

Research Article

Flux Effects in Metal Hydrogen Loading: Enhanced Mass Transfer

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Abstract

SRI has shown over hundreds of electrochemical experiments that the Fleischmann–Pons heat effect can be generated if high current, high loading and deuterium flux are present. Until the work of Dardik and the Energetics group, we were unable to generate the deuterium flux synthetically. Using Dardik's Superwave® method to generate deuterium flux, we have shown that excess heat is regularly seen in PdDx electrolysis cells, given the appropriate cathode metallurgy.

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1. Introduction

On March 23rd 1989 Fleischmann, Pons and Hawkins [1] publicly reported results of an anomalous heat effect resulting from the intensive, electrochemical insertion of deuterium into palladium cathodes occurring over an extended period of time. This was already a well-studied system, and the SRI team, having worked on Pd/D₂O for more than a decade, was better positioned than most to judge this claim experimentally. If anomalous large heat production was indeed present in palladium cathodes loaded electrolytically with D, then the only possibility was that this occurred in the very high loading regime with the atomic loading ratio D/Pd greater than about 0.8 where the system had been infrequently and poorly studied. This intuition regarding the effect of the D/Pd loading ratio on the excess power production was supported experimentally when the groups at SRI [2] and IMRA-Japan [3] reported simultaneously and independently the effect of threshold loading of D/Pd ~ 0.85 on the Fleischmann Pons Heat Effect (FPHE) for bulk Pd wire cathodes at ICCF3 in Nagoya in October 1992.

Several mysteries relating to the FPHE remained to be revealed and resolved at that time. The appearance of heat in excess of electrical input appeared to exhibit a threshold effect on current density at levels significantly greater than the current density of maximum loading [4]^a. A significant time delay separated complete deuterium saturation and the onset of thermal activities that suggested the initiation or incubation time of an unknown process presumably of chemical

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^aThreshold current densities of 100 mA cm⁻² or larger were observed, well beyond the current density of maximum loading that is between 15 and 25 mA cm⁻² for Pd cathodes in 0.1–1.0 M LiOD solutions typically used in these experiments [4].

or metallurgical origin. In 1995 it was discovered that there was another materials or electrochemical constraint on the demonstration of the FPHE [5]. Excess power was shown not to occur for equilibrium-loaded bulk-wire cathodes no matter how highly loaded, but did occur when a flux of deuterium was present. The excess power was roughly proportional to the flux of deuterium through the cathode interface^b independent of direction.

We will use the space here to discuss the materials and electrochemical significance of these observations with regard to demonstrating and hopefully utilizing the FPHE. We adopt an empirical approach and do not attempt to understand or explain the fundamental physical processes behind the need for high loading, high current, long times and high flux. Of pragmatic interest is how one can tailor the metallurgical and electrochemical processes to achieve these four conditions simultaneously.

2. The Flux Condition

SRI experiment M4 was performed in a helium leak-tight calorimeter [6] and employed a Johnson Matthey low platinum group metal palladium cathode 0.1 cm dia., $\times$ 10 cm long formed into the shape of a “lasoo” [6]. The electrolyte was 1.0 M LiOD with 200 ppm Al added initially. The cell was evacuated and electrolyte added with the power supply delivering 2 V cathodic. The cell was then filled with D₂ gas containing 0.34 ppm ⁴He to a pressure of 5 psig. Two slow current ramps were undertaken in an attempt to engender loading and exhibit an excess heat effect^c. The first current ramp from 70 to 210 h yielded excess power and energy below the measurement uncertainty ($P_{XS, Max} = 12 \pm 21$ mW and $E_{XS} = 12 \pm 18$ kJ) and the second from 350 to 390 h showed a small effect at the limit of calorimetric accuracy ($P_{XS, Max} = 53 \pm 25$ mW and $E_{XS} = 17 \pm 8$ kJ).

At 472 h and prior to the third current ramp an important change was observed in the properties of the measured cathode axial resistance ratio and, consequently, in the inferred loading; the measured resistance appeared to become spontaneously noisy^d. No change was made (intentionally or knowingly) to the electrical circuit at this time, other than repeating a previously performed current profile. A third current ramp was started at 504 h from 32 mA cm⁻² to 985 mA cm⁻² over a period of $\sim$ 60 h. Figure 1 shows the effect of this ramp on the loading inferred from the 4-wire resistance measurement [7]. While not particularly well loaded, the cathode responded positively to increasing current up to a surprisingly high value of current density and a maximum loading of D/Pd = 0.88 ± 0.01 was obtained at a current density of $\sim$ 376 mA cm⁻². What is of interest and was first seen in this data set, the loading appeared to fluctuate or oscillate with an amplitude that varied during the 240 h period of Fig. 1. The red line in Fig. 1 will be discussed below.

Figure 2 shows the effect of current, loading and loading oscillations on the measured excess power normalized to the cathode volume (0.079 cm³). Also shown in Fig. 2 is a fitting function

$$P_{XS} = M(x - x^\circ)^2(i - i^\circ)|i_D|, \quad (1)$$

where P_X is the excess power density (W cm⁻³), M is a proportionality constant (in this case 3×10^6), $x = D/Pd$, $x^\circ \sim 0.833$, i is the electrochemical current density for the cathode, $i^\circ = 0.45$ A cm⁻², and i_D is the absorption/desorption deuteron flux through the surface expressed as current density (A cm⁻²) that is required to load and unload the cathode during the period of the spontaneous loading oscillations.

With two adjustable parameters^e (x° and i°) the green function in Fig. 2 exhibits a cross correlation $r = 0.853$ with the measured excess power density indicating that $\sim$ 73% of the excess power is reflected linearly in the terms

^bOther fluxes may be important as well, notably axial fluxes of deuterons and electrons in the metal phase.

^cAt the end of each ramp the cathode surface was briefly and partially stripped anodically to remove surface deposits, and Cu was added to the electrolyte dissolved in LiOD.

^dOn closer examination this noise resolved into signal as discussed below.

^eThe scale factor M is not relevant to the cross correlation function. The adjustable parameters x° and i° are heavily constrained by physical reality,

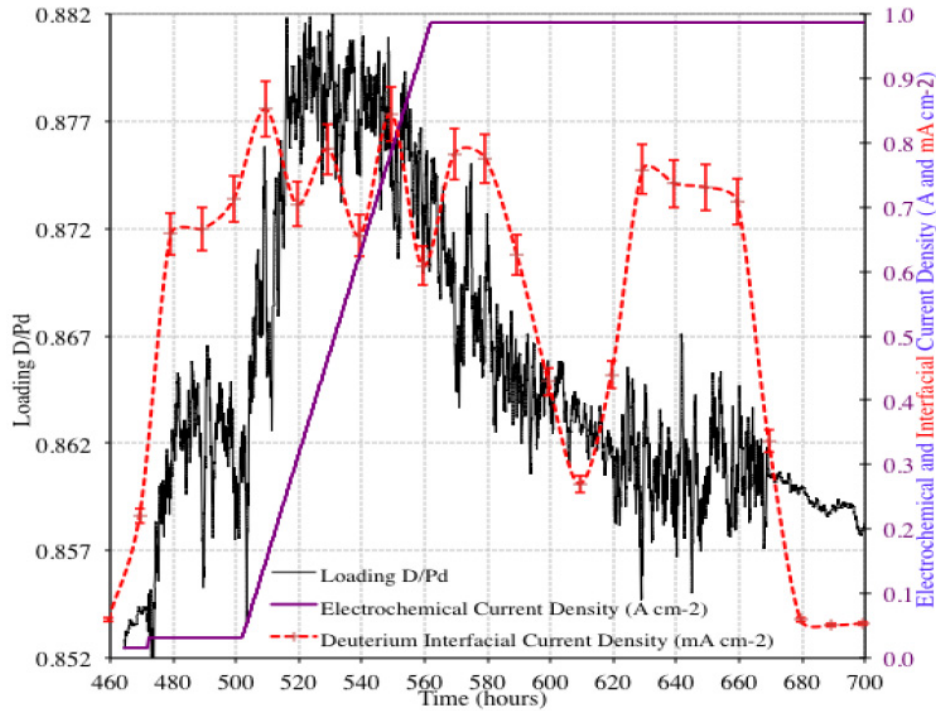


Figure 1. The response of loading and interfacial deuterium flux to a ramped increase in electrochemical current density in experiment M4.

of equation [1]. In fact, since the current is constant during most of the duration of excess power, the primary drivers are the slow decline of the average loading value, and the oscillation of loading (the dc and ac effects of loading, see Fig. 1). It is this data set, together with several subsequent sets primarily using 1 mm dia. wires and 50 μm thick foils^f that prompted us to consider the deuterium flux as a variable in excess heat production, and to attempt to find means to stimulate it.

First, what is the nature of the loading oscillation, and what is its range of amplitude? In the 24-hour period from 610 to 634 h there was no change in current density and very little change in average loading with a slight declining trend. Despite this the measured excess power rises from near zero values ($\sim 30 \text{ mW cm}^{-3}$) between the peak values shown in Fig. 2, to more than ten times this value at 634 h. Details of the loading variation and excess power can be seen in this period in Fig. 3. The loading oscillation at constant electrochemical current density appears in the shape of a rough sinusoid (with some harmonic distortion), with fixed period $\sim 2 \text{ h}$, and spontaneous variation in amplitude. It is this internally generated amplitude modulation that affects the last term in equation [1] and dominates the variability of excess power in this interval.

Why 2 h? Once inside the Pd metal phase the D atoms diffuse with critical dimension 0.05 cm determined by

^f Data from foils are not as easily handled for planar cathodes which invariably have non-uniform current distributions and non-uniform loading that results in a measured average value that may be well below the points of maximum loading where presumably the excess heat effects take place.

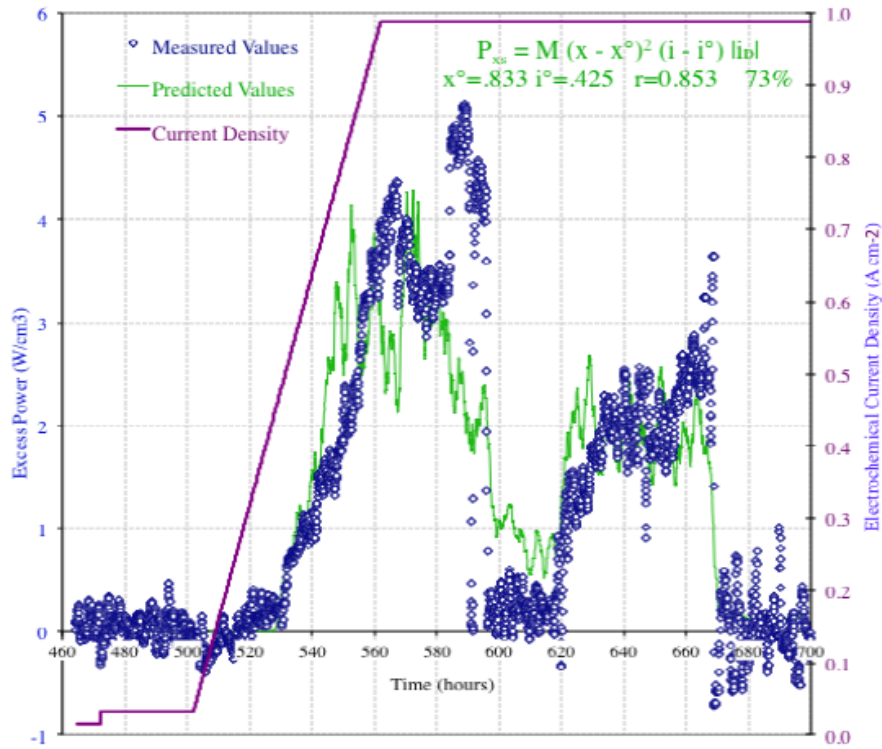


Figure 2. The observed and calculated excess power from Eq. (1) for a ramped increase in electrochemical current density in experiment M4.

the radius of the 1 mm dia. wire. There are approximately 14 peaks and valleys in the loading in Fig. 3 so that the average period is 1.71 h. Calculating the diffusion coefficient from this time constant for a penetration depth of 0.05 cm yields a value of $D_D = 2 \times 10^7$, exactly that of deuterium at high concentration in palladium. It appears that what was happening, *without our control or even knowledge at the time*, was that the cathode spontaneously absorbed D at a rate determined by the electrochemical kinetic control of the surface monolayer coverage (D surface activity). At the point that the cathode was “full”, and the inward flux no longer sustainable, either a condition of stress inside the lattice or an effect that reduced the deuterium surface activity causes the flux to reverse and complete the cycle. In the interval of Fig. 3 excess power is controlled by the amplitude of this oscillation. After many years we still do not know what caused the amplitude (and thus excess power density) to change.

What is happening and how can we affect it? The dashed red line in Fig. 1 plots the 10-hour averaged value of the flux of deuterium across the cathode interface that is required to cause the variation in bulk average loading⁸. Note the three order of magnitude difference in scale between i_D (the deutron interchange flux expressed in mA cm^{-2}) and i (the applied electrochemical current density expressed in A cm^{-2}). This scale difference indicates that essentially all

⁸For convenient reference this flux is plotted as a current density although the exchange of surface-adsorbed and bulk-absorbed D atoms is a chemical not electrochemical process.

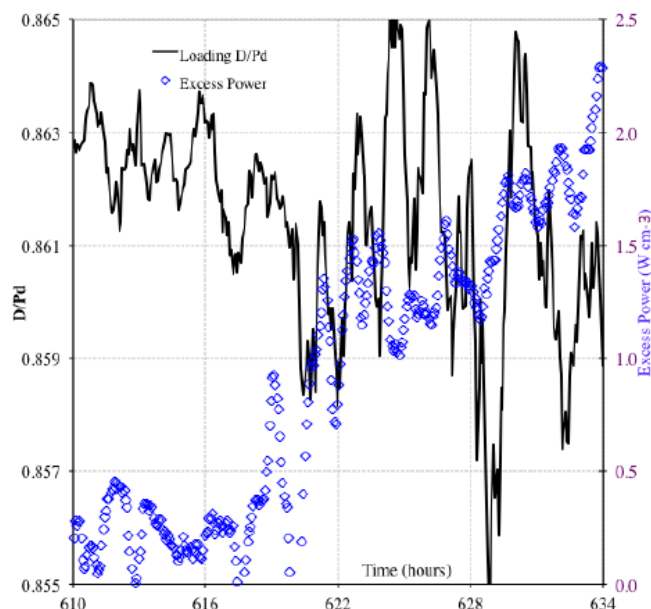


Figure 3. Detail of the spontaneous loading and excess power fluctuations in M4.

of the applied current results in D_2 molecule formation not loading. Despite this, the exchange flux of nearly 1 mA cm^{-2} is quite surprising, especially since in light of the fit to equation [1] in Fig. 2 this flux appears to control the rate of excess heat production in well-loaded cathodes after the incubation period.

This brings us to the central question: how can we take advantage of this knowledge to increase the reproducibility of our experiments and the power and energy density of the effect? The total excess energy produced in the two peaks (Fig. 2) of Ramp 3 was $82.5 \pm 27 \text{ kJ}$, a 3 sigma effect but more would be desirable. After brief stripping and a third Cu addition a fourth ramp was commenced at 758 h. The loading during Ramp 4 was better than Ramp 3 with D/Pd reaching a maximum of 0.898 ± 0.001 but the loading fluctuation seen in Figs. 1 and 3 was not present. An attempt was made to stimulate loading fluctuations electrochemically by modulating the current with increasing amplitude about a fixed cathodic point ultimately reaching a maximum of $3.1 \pm 1.0 \text{ A}$. This condition was maintained for 24 h but resulted in very little forced loading variation, a relatively rapid net loss of loading down to $D/Pd \sim 0.82$, and no excess power. The calorimeter maintained thermal balance with $P_{XS, \text{Max}} = 0 \pm 40 \text{ mW}$ and $E_{XS} = 4 \pm 26 \text{ kJ}$ in the approximately 300 h process of Ramp 4.

At 1077 h the cathode was stripped and 2 cm^3 of 1 M LiOD with 200 ppm Al was added to the cell, followed by 1 cm^3 of D_2O , with flowing D_2 . At 1078 h the cell was pressurized to $\sim 5 \text{ psig}$, the D_2 flow stopped and manifold sealed, and the current density was returned to 16 mA cm^{-2} . At 1174 h the fifth current ramp was started from 0.1 to 3.1 A at 25 mA/h. At 1334 h a further attempt was made to induce loading variation by switching the current on alternate measurement cycles (5 min) between 3.1 A cathodic and 0.001 A anodic. During the initial ramp the loading reached a maximum loading of $D/Pd = 0.918 \pm 0.001$. The introduction of cathodic/anodic pulsing at 1334 h produced a variability in loading, as desired, but the flux response was small, the net loading declined and the excess power and energy was within the calorimeter experimental uncertainty accuracy ($P_{XS, \text{Max}} = -25 \pm 25 \text{ mW}$ and $E_{XS} = -4 \pm 8 \text{ kJ}$).

Before the declared end of experiment M4 a total of 26 further attempts were made to find a waveform or pulse sequence that would allow us to induce a loading variability and thus a flux of D across the interface, while maintaining above-threshold loading. None was found [6] and a number of experiments were designed and operated over the next few years with similar null results. Although high loadings could be achieved with suitable electrochemical control and robust Pd metallurgy, and high loading variabilities could be achieved with some current schemes and scupulous control of the electrochemical interface, these two criteria were not met simultaneously with any waveform employed by us until 2003.

The paper delivered by El Boher at ICCF10 in 2003 with principal author Dardik remains one of the most interesting and important works in the CMNS field [8]. Two aspects of novelty were introduced by Energetics Technologies Inc. (ETI) in this paper:

- (1) The use of a palladium glow discharge in deuterium gas that produced 6.7 times more thermal output than input electrical energy in a well designed mass flow calorimeter.
- (2) Implementation of a highly novel multi-periodic waveform that the inventors designated as a “SuperWave”.

Not only were ETI scientists able by means of this SuperWave to (presumably) load and stimulate the Pd/D-plasma interface to achieve significant levels of excess energy production at useful temperatures^h, they were also able to use this function to load and modulate the loading in electrolytic Pd/D₂O cells. As a result of this an extended and successful campaign of experimentation was mounted to explore the use of SuperWaves in loading Pd with D in electrolytic cells and excess heat production by ETI in Israel, SRI in the US and ENEA (Frascati) in Italy [9].

What is a SuperWave and what is it good for? SuperWaves are a new class of function, somewhat related to Brown Noise, generated by the self similar superposition of higher frequency replicates of a kernel function on itself according to the following rule. As the amplitude of the kernel function increases, the frequency and amplitude of the superimposed higher frequency replicate also increase. This generates a new kernel function; this recursion process can be replicated as many times as desired but from experience with electrochemical systems little benefit is gained beyond the fourth or fifth modulation level. What results is a function with lowest frequency determined by the period of the initial kernel, highest frequency governed by the selected scaling factorsⁱ, and all frequencies in between (and all amplitudes) are represented in the function. Figure 4 shows this process in operation using a $\sin^2$ function as a kernel (the dark blue line).

The function shown in Fig. 4 and closely similar functions generated using varied parameters has been widely explored at SRI in the past decade for loading and excess heat generation. Another way of representing the SuperWave mathematically is as follows,

$$F(t) = A_0 \sin^2(\omega_0 t) [1 + A_1 \sin^2(\omega_1 t)] [1 + A_2 \sin^2(\omega_2 t)] [1 + A_3 \sin^2(\omega_3 t)] \dots \quad (2)$$

More than 1000 experiments have been performed in the laboratories mentioned above^j to test the power and benefits of SuperWaves in electrochemical and other systems. The advantages are best shown by example. Figure 5 shows the use of a SuperWave in an electrochemical cell and calorimeter of ETI design [9,10] during a DARPA-sponsored replication activity [11]. In this case the cathode was a 50 μm thick foil of area 8.6 cm^2 prepared by Violante at ENEA (Frascati) and the electrolyte was 0.1 M LiOD with no deliberate additions. The red data points plot the average,

^hThe water in the mass flow calorimeter was raised to the boiling point and the temperature inside in the plasma was obviously much higher.

ⁱThe highest frequency is practically constrained by the ability of power systems to deliver signal to the system under test, and the ability of the measurement system to interrogate and resolve the input and output signals.

^jPrimarily by ETI in Israel which is now constituted as the Sidney Kimmel Institute for Nuclear Renaissance (SKINR) at the University of Missouri, Columbia.

maximum and minimum loading obtained during the 20-minute SuperWave cycle^k of experiment ETI 035-7. It can easily be seen that the SuperWave allows or facilitates loading up to extreme values for this cathode, and that this high loading persists to both for long times and at high currents. The maximum loading observed during the 540-hour interval of Fig. 4 was an impressive value of $D/Pd_{Max.} = 1.010$ with a maximum 20-minute average value of $D/Pd_{MAV.} = 0.982$, both at the maximum average current of 1.75 A or electrochemical current density of 203 mA cm^{-2} .

Connecting the minima and maxima of D/Pd for each SuperWave cycle is a bidirectional flux of deuterium through the large surface area. Although scattered, the black circle points in Fig. 5 show the very impressive response of a highly facile electrochemical interface. The largest response of over 4 mA cm^{-2} of deuterium interfacial flux occurred at $\sim 160 \text{ h}$ when the cathode was deliberately partially stripped and at intermediate currents of 470 mA or 55 mA cm^{-2} . An analysis of the excess power measured in this experiment in terms of Eq. (1) yielded the following constants [11]: $x^\circ = 0.875 \text{ D/Pd}$; $i^\circ = 35 \text{ mA cm}^{-2}$. That is, in terms of Eq. (1), the foil cathode in experiment ETI 035-7 behaved very similarly to the wire cathode of experiment M4 discussed above, but with a significantly lower current threshold (35 cf. 450 mA cm^{-2} for M4) and a very much lower proportionality constant M (10^3 cf. 3×10^6 for M4). Both factors suggest that a much smaller fraction of the total surface area was involved in excess heat production for the foil cathode. The reasons for this are reasonably well understood and described in reference [11], but are beyond the scope of this work.

^k20 minutes or 1200 s corresponds to a frequency of 0.83 mHz which is below the lowest frequency at which mass transport processes (the slowest relevant electrochemical process) are relevant.

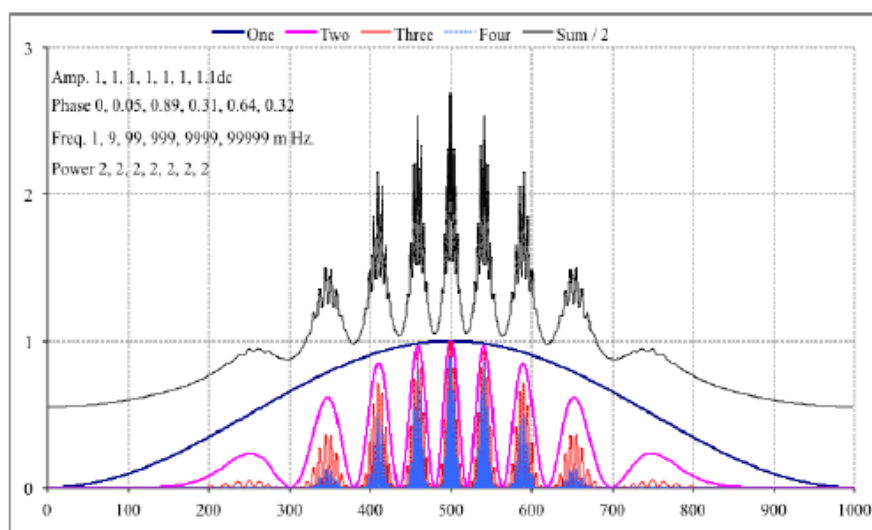


Figure 4. Generation of a SuperWave of 1000 second period, covering the range 1 mHz. to 100 Hz. with dc offset for electrochemical use.

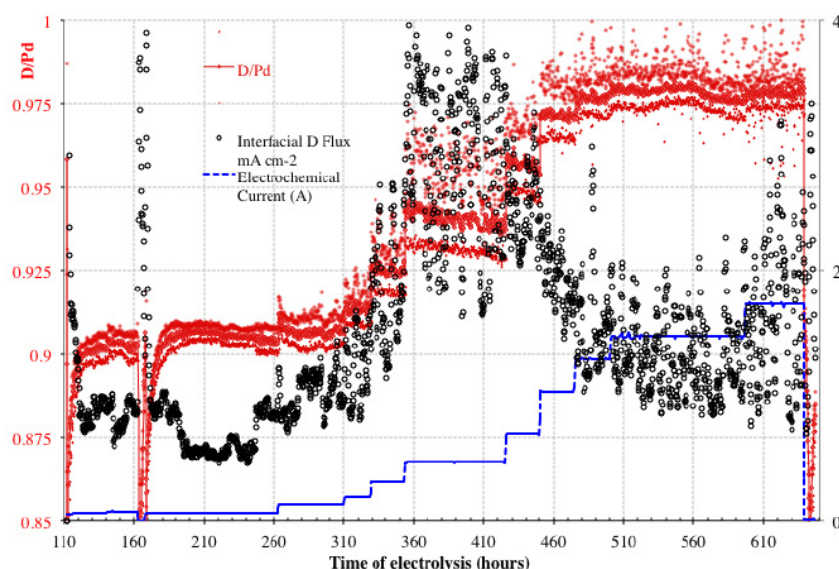


Figure 5. The interfacial impedance of an excess heat-producing Pd cathode 4 mm in dia. and 4.5 cm long at 1000 psig of D_2 pressure and 4°C using 1.0 M LiOD.

3. Discussion

What is relevant here is the clearly demonstrated ability of SuperWaves to engender high loading and high flux at high currents in a well prepared cathode. Since these are three recognized conditions of excess heat production it is pertinent to ask why the SuperWave is capable of producing this result, especially since no other waveforms that we have evaluated are? What is the SuperWave speaking to in the electrochemical system? One clue possibly was revealed in very early results obtained of the electrochemical impedance response of cathodes capable of excess heat production. Figure 6 shows data obtained for SRI Cell P2 in 1989 that was first published at ICCF1 (ACCF) in 1990 [12]. The first quadrant near semi-circular response¹ is the expected behaviour of an electrochemical charge transfer impedance in parallel with the electrochemical double layer capacitance.

The appearance of a second semi-circle under the real axis at low frequencies^m is a relatively rare feature in electrochemical systems. It is sometimes referred to as an “inductive loop” since it conforms to the mathematics of a low frequency inductor but this makes no physical sense as energy is not stored in magnetic fields in electrochemical systems. This feature is better thought of as a combination of negative capacitance and negative resistance indicating the presence of positive feedback. Each of the impedance loops in Fig. 6 has a characteristic frequency, the loop above the real axis at a few hundred Hertz, the loop below the real axis at a few hundred milli-Hertz. One conjecture is that the SuperWave used has sufficient and appropriate dynamics to modulate both of these resonancesⁿ, one associated with electrochemical kinetics (loading) and the other associated with positive feedback (flux).

¹Actually the fourth quadrant as the imaginary impedance axis (vertical) is plotted by convention as $-X$.

^mFrequency is not an explicit variable in this type of plot but each point is generated at a different frequency with frequency decreasing logarithmically from kHz to mHz in a clockwise fashion.

ⁿIt is likely that several other resonances also are crucial in producing the FPHE in electrolytic systems.

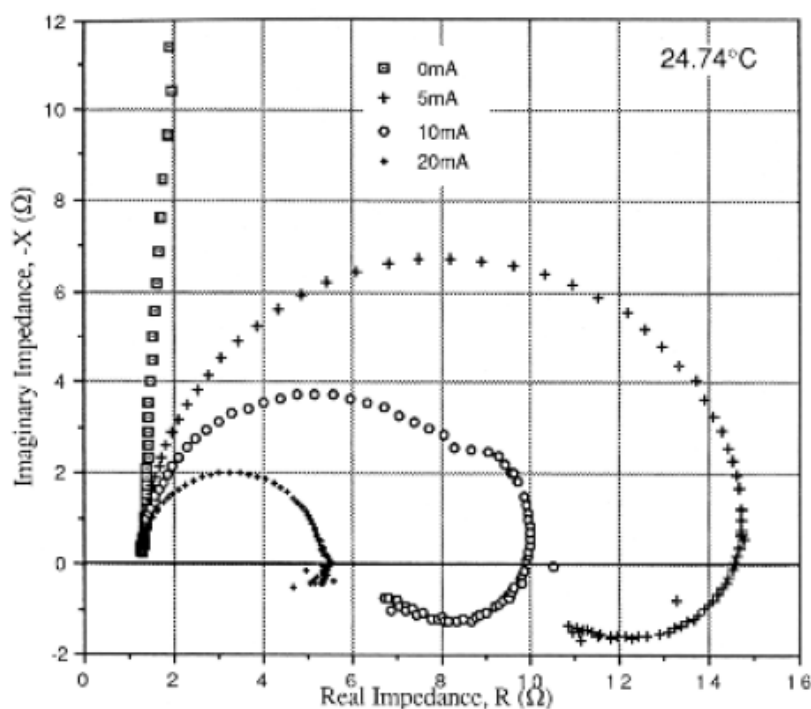


Figure 6. The interfacial impedance of an excess heat-producing Pd cathode 4 mm in dia. and 4.5 cm long at 1000 psig of D_2 pressure and $4^\circ C$ using 1.0 M LiOD.

4. Conclusions

The empirical requirements of high loading, high current and high interfacial deuterium flux to produce the FPHE in electrolysis experiments are in mutual conflict. However, systems have been observed to exhibit spontaneous flux driven loading oscillations, and at least one function, the SuperWave proposed and developed by Dardik [8–11] and ETI (now SKINR), has been observed to be capable of meeting and sustaining these conditions synthetically. With regard to demonstrating and hopefully utilizing the FPHE it would appear to be important to understand the role of resonant effects in electrochemical kinetic processes, as well as other system resonances not discussed here. We are pursuing these concepts further in ongoing collaboration with Violante (ENEA) and La Gatta (TSEM) in Italy [13].

Acknowledgements

In addition to the SRI team the progress briefly outlined above has been critically dependent of the vision, courage and dogged tenacity of two individuals: Dr. Irving Dardik's novel conception and understanding of the basic form of the SuperWave and its potential role in FPHE studies; and Dr. Vittorio Violante's tireless pursuit of the metallurgical variables that control the ability of bulk palladium to accept and retain very high deuterium loadings. Both men were supported by highly capable research teams.

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