Excess Power Observations in Electrochemical Studies of the D/Pd System; the Operating Parameter Space

M.C.H. McKubre
SRI International, Menlo Park, California.

Abstract. The research activity into the Fleischmann-Pons Effect, FPE [1] at SRI has now accumulating more than 60 man-years of research. Here we focus attention on aspects of that work that lead to an improved understanding of the parameter space in which the FPE occurs.

1. Introduction

Researchers at SRI first focused attention on the critical importance of deuterium loading, the role of chemical poisons and additives in controlling the electrochemical interface, in order to achieve and maintain high D/Pd loading. We studied the correlation of excess power production with loading and reported simultaneously with IMRA-Japan [2,3] the threshold onset of the FPE reproduced as Figure 1. We designed and built a novel, high-accuracy, fully automated mass flow calorimeter, and set out to perform replication studies of the Fleischmann and Pons heat effect, first to confirm the existence the effect and second to better define the physical conditions under which it can be observed.

Fig. 1. - Excess power density in W/cm² versus average D/Pd atomic ratio measured from the axial resistance for a Johnson Matthey wire cathode 30 cm long and 1 mm diameter in 1.0 M LiOD containing 200 ppm Al.

As a second thrust of activity SRI embarked on a formal program of laboratory replication already discussed in several papers [4-7]. We successfully replicated:

i. calorimetric evidence of the Fleischmann and Pons heat effect [8,9],
ii. pioneering Miles/Bush FPE heat/helium correlations [4,10],
iii. heat (and helium) results of gas loading studies reported initially by Case [10],
iv. Arata & Zhang double structured cathode electrolysis heat (and helium) results [10],
v. Energetics Technologies startling amplification of the power and energy gain of the FPE using innovating current (and other) modulation first elucidated by Dardik [7,11].

To accomplish these tasks the SRI team encouraged and contributed in a number of scientific partnerships. Obviously in approaching any difficult problem it is important to attract a critical mass of all the people who might contribute to the resolution of these effects. Specifically and ongoing we have a long established collaboration with Peter Hagelstein and his colleagues at MIT and over a decade of continuous, active, formal collaboration with Vittorio Violante and his group at ENEA Frascati. The Energetics team we have been collaborating actively with since about 2006, and more recently with the Naval Research Laboratory, NRL.
2. Experimental

At SRI, it was decided in early experiments to pursue excess power measurements based on flow calorimetry so that measurements of thermal power were obtained from measurements of the input and output (water) temperature, mass flow rate, and knowledge of the (water) heat capacity. In the SRI calorimetry of the early 1990s, about 95% of the thermal power was captured in the flow. The power not captured by the flow calorimetry was estimated using a Fick’s law measurement, resulting in total power measurements with errors on the order of 0.5% in the case of 95% capture by the flow. In later designs, specifically the Labyrinth (L) and helium leak tight (M) calorimeter designs greater than 99% of the evolving heat was captured in the convecting fluid flow resulting in accuracies better than ±0.35%.

To perform excess power measurements in this kind of calorimeter, closed cell operation was required, which necessitated the recombination of all gases generated in association with the electrochemistry. A further advantage of this choice is the retention of D₂O and products for analysis. It is worth noting that mass flow calorimetry and closed cell operation were not the methods adopted by Fleischmann and Pons. Much has been made of this difference but these choices reflected no disapproval of earlier principles and procedures of calorimetry. Although we were not aware of the details at the time, Fleischmann and Pons designed and built a beautiful calorimeter. It was very subtle and very sophisticated, requiring a sophisticated analysis and understanding. Unfortunately most of the people who remained skeptical in 1898 and 1990 had no means of achieving that sophisticated understanding.

In order to achieve high loading values (D/Pd ratios >> 0.9) one needs to take strong control of the impurity aspects of the electrochemical cell. At SRI the various elementary constraints evolved a particular cell design shown in Figure 2. We employed mostly one molar LiOD, where the original work [1] employed 0.1 M. Again, no judgment is implied. We selected the electrolyte we believed best able to test our hypothesis that high D/Pd loadings prompted or promoted the excess heat effect. Most early SRI experiments were performed with 1 and 3 mm diameter wires, either 3 or 5 cm long. Loading is inferred from measurements of the resistance in the axial direction, expressed as a ratio of the unloaded resistance.

![Fig. 2. - SRI Degree of Loading (DoL) electrochemical cell shown in hermetic closure.](image)

In its calorimetric use the cell of Figure 2 is placed inside the calorimeter as shown in Figure 3. The calorimeter was submerged inside a large (~1 m³), water bath that was well stirred and well regulated. This bath was placed in the center of an isolated, temperature controlled room. The mass flow fluid (water) was drawn from the bath past two inlet RTD sensors placed directly in the flow stream, past the submersed
electrochemical cell and emerges past outlet temperature sensors situated within the axial outflow channel, directly in contact with the outgoing fluid. Two outlet RTD sensors were used, identical to the two at the inlet, to provide a redundant measurement of $\Delta T$.

Fig. 3. - SRI Labyrinth (L) Mass Flow Calorimeter showing internal hermetically sealed electrochemical cell.

Many excess heat bursts were detected over the years in Fleischmann Pons experiments run in the SRI flow calorimeters. An example is illustrated in Figure 4, where two cells (a light water cell and a heavy water cell) were run electrically in series. Excess power was observed in heavy water cells at SRI, but not in light water cells, consistent with the results presented in this figure. In addition, the excess power effect appears to vary in response to the current density applied as shown in Figure 5. One observes a threshold in current density, where no excess power is present below 270 mA/cm$^2$, and where the excess power appears to increase roughly linearly above this threshold. The appearance of a threshold in current density is typical in FPE experiments, although the specific current threshold is different for different cathodes, and depends strongly on whether the cathode is a rod or foil [12].

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1 In some experiments two additional thermistor sensors were used at the outlet to provide an alternative measurement method.
Fig. 4. - Excess power in Fleischmann-Pons experiments as a function of time in twin cells and calorimeters, driven with a common current, one with heavy water (upper data points) and one with light water (lower data points). The applied current density is shown as a solid line.

Fig. 5. - Excess power as a function of current density for Fleischmann-Pons cells with heavy water (upper data points) and with light water (lower data points).

Figure 6 presents not a typical result but a good result from later series SRI FPE experiments. With total input power\(^2\) 12 W, we observe the output power increasing up to 6 W, with peak excess power of 50% with respect to the total input power. Also plotted is a pseudo-reference voltage exhibiting structure and detail reflecting extreme and at times bi-stable conditions at the electrochemical interface of the cathode, somewhat correlated to excess power. The period from ~700 hours onwards was more or less steady electrochemically, but the thermal and voltametric responses are dynamic.

It was found that changes in the operating parameters could initiate a heat burst in addition to the apparently self-stimulated dynamics of the cathode overvoltage and excess power. This observation may be related to a more general correlation between excess heat and a net deuterium flux either into or out of the metal. Figure 7 plots loading and excess power for a 24 hour period of constant electrochemical condition for (temperature and current density) a 1 mm dia. Pd wire cathode exhibiting variable excess power. The loading can be seen to vary in a somewhat sinusoidal “breathing” mode with ~2 hour period as the cathode apparently spontaneously absorbs and desorbs deuterium.

\(^2\) Experiments were operated in pseudo-isothermal condition by holding the sum of the electrochemical and joule heater input power constant.
Fig. 6. - Excess power as a function of time for Fleischmann-Pons cells with LiOD electrolyte containing 200 ppm Al. The solid green line plots electrochemical current density, the square blue points are cathode voltage measured vs. proximate open-circuit Pt pseudo-reference electrode. The solid black line is the average excess power raw data points plotted in orange.

Fig. 7. - Correlation of the amplitude of loading oscillations with the magnitude of excess power in experiment M4.

While the frequency remains fixed, the amplitude of this “breathing” closely correlates with the amplitude of the excess power signal. We do not have an accurate knowledge of the diffusion coefficient of D under the prevailing loading condition but a time constant of 2 hours corresponds with a diffusion coefficient of \( \sim 5 \times 10^{-7} \) cm² s⁻¹ traversing the full radius of the electrode. We do not know what caused this to occur, and all attempts to stimulate such oscillatory fluxing in the high loading condition have failed (with one notable exception discussed below).

3. Conclusions

The clear evidence of both intense and extended experimental investigation is that the FPE heat effect occurs as a consequence of four conditions in the electrochemical palladium-deuterium system:
i. electrodes must attain and maintain D/Pd loading above a (high) threshold value, for
ii. periods longer than an initiation time that is long compared to deuterium in-diffusion
iii. while being subjected to a high electrochemical current that is in general larger than the
current density of maximum loading
iv. maintaining an electrode/electrolyte interface kinetically free enough to facilitate high rates of
deuterium absorption/desorption (flux).

This set of observations prompted the development of an empirical expression for the simplest and most
widely observed mode of excess heat production (designated by us as Mode A).

\[ P_{ss} = M \left( x-x^0 \right)^2 \left( i-i^0 \right) |i_D| \]  \[ \text{[1]} \]

where \( x = \text{D/Pd}, x^0 \) is the threshold value typically \(-0.875\), the current density threshold \( i^0 \) for wire cathodes
typically falls in the range \( 75 < i^0 < 450 \text{mA cm}^{-2} \), the deuterium interfacial flux \( i_D = 2-20 \text{mA cm}^{-2} \).

In conclusion it should be noted that the simultaneous attainment of the above specified conditions has
been found to require patient and rigorous attention to: system electrochemistry; bulk palladium
metallurgy; electrode surface morphology and crystal orientation. Much, if not all of the apparent and
“famous” irreproducibility of the Fleischmann-Pons heat effect can be traced directly to the failure to
recognize and meet one or more of these conditions.

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