are capable of sustaining high loading at high current densities. Only when we are able to achieve and maintain these conditions reliably and repeatedly, will we be able to test satisfactorily the hypothesized association of the high-current/high-loading condition with the appearance of anomalous excess heat production.

5. References

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