Excess Power Observations in Electrochemical Studies of the D/Pd System; the Influence of Loading

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ABSTRACT

Excess power measurements have been carried out on a deuterium-based electrochemical system of novel design. The excess power generation is reported as a function of electrochemical current and cathode loading. A phenomenological model for excess power production is introduced and briefly discussed.

INTRODUCTION

An experimental programme was undertaken to test the hypothesis that anomalous thermal processes occur when deuterium is loaded by electrochemical means into palladium to high atomic (D/Pd) ratios. Based on calorimetric results obtained to date[1–3], it appears that one criterion (amongst others) for the observation of anomalous power generation is the attainment of average deuterium loadings of approximately 0.9 or greater. In view of the importance attached to the loading-related aspects of excess power production, a considerable amount of effort has been expended thus far on the characterization of the kinetic features of the loading process and means to achieve, maintain and measure *in situ* high deuterium loadings. Some aspects of these studies have been reported previously[4]; additional aspects are discussed further below.

Here, the results of calorimetric measurements on an electrochemical cell of novel design are reported. These results enable apparent correlations to be established between the excess power generation, the electrochemical current and the average deuterium loading. These correlations are discussed in terms of the phenomenological model for excess power generation introduced previously[2, 3].

EXPERIMENTAL METHODS

Maintenance of high deuterium loading

The ability to maintain a high steady-state loading is determined essentially by the extent to which the rates of the reactions which lead to the loss of deuterium from the cathode can be suppressed. Important in this regard is the imposition of a uniform current density distribution over as much of the cathode surface as practical. This is partly achievable with suitable cell design; in particular, appropriate relative cathode / anode disposition. In addition, the production of cracks on the cathode surface (either directly or via the expansion of internal voids) inevitably leads to a disruption of the local current density and loss of deuterium. Thus processes likely to result in cracking, for example repeated cycling through the α/ß phase transition in the case of palladium, should be avoided.

Classically, a number of so-called "recombination poisons" (typically, sulphur-containing compounds, e.g. thiourea) have been employed to retard the rate of gaseous hydrogen evolution from the cathode surface, and thereby enhance the net loading rate. However, such electrolyte additives have little effect on the maintenance of high loadings due to their volatility or electrochemical decomposition over long time-periods. As a possible solution to this problem, we have observed that the addition of small amounts (typically 200 ppm) of non-classical additives, such as aluminium or silicon (in metallic and oxide form, respectively), to the electrolyte, results in the ability to maintain high loadings for longer periods, without impeding the initial attainment of high loadings. In this context, it should be mentioned that, in cells which utilize glass components, silicon-containing species will accumulate in basic electrolytes over extended time-periods.

Electrochemical cell design

The following cell design, Figure 1, was employed in this study. The cell body was made of stainless steel for convenience in manufacture and to ensure good thermal contact between the cell and the heat transfer fluid. A PTFE liner was employed in order to prevent the highly corrosive electrolyte, 1 M LiOD + 200 ppm Al, from making contact with the metal cell body.

Two concentric-cylinder palladium sheet anodes were used. These were 25 μm thick, approximately 5 cm high, 2 and 4 cm diameter, respectively. A 1

mm diameter vacuum-annealed palladium wire cathode, approximately 45 cm long (with 36 cm submerged in the electrolyte), was secured by four PTFE pegs from below and mounted between the concentric anodes in the manner shown in Figure 1. The anodes were mounted between two parallel PTFE plates which were themselves held in position by a PTFE pillar placed inside the inner anode, and a series of PTFE posts placed outside the outer anode.
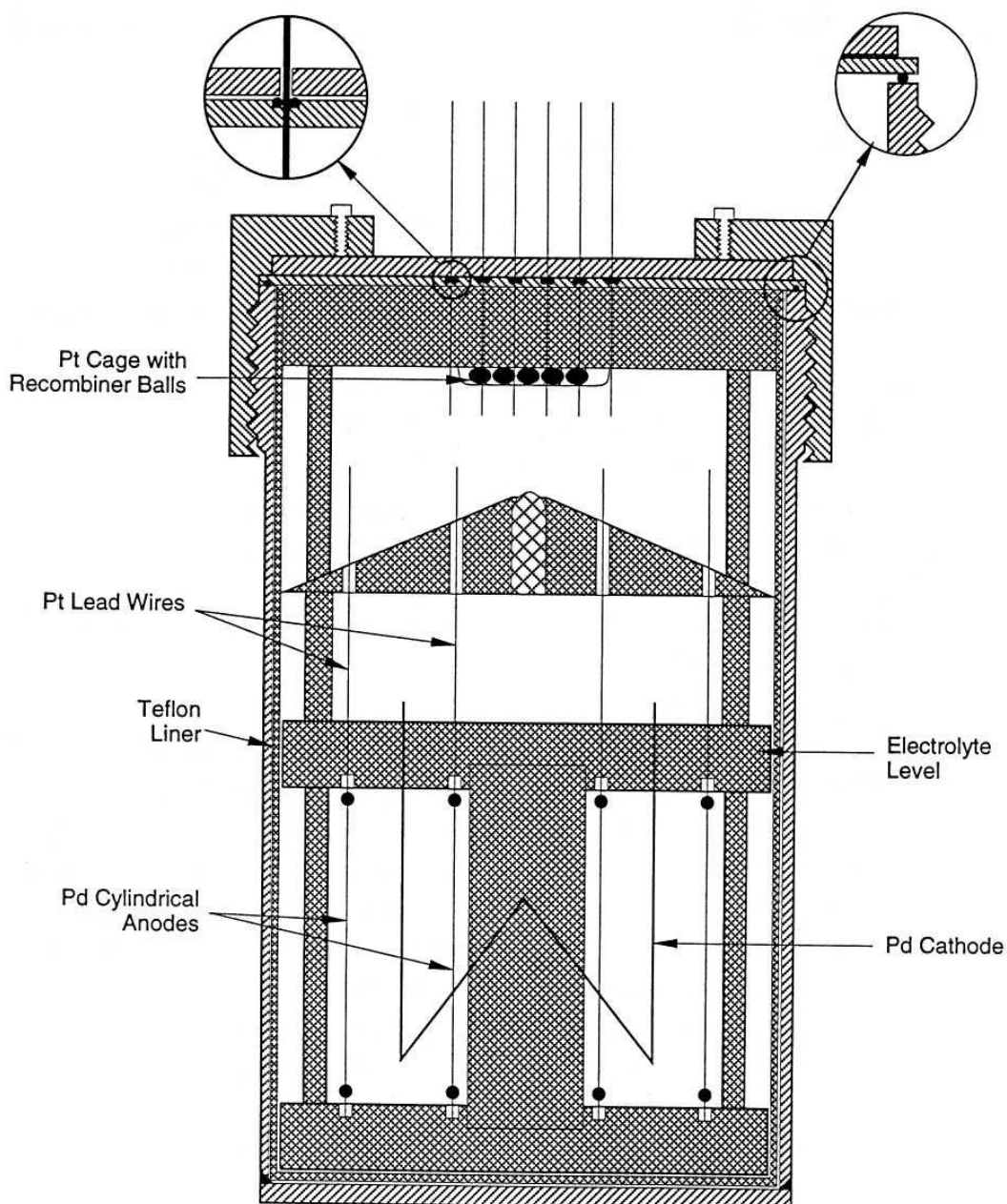

Fig. 1. Electrochemical cell design

Recombination of the evolved deuterium and oxygen was achieved using porous, platinum coated alumina spheres held within a wide-mesh platinum cage. The cage was suspended below a PTFE plate at the top of the cell. The collapse of deuterium and oxygen bubbles above the electrolyte surface projects liquid a considerable vertical distance during the operation of the cell at high current. In the absence of suitable precautions, the head space of the cell would fill with LiOD-saturated mist, possibly affecting the recombiner function. In order to prevent this, a PTFE cone was mounted between the electrodes and the recombiner. The center of the cone was removed and a static mixer inserted in order to remove LiOD-containing droplets from the gas stream reaching the recombiner. Small holes were drilled in the periphery of the cone in order that recombined D_2O could drip back into the electrolyte.

A pressure pipe connected the inside of the cell to a pressure transducer mounted above the calorimeter. The cell body was sheathed with a brass cylinder containing a resistive heater. In order to ensure good thermal contact with the calorimetric fluid, cooling fins were brazed to the outside of the brass cylinder.

Once assembled, approximately 200 cm^3 of electrolyte was added to the cell, reaching a level just below the bottom of the PTFE cone. The residual head-space within the cell was approximately 100 cm^3.

Initially, before sealing, the cell was filled with deuterium gas at approximately 1 atm pressure.

Calorimetry

The electrochemical cell described above was contained within a mass flow calorimeter, Figure 2, the design and operation of which have been described previously.[2,3] Briefly, the calorimeter consisted of an approximately adiabatic enclosure - comprised largely of a silvered, evacuated Dewar - which contained the electrochemical cell and through which the calorimetric fluid (water) was pumped. The calorimeter was situated in a constant temperature bath, maintained at 30 ± 0.003ºC, which also served as the source of the calorimetric fluid. The mass flow rate of the calorimetric fluid was determined gravimetrically, using an auto-siphon device mounted on an electronic balance, after passing through the calorimeter. The internal heater, described above, permitted operation at constant total input power, so as to

maintain approximately constant the mean electrochemical cell temperature. The power output from the calorimeter was determined essentially by the mass flow rate, the change in the temperature of the calorimetric fluid on its transit through the calorimeter, and a power loss term, discussed further below. Experimental control and data acquisition were achieved with a Macintosh microcomputer.
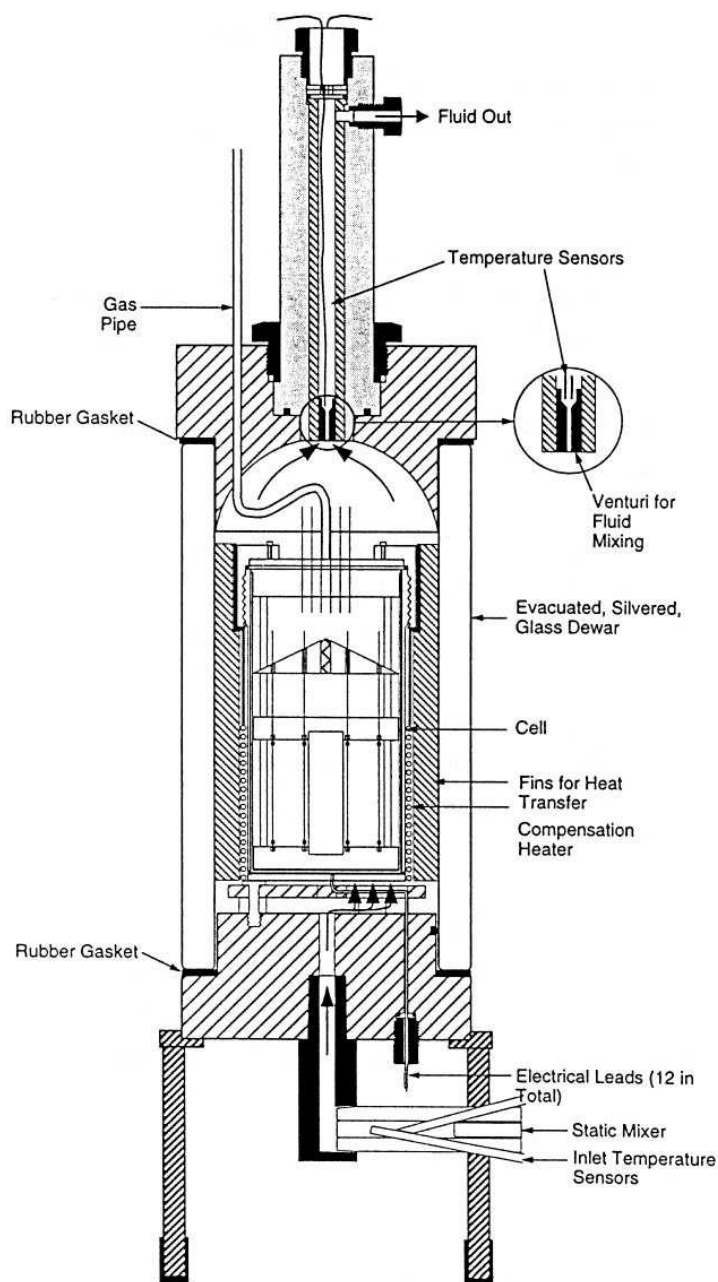

Fig. 2.　Calorimeter containing electrochemical cell

Data analysis

The difference between the output power and the power input to the calorimeter (both electrochemical and heater) may be referred to as an "excess power", P_{xs}. For the calorimetric system employed here, this quantity is given by

$$P_{sx} = (C_p \, \delta m/\delta t + k')(T_{out} - T_{in}) - P_{el} - P_h$$

where C_p is the heat capacity of water, $\delta m/\delta t$ the mass flow rate, T_{out} the outlet temperature of the calorimetric fluid, T_{in} the corresponding inlet temperature, P_{el} the input electrochemical power and P_h the input heater power. The power loss term k' is retained in order to account for the fact that the adiabatic calorimeter boundary is inevitably imperfect, and some conductive heat loss is expected. The methods employed both for the determination of k' at the outset of an experiment, and for the confirmation of its constancy during the course of an experiment, have been described[2, 3]. Similarly, the exact means employed for the measurement of the other quantities in the above equation, and the steps taken to reduce systematic errors in their respective measurements, have been discussed[2,3]. The measurement uncertainty in the excess power, treated as an example of a single-sample measurement,[5] was calculated as described previously[3] and is quoted (approximately) at the 95% confidence level ($\pm 2\sigma$).

RESULTS

Electrochemical and calorimetric data for the experiment described here during the time period 300 – 780 h are presented in Figures 3 to 5. Prior to 300 h, either statistically significant quantities of excess power were not produced, or complete calorimetric data were not obtained (due to a bath malfunction). For the calorimeter employed in this experiment, k′ was 0.46 ± 0.05 W K^{-1}. Figure 3 shows the variation of input electrochemical and heater powers, and the resulting total input power. Figure 4 describes the measured cell voltage and the electrochemical current during the time period 300 – 780 h. Note that a cell current of, for example, 5 A is equivalent to a current density of 0.44 A cm^{-2}. The calculated excess power with its associated measurement uncertainty and the average cathode loading are shown in Figure 5.
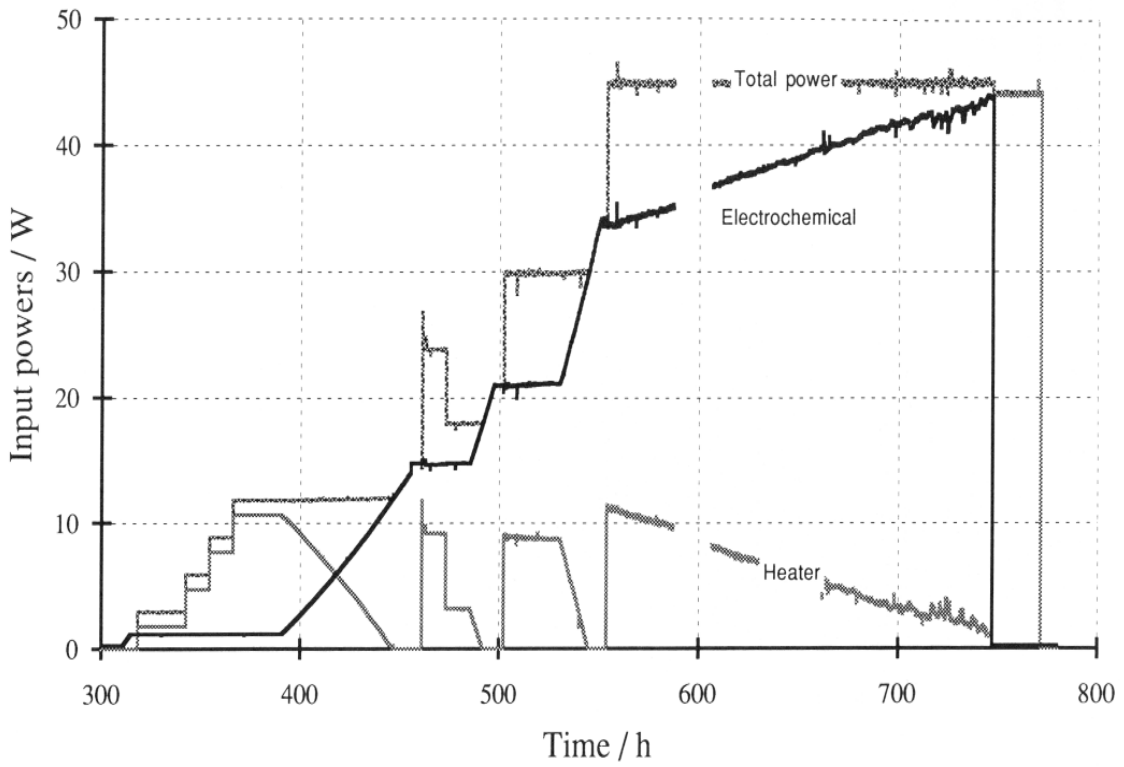
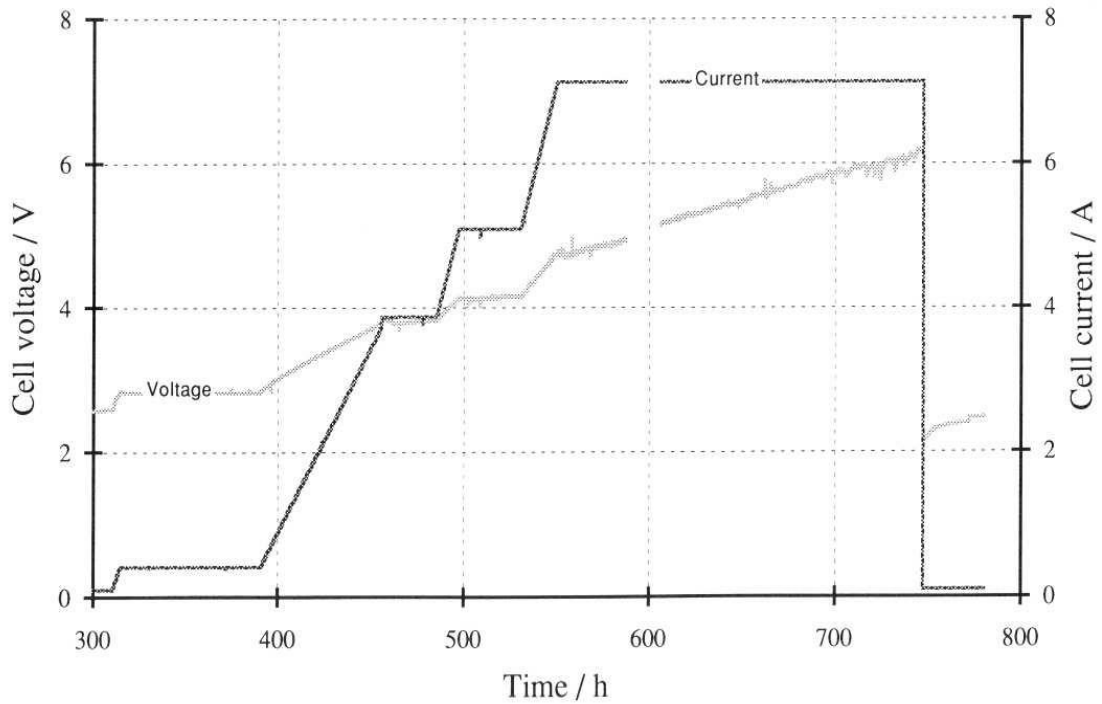Fig. 3. Variation of input powers with time

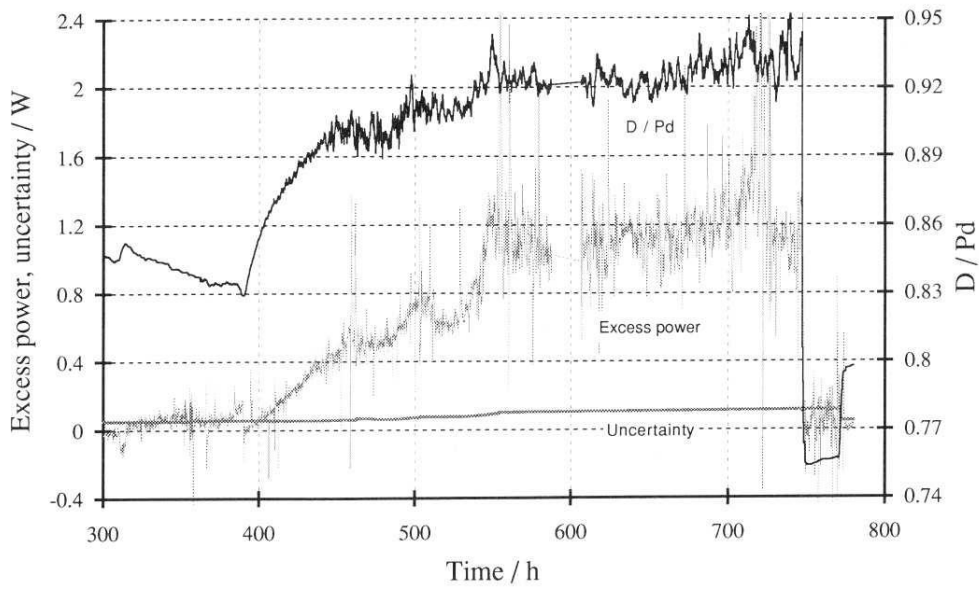Fig. 4. Variation of cell voltage and current with time

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Fig. 5. Variation of excess power, uncertainty and loading

Figures 6 and 7 depict the variation of excess power with electrochemical current and average cathode loading, respectively.
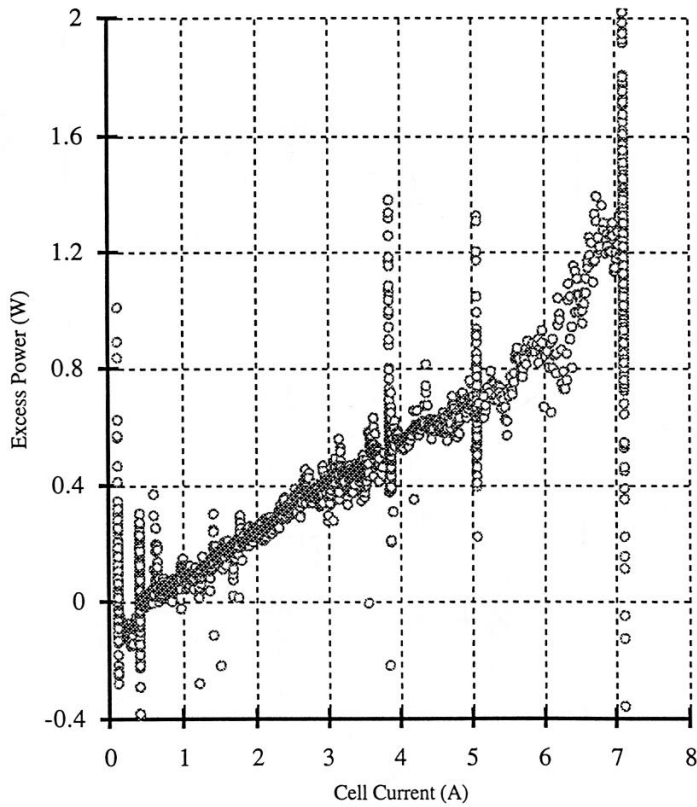

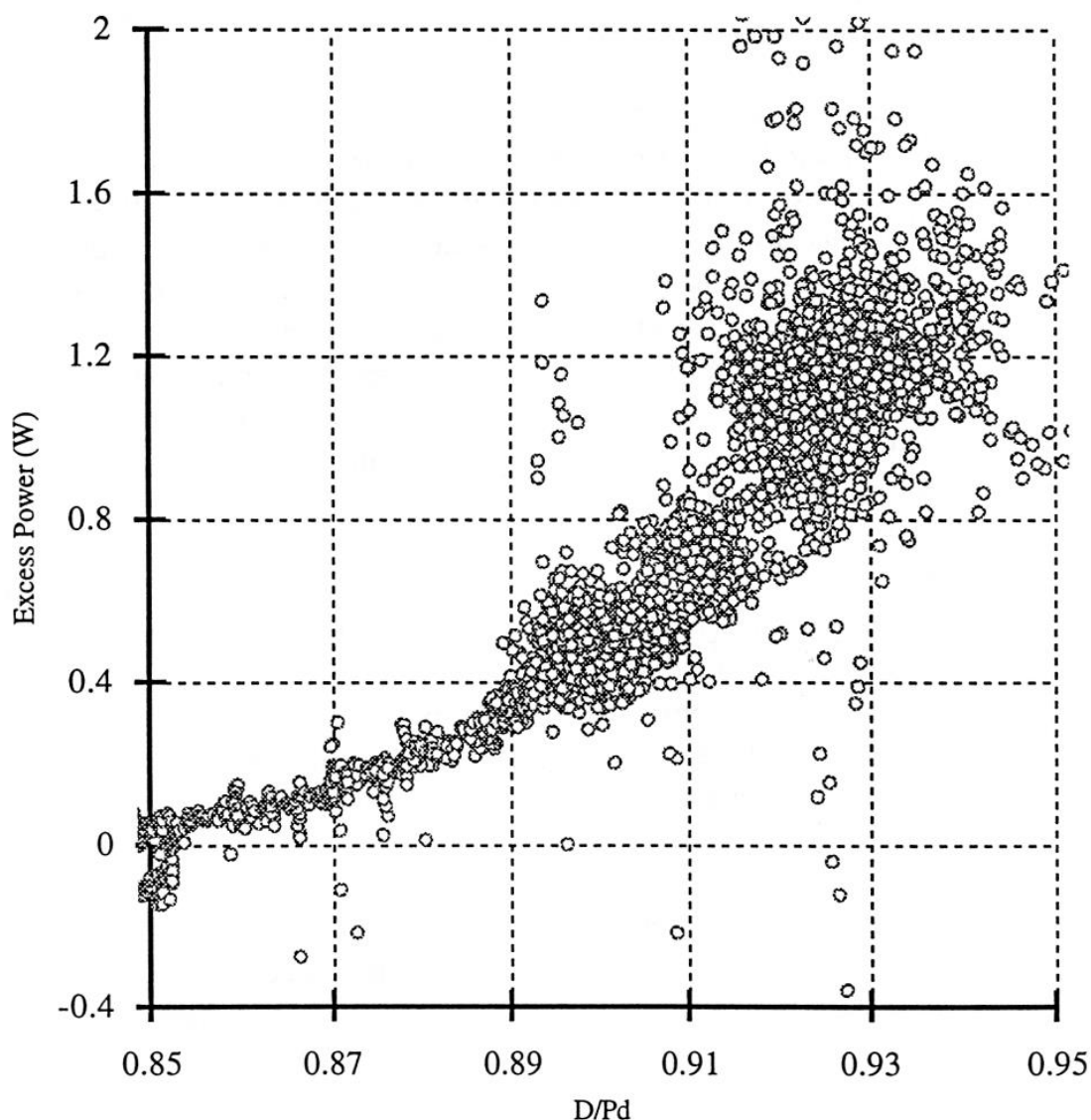Fig. 6. Variation of excess power with cell current

Fig. 7. Variation of excess power with loading

DISCUSSION

During the time period of interest, excess power up to approximately 1.2 W was produced. Although significant with respect to the measurement uncertainty, the excess power in this particular experiment was relatively small, in particular when compared to the total input power. The excess energy produced *during the time period of interest* was 1.2 ± 0.3 MJ or approximately 4.3 MJ cm^{-3} of palladium cathode. During this period, the total input electrochemical and heater energies were 36.3 ± 0.07 and 12.6 ± 0.03 MJ, respectively.

In common with previous experiments[2, 3], the excess power production observed here appears to conform to a certain phenomenology, discussed below. In addition, for the experimental configuration utilized here, the excess power is observed to vary systematically with current and in a second order manner (approximately) with average loading, above a loading threshold.

Using a different calorimetric system, a higher than first order dependence has been reported previously[6] for the variation of excess power with electrochemical current. An important distinction between this previous study and the results reported here is that, in the former case, the calorimetric system was not operated, as here, at constant total input power with an efficient heat removal mechanism, thereby ensuring an approximately constant mean cell temperature. Instead the system was operated at constant electrochemical current in a heat-retaining calorimeter design, thereby forcing the mean cell temperature to increase with increasing current. Clearly, further work is required in order to elucidate the nature of this apparent temperature dependence of the excess power. The approximately quadratic dependence of excess power on average cathode loading reported here serves to reinforce the remarks made above concerning the need for care in cell design and operation, if high loading are to be realized. At present, since the origin of the excess power production phenomenon in electrochemical systems utilizing deuterated palladium cathodes is unknown, the significance, if any, of the data in Figure 7, remains unclear. The data are, nonetheless, intriguing.

Phenomenological model

Based on our calorimetric studies carried out to-date, we may construct a phenomenological model for excess power production from deuterium-based electrochemical systems employing palladium cathodes. For an (initially) unalloyed cathode, the following three factors (at least) are associated with the observation of excess power production: **i)** The average cathode loading should exceed (approximately) 0.9; **ii)** an initiation time (typically, several hundred hours) is required which is long when compared with the time required for initial deuterium loading; **iii)** changes in the excess power level are usually associated with departures from the electrochemical steady-state, caused primarily by varying the current. Although the mechanistic

significance, if any, and interdependence of these factors are presently unknown, the following supplementary, necessarily somewhat speculative, suggestions may be noted:

Firstly, due to current density inhomogeneities on the cathode surface, it is likely that regions exist within the cathode where the loading exceeds the average value, perhaps significantly. Thus, it may be possible for the local loading, in certain regions, to approach unity in a cathode with a high average loading. In this connection, the development of new methods to further increase and maintain loading may be important. In addition, techniques for the accurate characterization of loading inhomogeneities may prove useful.

In the studies carried out here, the cathode dimensions were such that deuterium loading was achieved on the time-scale of hours, certainly much sooner than the several hundred hours required for the production of excess power. This observation raises the interesting possibility that one or more species, other than deuterium, are required to be present in the cathode in order to observe excess power, species which are not present initially and are thus required to diffuse into the cathode, presumably from the electrolyte. Analyses of used cathodes have revealed the presence of several light elements in the near-surface region (to a depth of several microns); in particular, lithium. Clearly, calorimetric experiments involving the use of selectively pre-alloyed cathodes are of interest.

For a cathode initially in the steady-state (with respect to loading), a departure from this state will lead to the modification of the deuterium fluxes within the electrode. Since it has been observed that excess power levels generally increase with increasing current density, the possible role of the interplay between the ionic and electronic fluxes within the metal merits consideration, particularly with respect to its influence on the (local) loading.

In order to understand the origin and/or mechanism of the excess power phenomenon, it is clearly essential to identify either the fuel(s) or the product(s) (preferably both) of the energy producing process, assuming, for the moment, that it is non-artifactual in nature. This task is made easier if the excess power (and, hence, the integrated excess energy) levels are caused to increase intensively. We are presently investigating the utilization of the phenomenological model described here, to achieve the intensive scale-up of the excess power effect.

Approximately 70 hours after the excess power event described here, an accident occurred which caused termination of the experiment. The cause of this accident is discussed in a paper published elsewhere in these Proceedings.

ACKNOWLEDGEMENT

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