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NEW HYDROGEN ENERGY RESEARCH AT SRI

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Abstract

With financial support from the Institute for Applied Energy (IAE), SRI International has undertaken a research and development program in the field of New Hydrogen Energy production. The long-term goals of this program are: (i) to understand the phenomenology and identify the mechanism(s) of new hydrogen energy production, and (ii) to increase the rate of energy production to useful levels. To these ends, in addition to research at SRI International, collaborative research with IAE has been undertaken at SRI and IAE's facility in Sapporo.

Research has been performed in a number of areas: Firstly, calorimetric studies of the palladium/heavy water system have been carried out using electrochemical cells housed in well-qualified mass flow calorimeters, one design of which is capable of accurate measurement of the helium content of the cell. Although most results have been obtained for electrolyte temperatures in the range 25-40°C, some experiments have been undertaken in the vicinity of the boiling point of heavy water. In addition to these calorimetric experiments, extensive studies have been made of the electrochemical loading of deuterium into palladium obtained from a variety of sources.

While the results obtained are consistent with those obtained previously, by various researchers, it is clear that attainment of the necessary conditions for excess heat production is greatly impeded by a materials-induced variability of a critical parameter which is not presently under our control.

1. Introduction

For the past two years, SRI International has participated in the New Hydrogen Energy (NHE) program, run under the auspices of NEDO, Japan. The underlying goal of this program is to understand the origin of the various calorimetric and nuclear anomalies which have been reported recently in connection mostly with the electrochemical insertion of deuterium into palladium.

An important aspect of any experimental program is the need to achieve consistency and replicability of results. The studies carried out under the NHE program have necessarily been tightly focused on the achievement of the immediate project goals: the reproducible attainment of excess heat, or, failing this, to obtain an explanation for the apparent absence of replicability.

In previous experiments we have established empirically a hypothesis or phenomenological model for the occurrence of "excess heat" in the D/Pd system. This model predicts that, for 1 and 3 mm diameter, pure palladium wires, loaded electrochemically with deuterium in 1 M LiOD electrolytes, we expect[1] to observe anomalous "excess" heat if we meet the following four criteria:

i)   we need to achieve and maintain a D/Pd loading at or above some critical value (0.85-0.90)

ii) for periods of time (several hundred hours) substantially longer than the diffusional time constant of D in the Pd lattice

iii) at currents (or current densities) above some threshold value (several hundred mA or mA cm^{-2})

iv) in the presence of some flux of D passing through the interface.

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$$P_{xs} \propto (I - I^\circ)(x - x^\circ)^2 \frac{\delta x}{\delta t} \qquad [1]$$

There is no fundamental basis for equation [1], although the terms are consistent with some theoretical descriptions of heat production via lattice-induced nuclear processes.[2] Equation [1] is almost certainly overly simple, and suffers from the added difficulty that its terms are not orthogonal: the current affects the flux, the flux affects the loading, and the current affects the loading. It is the character of this last interrelationship, which is both surprising and unfortunate, that is the subject of this paper.

2. Experimental

A feature of our D/Pd experiments is that, despite nominally and apparently identical metal source, metal preparation and electrolytes, different cathodes exhibit different loading and overvoltage responses to the same electrochemical treatments.[3] Until we can control this variability, we have adopted what we call a "farmed" approach to our calorimetric experiments. Typically, six experiments are started together in "farms" which are intended to perform two functions: (i) explore in a statistical way,[3] the role of various variables affecting loading; (ii) identify two candidate cells, adventitiously well loaded, to be studied in two stations of our L-series mass flow calorimeters.[1]

Table 1 summarizes the results of calorimetry performed in this way, since ICCF5. This table is broken horizontally into three data blocks: cathode source and size; important characteristics of the behavior of the cathode in the degree of loading (DoL) farm; some features of the behavior in the calorimeter. Where cells do not have an entry in the DoL columns, they were started directly in the calorimeters.

Table 1 reveals several important details in the context of the hypothesis regarding excess heat production, that we are attempting to test. In all cases the maximum current experienced by the cathode exceeded the maximum threshold current previously observed for excess heat production. In almost all cases, the experiment duration exceeded the minimum initiation period. In many cases, the maximum loading inferred from the measured resistance- ratio/loading functionality,[4] was certainly at the level where excess heat might be expected. Despite the separate attainment in many experiments of most of the criteria that we have identified as being important, none of the 13 experiments listed in Table 1 displayed excess power outside the range of measurement uncertainty, during steady state operation.

One possible explanation for this failure can be found in footnote 2 in Table 1. In general, the current density of maximum loading was ~100 mA cm^{-2}. As the current was raised significantly above this level in the attempt to generate excess power, the cathodes de-loaded; in some cases, this de-loading was precipitous.

Such rapid de-loading has not always been observed. Figure 1 shows results from two experiments published previously.[5] Experiments P15 and P16 were prepared identically and operated simultaneously. Both employed Engelhard Lot #1 palladium (1/8" machined to 3 mm diameter and 3 cm long) in 1 M LiOD containing 200 ppm Al. The surface of the cathode P16 was modified by implantation of ^{3}He, although this detail is not regarded as salient in the following discussion.

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Table 1. L-Series Calorimetry - Summary of Results

Batch	Cathode dia. (mm)	length (mm)	Degree Start	of Loading Farm Cell	Duration (days)	Max D/Pd	Calorimeter Duration[1] (days)	Maximum[2] D/Pd	I(A)
LL5 Eng.#3	3	30	Apr-95	S3	20	0.92	22	>0.96	3
LL6 Eng.#3	3	30	Apr-95	S4	20	0.93	22	0.91	3
LL7[3] Eng.#5	3	30	Jun-95				7	<.85	1.15
LL8[3] Eng.#5	3	30	Jun-95				7	<.85	1.15
LL9 Engelhard	1	30	Jun-95				60	0.92	2
LL10 Engelhard	1	30	Jun-95				60	0.92	2
LL11 IMRA	1	30	Jul-95	U4	76	>.97	65	0.94	1.5
LL12 IMRA	2	30	Jul-95	U1	76	>.97	64	0.93	3
LL13 IMRA	1	30	Sep-95	V4	40	>.95	39	0.92	1.5
LL14 JM(Z)	1	30	Sep-95	V2	40	0.95	39	0.95	1.5
LL15 IMRA	1	30	Oct-95	W3	36	>.95	84	0.97	1.5
LL16 IMRA	1	30	Oct-95	W4	36	0.94	84	0.94	1.5
LL17 Pt	1	30	Mar-96				14		2.5
LL18 IMRA	1	30	Apr-96	X3	75	0.96	36	0.9	3
LL19 Pt	1	30	Apr-96				36		2.5
LL20 Pd sheet	1 x 10	20	Jun-96				43		2
LL21 Pd sheet	1 x 10	20	Jun-96				43		2
LL22 JM(Z)	2	30	Aug-96	Z2	21	0.94	38	0.9	2
LL23 JM(Z)	2	30	Aug-96	Z5	21	0.92	38	0/9	2
					461		801		

[1] Duration addition to any time spent in DoL Farm.
[2] In general, cathodes begin to deload at current densities above approximately $100 \, mA \, cm^{2}$, *i.e.* maximum current and maximum loading do not occur simultaneously
[3] LL7 and LL8 terminated early due to mechanical problems.

Figure 1 shows time series data in a 100 hour interval during which the cathodes were subjected to their third current ramp (the first with any evidence of excess power). The current is the thick line referenced to the right axis. The left axis show the resistance ratio together with values of the average loading inferred from previous calibrations.[4]

In response to the current ramp, cathode P16, initially well loaded, accepts further loading until the current reaches its plateau value of 1.5A (~500 mA cm^{-2}). During the current plateau, the resistance of cathode P16 starts slowly to increase. There is a period of lost data indicated by the dashed line, and when the cathode is observed again at ~780 hours the resistance ratio has risen to ~1.7, a loading of ~0.925. During this period, P16 gave no indication of excess power within the measurement uncertainty (±50 mW).

A similar, but rather more satisfactory response to the current ramp is observed for cathode P15. Initially slightly better loaded than P16, this advantage persists through the current ramp. More significantly, during the plateau at 1.5A, cathode P15 shows no indication of de-loading, and even loads further to a value of nearly 0.97. A small amount of de-loading occurs when the current is raised from 1.5 to 1.65 A, but for almost the entire interval the loading remains above 0.95. The excess power for P15, referenced to the right axis, is clearly significant compared with the measurement uncertainty, (±50 mW).
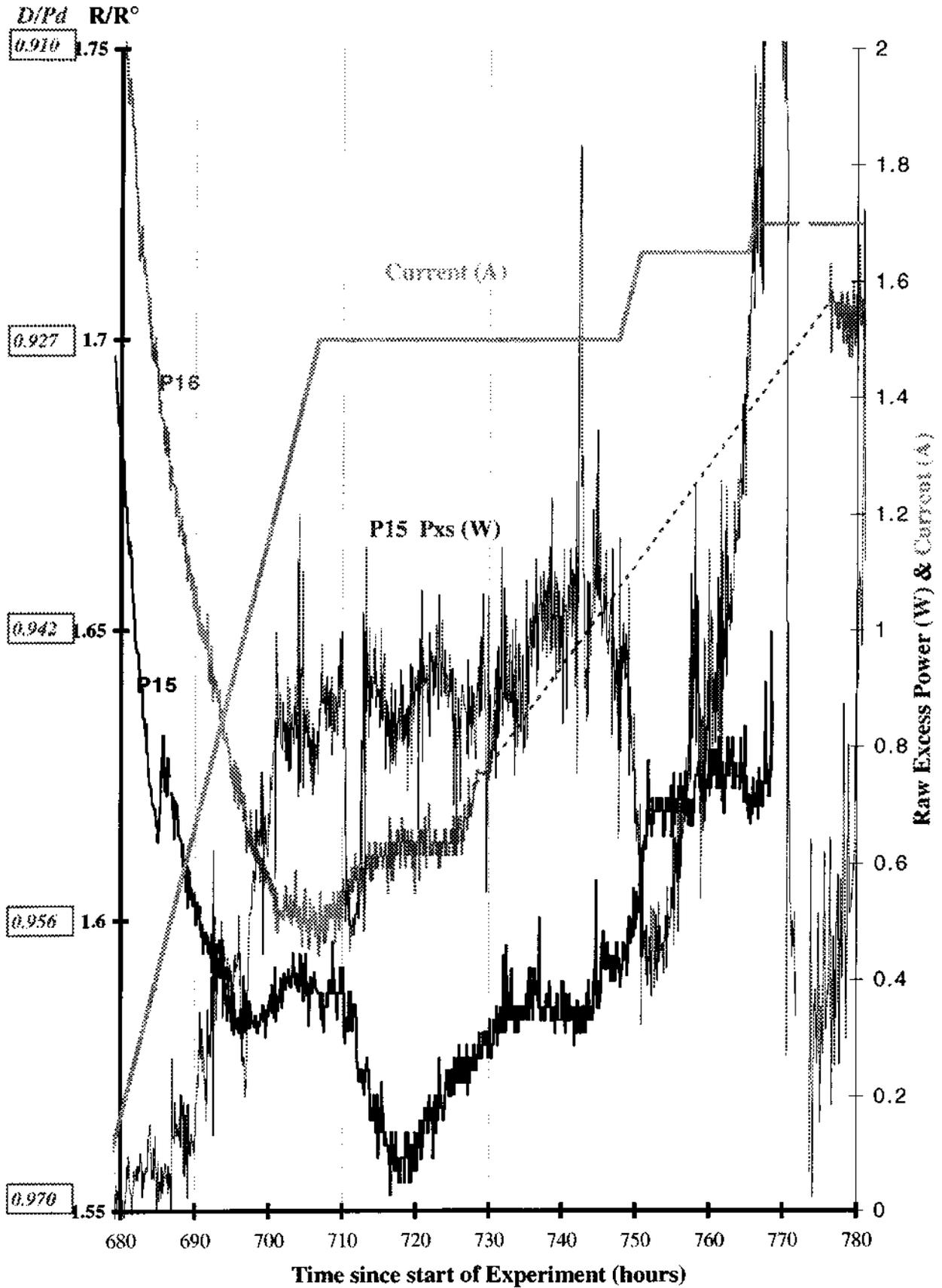
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Figure 1   Experiments P15 and P16 Current, Resistance Ratio and Excess Power.

Figure 2 shows the loading and excess power response of LL5, the best performing cathode in Table 1. This cathode also was 3 mm in diameter and 3 cm long pure Engelhard palladium, in this case Lot #3. When transferred from the DoL farm after 20 days of observation, the resistance ratio initially was at the maximum ($R/R^\circ = 2.0$, see Figure 2). During ~12 hours at open circuit, cathode LL5 de-loaded to the left side of the resistance maximum ($D/Pd < 0.725$). The response to small current steps to 50, 100 and 150 mA (17, 33 and 50 mA cm^{-2}) was encouraging, with the cathode exhibiting a rapid uptake followed by an asymptotic approach to some limit at each new current value.

Figure 2b shows a 100 hour data interval for cathode LL5 to allow more direct comparison with Figure 1. With the onset of the current ramp the cathode LL5 initially starts to load, and obtains a value almost identical to the maximum obtained by P15. A significant difference is that, for P15, this maximum loading was attained at 1.5A (~500 mA cm^{-2}), while for LL5 this maximum was held only for currents between 0.3 and 0.6 A (~100-200 mA cm^{-2}). A more glaring difference is apparent in Figure 2b, and one of more urgent concern. When the current is ramped above 0.6A, cathode LL5 de-loads, first abruptly, and then steadily as the current ramp proceeds.

Measured excess power is referenced to the right axis in Figures 2a and 2b. The small, flat endotherm from 90 to 190 hours in Figure 2a, coinciding with the current ramp, is due to the departure of the calorimeter from its steady and initial state, as the calorimeter and its contents are heated by the input electrochemical power. This energy is yielded during the exothermic "spikes" at ~200 and ~230 hours as the electrochemical and heater currents are turned off, and the calorimeter returns to its initial state. In Figure 2b a simple correction has been made to the excess power for this departure from the steady state, by adding a term:

$$P_{Non-SS} = \overline{m\ C_p}\ \delta T_e/\delta t$$

where $\overline{m\ C_p}$ is the heat capacity of the cell and its contents, and $\delta T_e/\delta t$ is the (measured) rate of change of the electrolyte temperature during the current ramp. Figures 2a and 2b indicate no evidence of anomalous excess power in cathode LL5, a situation clearly different from that manifest by cathode P15 in Figure 1.

The de-loading observed for cathode LL5, beginning at ~103 hours (Figure 2) is both rapid and undesired. From the time series data it is possible to extract further information that may allow us at least to understand, and potentially to prevent, such precipitous de-loading.

Figure 2c shows on an expanded scale the current density and measured resistance ratio for 6 hours, covering the period of the most abrupt de-load during the initial stages of the current ramp. The resistance ratio increases from ~1.55 ($D/Pd \approx 0.97$) to ~1.75 ($D/Pd \approx 0.90$) in a period of about 3 hours. Since the maximum possible resistance ratio is ~2.0, a natural question is; how can such a rapid change in resistance occur?

In an electrode devoid of pores and cracks, all de-loading occurs by diffusion of atoms in the solid phase to, and evolution of molecules from, the surface. We have developed a simple model to account for the observed resistance gain and deuterium loss from the cathode based on the following conditions and assumptions:

i)   Before the period of rapid de-loading the composition in the cathode is approximately uniform, with $R/R^\circ = 1.55$ and $D/Pd = 0.97$.

ii)   During this time the activity of deuterium adsorbed on the surface of the cathode (controlled by the electrochemical process) is everywhere equal; the chemical potentials of adsorbed and absorbed D are equal; there is no net absorption or desorption.

iii)   At the onset of de-loading, the activity of adsorbed deuterium is reduced to a value capable of supporting a much lower D/Pd loading; this change occurs instantly, and everywhere on the cathode surface.
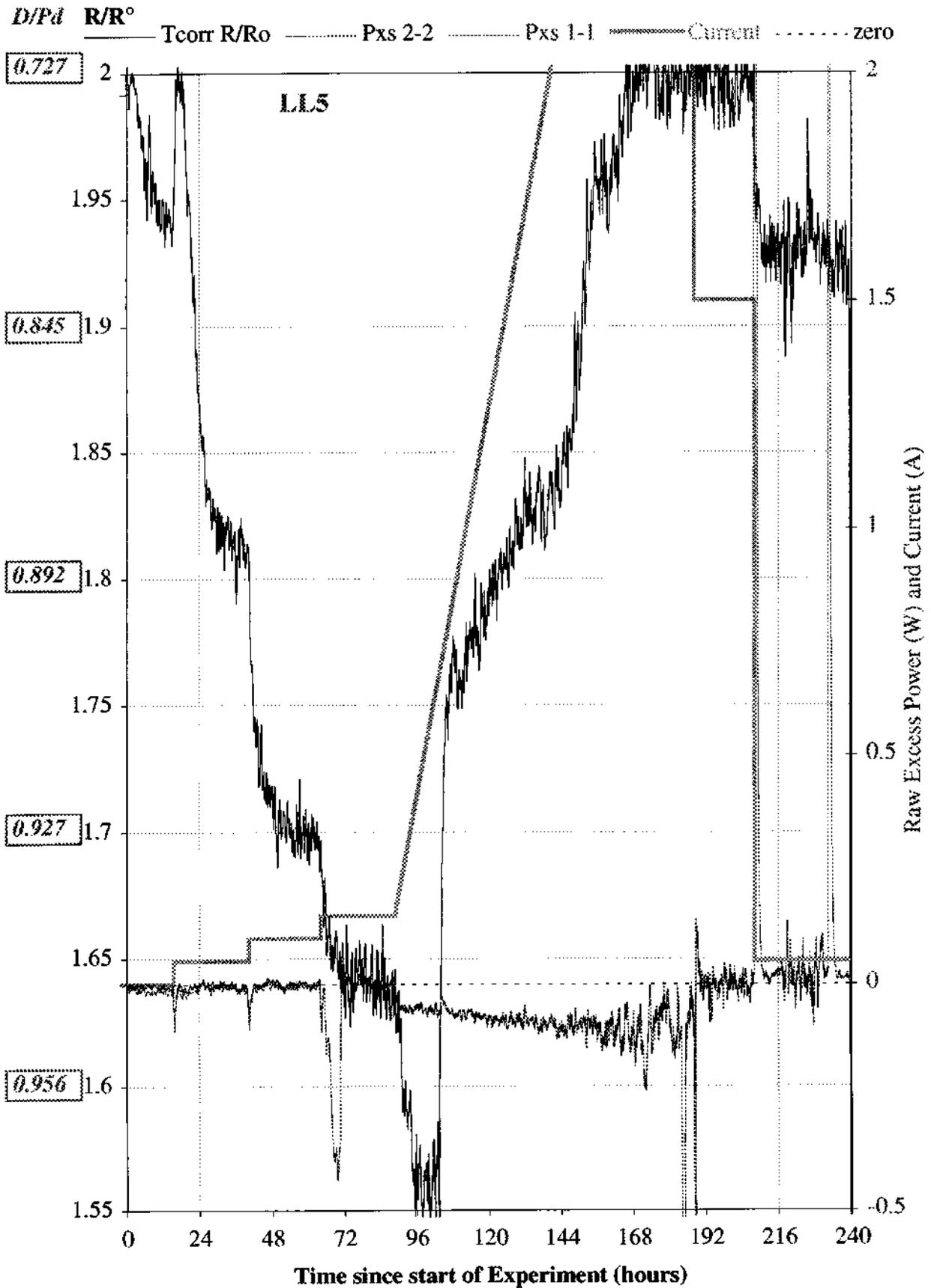
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Figure 2a   Experiment LL5; Current Density, Resistance Ratio and Excess Power.
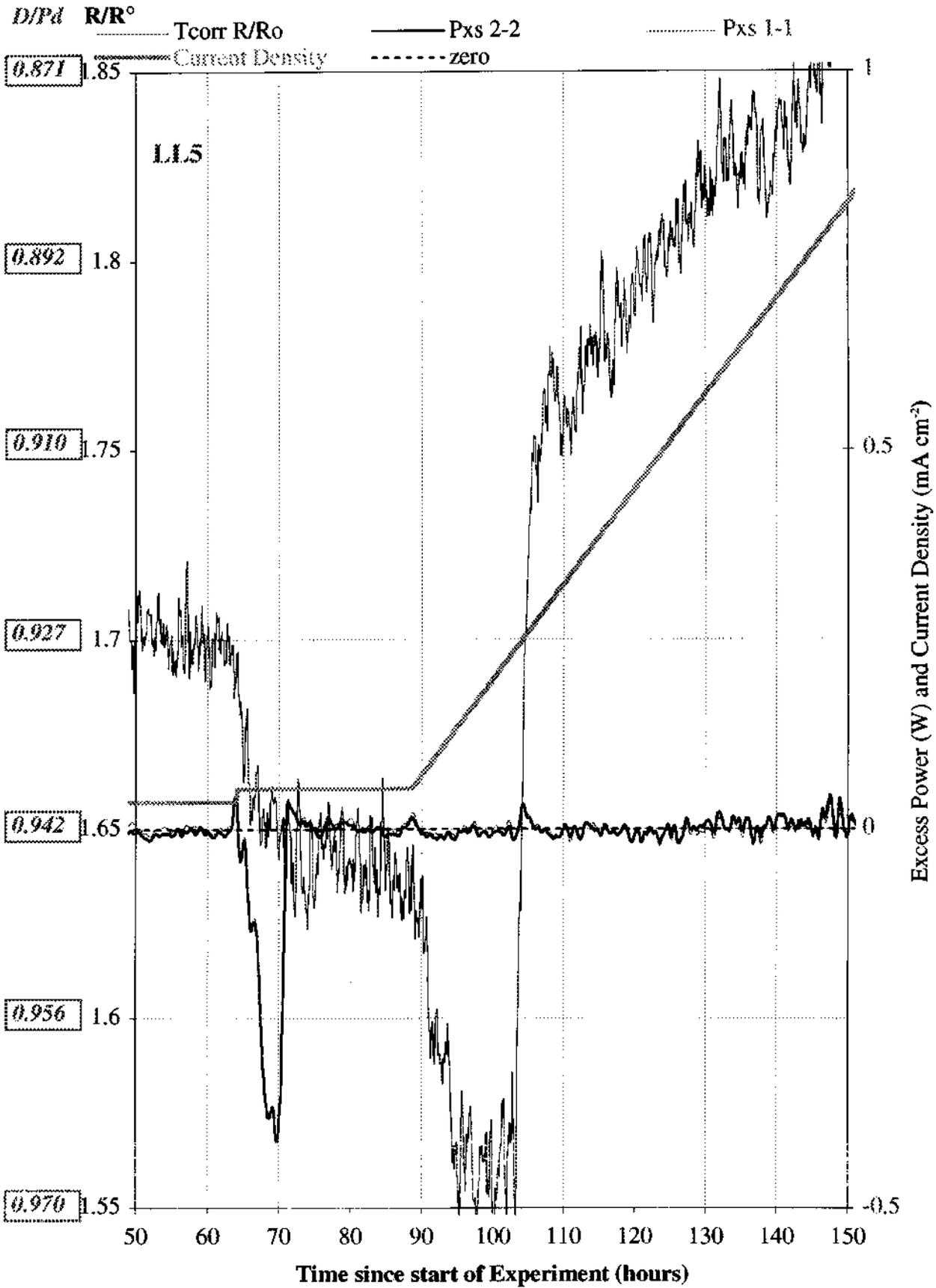
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Figure 2b   Experiment LL5: Current, Resistance Ratio and Excess Power.
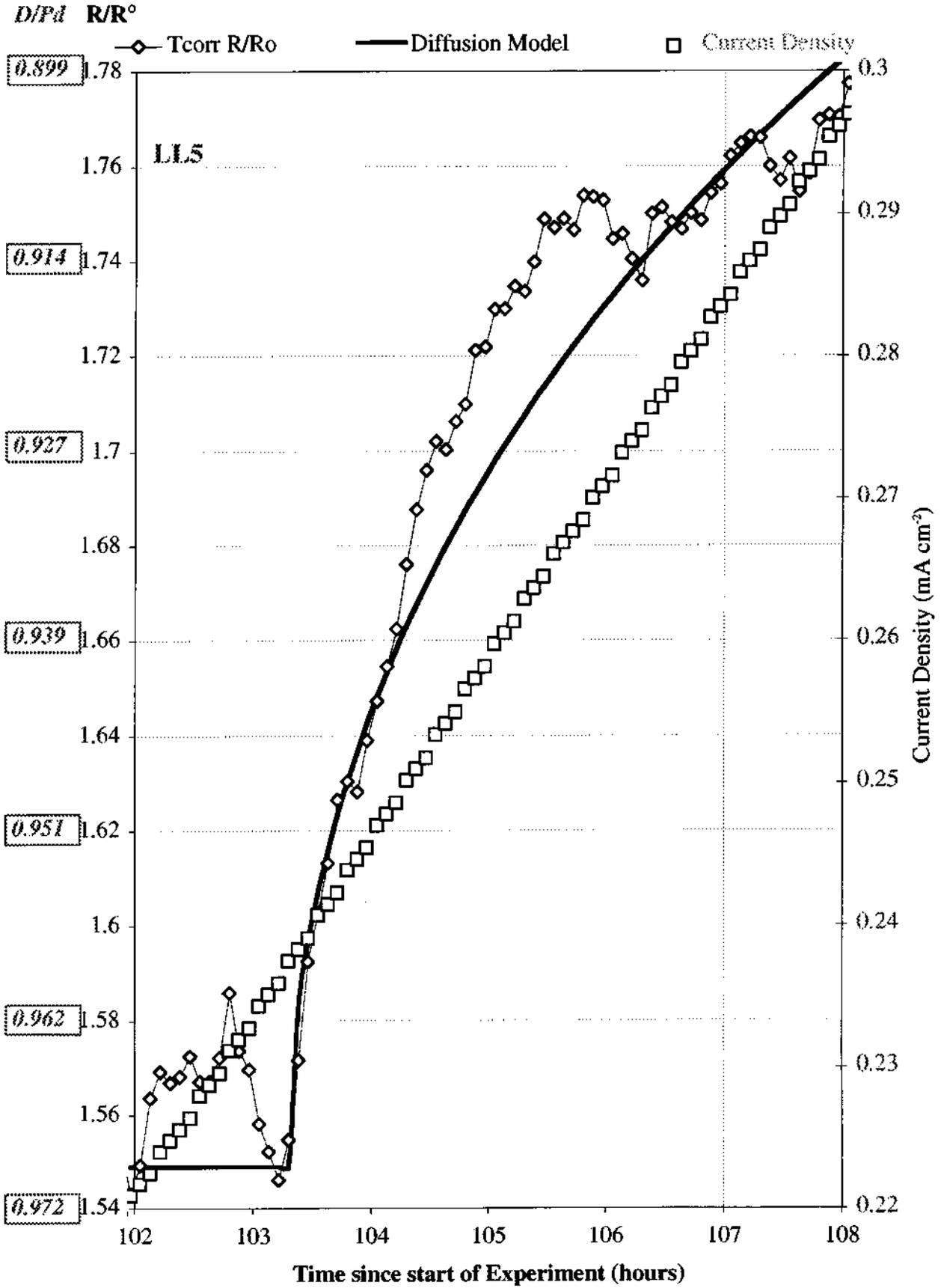
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Figure 2c   Experiment LL5: Current Density and Resistance Ratio: Measured and Predicted.

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iv)   Diffusion of deuterium occurs in response to the established gradient of chemical potential; the de-loading rate is controlled by the mass transport of deuterium atoms to the cathode surface.

The solid line in Figure 2c shows the results of a model calculation for the radial symmetry of the (3 mm diameter) cathode, with the two additional constraints:

v)   The diffusion coefficient for D in PdD_x is taken to be 1.7×10^{-7} cm^2 s^{-1}.

vi)   At t = 103.4 hours, the boundary concentration steps from D/Pd = 0.97 to D/Pd = 0.725.

Selection of the value of 0.725 for the final surface D/Pd loading requires some further comment. A difficulty in the modeling is explaining how the resistance can rise so quickly. The de-loading process cannot occur faster than diffusion brings species to the surface, so our assumption is that mass transport is rate limiting. The de-loading rate is proportional to the participating area, so the assumption is made that all of the surface is involved. The resistance ratio cannot rise higher than its value at the maximum ($R/R°=2.0$ at D/Pd=0.725), so our assumption is that 0.725 is the final value attained. There are several other reasons, however, which justify this last choice: (i) $R/R° = 2.0$ is the value finally obtained for the average loading in the bulk (see Figure 2a); (ii) this is the value "normally" obtained by "poor" loading cathodes; (iii) the roughly parabolic shape of the $R/R°$ versus D/Pd functionality makes it relatively insensitive to composition in the vicinity of the resistance maximum.

For the reasons given in the preceding paragraph, it is hard to imagine a model that would or could give a faster rate of de-loading, than the one which we have employed. While not exact, there is a close conformity in Figure 2c between the diamonds (measured) and the solid line (predicted) values of R/R. This agreement suggests that the model described by conditions and assumptions (i) - (vi), above, closely reflects the situation of this cathode, in the time period shown. That is, abruptly and apparently spontaneously, the activity of deuterium in the surface layer drops from one previously held high value, over all the surface of the cathode, to a second much lower value, which is maintained even in the presence of an increasing electrochemical current density.

3.   Discussion

Four years separate experiments P15 and LL5. Experiment P15, while slightly better performing than its replicate, P16, exhibits a loading behavior which is by no means atypical of the set in which it was performed. Similarly, cathode LL5 performed better than average but the response of loading to current was reproduced, qualitatively, in every experiment in Table 1, involving a Pd wire cathode. It is clear that something has changed. An important, perhaps critical, component of our experiments is not under our control. Contributing complexity to the resolution of this problem is the probability that elements of irreproducibility exist in the electrolyte (impurities and additives), in the surface preparation, and in the metallurgy of our palladium samples. Very significant effort has been expended in understanding the electrochemical factors which affect loading; some of our findings are discussed in a companion paper.[3] Despite this effort and the time that has been spent in attaining understanding and attempting to obtain control of the electrochemical insertion of deuterium into palladium, one of the clear imperatives in the field latterly called "New Hydrogen Energy", is the need to achieve replicability in our experiments, or understand its absence.

One manifestation of the observed irreproducibility, is the ability of cathodes to maintain high states of D/Pd loading, at high electrochemical current densities. A model has been developed which describes, adequately, the circumstance of the rapid de-loading of cathode LL5. A sudden, and apparently spontaneous change occurred on the cathode surface during the course of a very slow current "staircase". In a period of less than 4 minutes, and with a current density difference of less than 1 mA cm^{-2}, a catastrophic change occurred all over the cathode surface from a state capable of sustaining a very high loading and an extraordinary chemical activity, to one where the loading is uninteresting, and the activity close to unity. A sudden drop in the activity of surface-adsorbed H

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atoms is most easily explained in terms of a change in electrochemical mechanism from that of "fast discharge-slow desorption" to that of "slow-discharge-fast desorption". The former is capable of sustaining high activities; the latter not. ("Desorption" in this context refers to either the Tafel or Heyrovsky steps[6]).

Unfortunately, such an explanation only begs the question of what causes the mechanism to change suddenly or, more precisely, what causes the relative rate constants for the various mechanistic steps to change. That the transition occurs catastrophically and over all the cathode surface suggests the critical involvement of an easily disturbed, fragile structure, other than the electrolyte and solid phases. Here, we shall refer to this structure as a "film", formed adventitiously from impurity species initially present in the electrolyte or leached from the solid surfaces within the cell, including the Pd. We speculate that attainment of the high loading state is possible (perhaps only) in the presence of this film. Failure of the film, mechanically, electrically or electrochemically, at least one part of the cathode surface results in a change in electrochemical mechanism to that which is more appropriate to a "clean" surface. The result is sudden de-loading, the rapid formation of gas bubbles at the metal/film interface, and mechanical disruption of the film over a wider area. Evidence for the presence and critical role of a surface film is provided by studies of well-loaded cathodes under ultrasonic irradiation.[7] Such electrodes, even while maintained cathodically polarized, deload on irradiation, presumably due to the removal of a critical surface structure or agent.

An auto-catalytic process such as that postulated in the previous paragraph obviously is capable of explaining a catastrophic loss of loading. This loss is precisely what we wish to avoid. If our model is correct, then it behooves us to examine more closely the surface structure, its constitution and character, and seek methods of controlling its properties so that we can assert reproducible control over loading.

4. Acknowledgments

5. References

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