Material Science on Pd-D System to Study the Occurrence of Excess Power

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Abstract

A recent joint work [1] identified the crucial role of material science in improving control of the Pd-D system to enhance the production of excess power during electrochemical loading of palladium foils with deuterium. Very high reproducibility, close to 100%, in loading Pd up to D/Pd ~1 (atomic fraction) was achieved. High loading about the threshold value of 0.9 is considered necessary to achieve the effect. This work demonstrated it is necessary but not sufficient. As a consequence, the focus of our research moved to the material properties of cathodes, especially surface characteristics, and an effort to correlate these properties with cathode performance during electrolysis. This paper describes the material properties examined that appear to produce excess heat.

Introduction

Recent evidence indicates that the Pd material plays a fundamental role in the occurrence of excess heat production during electrochemical loading of palladium cathodes with deuterium. This evidence has created a mounting interest in aspects of research related to material science.

A broad effort was carried out in the past to identify the mechanisms controlling hydrogen isotope dissolution into the palladium lattice during the loading process. The study helped define a proper metallurgical treatment to obtain the most suitable metallurgy to facilitate hydrogen absorption into the palladium cathode [2]. This work generated almost 100% reproducibility in achieving a deuterium concentration larger than 0.9 (atomic fraction) that is considered to be the threshold value for observing the effect.

This experimental work also demonstrated that the concentration threshold is a necessary condition for excess heat production, but not necessarily a sufficient one. Such evidence led to a systematic effort to improve knowledge about the status of the material that is required to have the effect.

Let us start from the most significant experimental evidence obtained from a statistical analysis of the data. Three different behaviors were observed with Pd cathodes loaded above the threshold D/Pd = 0.9:

(1) High power gain during the excess.
(2) Low power gain during the excess.
(3) No excess.

McKubre identified two types of excess power production:

Type A: excess power begins after several days of electrolysis and, in general, depends on the current density.

Type B: excess begins very soon and does not always depend on the current density.

The research described in this work is largely oriented to studying the main differences in materials that produce these two different types of excess power.

Lot-1 and Lot-2

Two different lots of palladium, obtained from the same producer, exhibited remarkably different behavior during the experiments, even though both lots underwent the same metallurgical procedures.
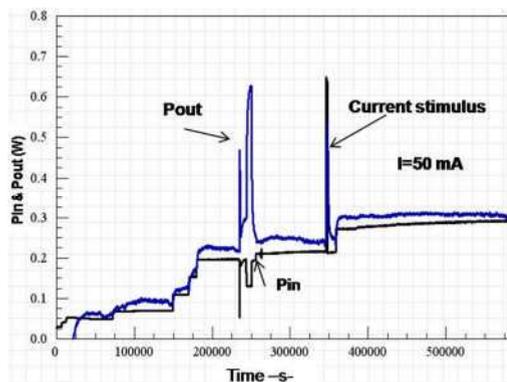

Figure 1. Experiment L17, evolution of input and output power: excess 500%
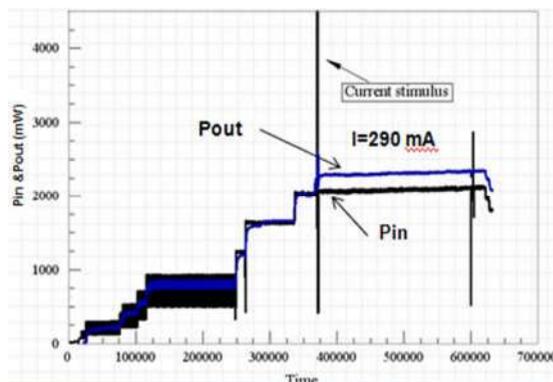
Figure 2. Evolution of input and output power in experiment L39

These two materials served as references in the investigation to identify material that produces the Fleishmann-Pons (FP) effect. The two lots are designated Lot-1 and Lot-2. Lot-1 gave Type B excess power with, in some cases, power gains well above 100%. Figure 1 shows the evolution of the input and output power in experiment L17, performed with a sample from Lot-1. During the main burst that continued long enough to allow the calorimeter to reach a fairly steady state condition, the power gain was up to 500%. The reduction of the input power during the burst occurred because the excess power increased the electrolyte temperature, causing a reduction of impedance of the electrolyte, so that the galvanostat reduced the voltage to maintain the current at the set point value. This lot successful produced excess heat in 75% of tests at SRI and up to 60% at ENEA.

Different behavior was produced by samples from Lot-2. As mentioned above, this lot was obtained from the same producer and had identical characteristics and purity (both 99.95%). Lot-2 gave Type A behavior with excess power of less than 20%. Loading up to the threshold

level required higher current compared to samples from Lot-1, and the reproducibility of excess power production was lower (less than 20%). Figure 2 shows evolution of the input and output power in the experiment L39, performed with Lot-2 material.

Such an experimental difference, based on a significant number of experiments (more than 40), led to a comparative analysis of both raw as-received samples and samples following metallurgical treatments. The first test was a qualitative check for the spectrum of contaminants in the two lots. Fig. 3 shows such a spectra, obtained with SIMS analysis (with sputter erosion). It is evident that some species that are completely absent in Lot-1 are contained as contaminants in Lot-2, for instance Zr. Contaminants may act on grain size, crystal orientation and grain boundaries, so that a different metallurgy may be expected for samples obtained from the two different raw materials, based on differences in the spectra of contaminants.

Scanning electron microscopy (SEM) performed on samples obtained from Lot-1 and Lot-2 after the same treatment steps are confirming this effect. Fig. 4 and Fig. 5 show the metallurgy of samples obtained from Lot-1 and Lot-2, respectively. The main difference is the grain size, being larger for the sample from Lot-1. This difference may be ascribed to the different spectrum of contaminants, with Lot-1 containing fewer grain boundary pinning constituents.
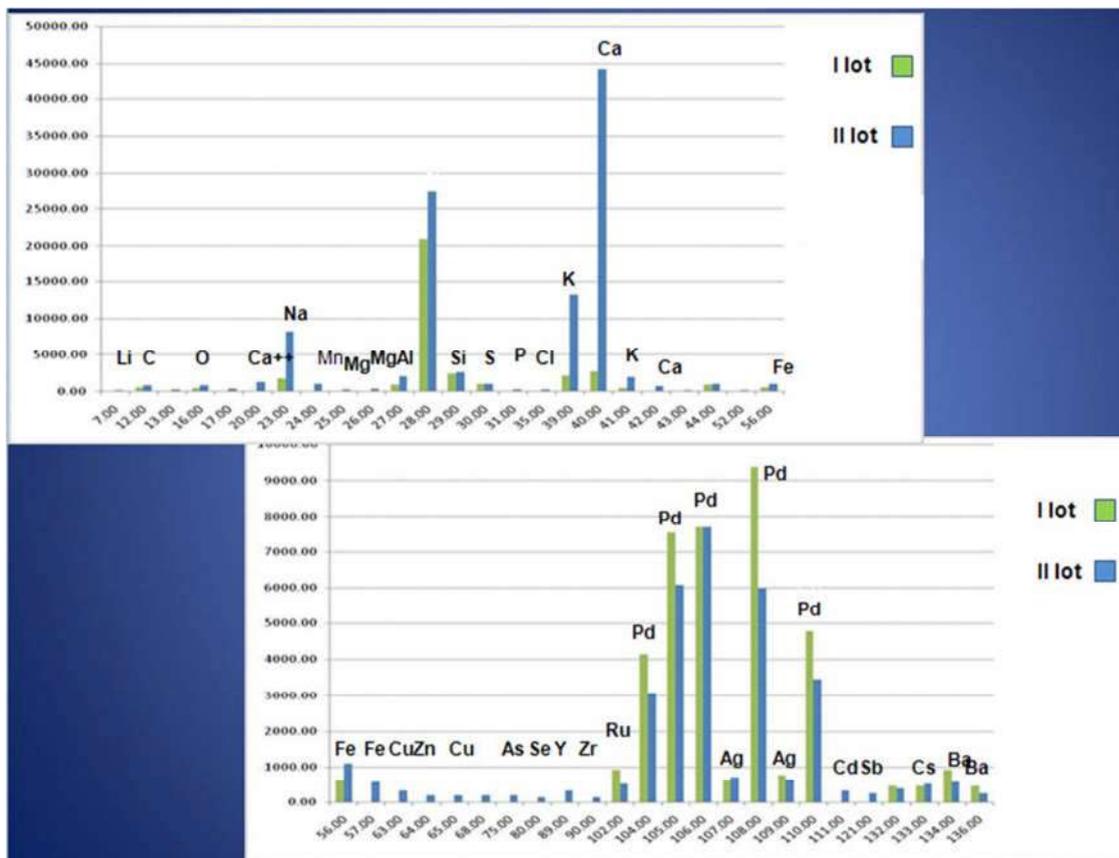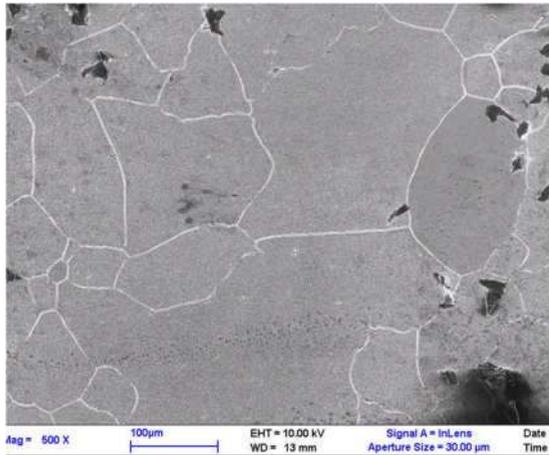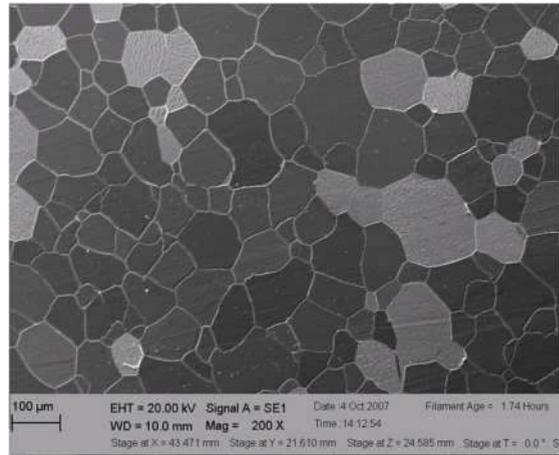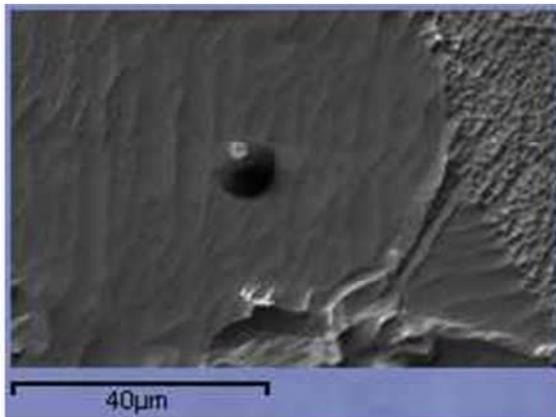

Figure 3. Spectra of impurities for Lot-1 and Lot-2, qualitative analysis (SIMS with erosion)
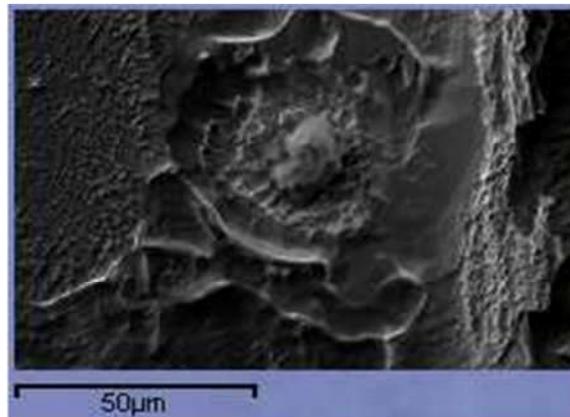
Figure 4. SEM microscopy of a sample from Lot-1

Figure 5. SEM microscopy of a sample from Lot-2

Figure 6. Effect of an iron particle on etching

Figure 7. Effect of a dust particle on etching

Crystal orientation after metallurgical treatment was studied by means of X-ray diffraction. The results for Lot-1 indicated these samples to have a well-aligned <100> surface normal, as shown by very sharp X-ray spectra with little or no <110> present. Lot-2 samples had a mix of <100> and <110> surface normals, with the spectra not as sharp as for Lot-1. A third lot of material with a different spectrum of contaminants underwent the same metallurgical and thermal procedure, yet revealed instead mostly <110> and very little <100> surface normal orientation. Cathodes fabricated from this third lot produced no excess power.

A statistical analysis of the collected experimental data revealed that Type B excess power was correlated with <100>-crystal orientation with a correlation factor very close to 0.8 [3]. The different experimental behaviours observed indicate that crystal orientation may be considered a second condition required to produce excess power.

It is very well known from the literature that contaminants modify the effect of chemical etching on surface morphology [4]; Fig 6 and Fig.7 show the effect of etching a Pd sample with either an iron or dust particle, respectively. Also, crystal orientation has an effect on the surface

morphology, and surface morphology as well as crystal orientation has a non-negligible role on electrode kinetics [5]. Observations of different Pd surface activity were identified by Rolison using SEM of etched Pd foils [6].

Material Status and Excess Heat Production

The resulting question is: how do these differences in the status of the material relate to excess power production? The first answer is that the excess power is correlated to the loading dynamics, and the loading dynamics depend on the material status. The evidence is highlighted by the following analysis. Figure 8 shows the ratio between the maximum loading value and the current required for such a loading, an indicator of ease of loading. Cathodes showing good loading at low current, in general, have produced excess power. Furthermore, the easier the loading, the higher the probability is that Type B (red bar) excess power will occur. The correlation factor between the occurrence of the Type B excess heat and easy loading is g=0.813. See ref [3] for additional statistical data.

Preliminary statistics from this report show that:

(1) Contaminants control the crystal orientation during annealing.
(2) Crystal orientation and specific contaminants modify the effect of chemical etching, leading to a different surface status.
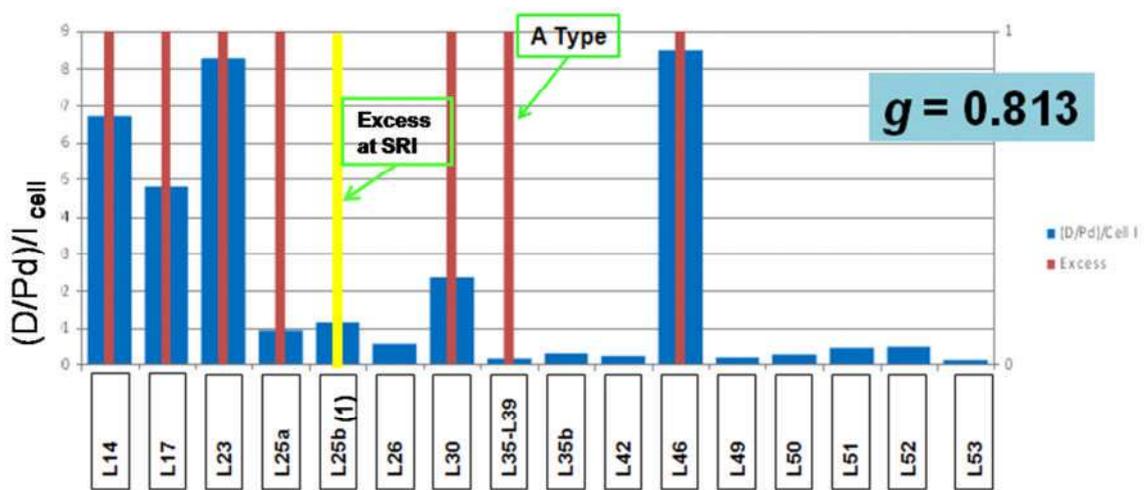(3) The surface morphology modifies the operating conditions in the electrochemical process.

**Figure 8. Ratio between the maximum loading value and the current required for such a loading.**

We conclude that the status of the surface is a third condition needed to produce excess heat. The Power Spectral Density function (PSD), defined as the squared modulus of the surface roughness Fourier transform, was chosen as a figure of merit representing the status of the surface [7]. The PSD function, after surface etching, was found for samples giving excess power, as in Fig. 9, to have peaks in the wave vector interval $10^6 - 10^7 \mathrm{m}^{-1}$. The statistics also revealed that the amplitude of the excess power correlates with the amplitude of the PSD peaks.

On the basis of the results described here, work was carried out to produce material characterized by:

(1) Spectrum of contaminants quite close to the Lot-1 spectrum.
(2) <100> crystal orientation.
(3) Proper metallurgy for easy loading.
(4) PSD characterized by the presence of peaks in the wave vector range $10^6 - 10^7$ m^{-1}.
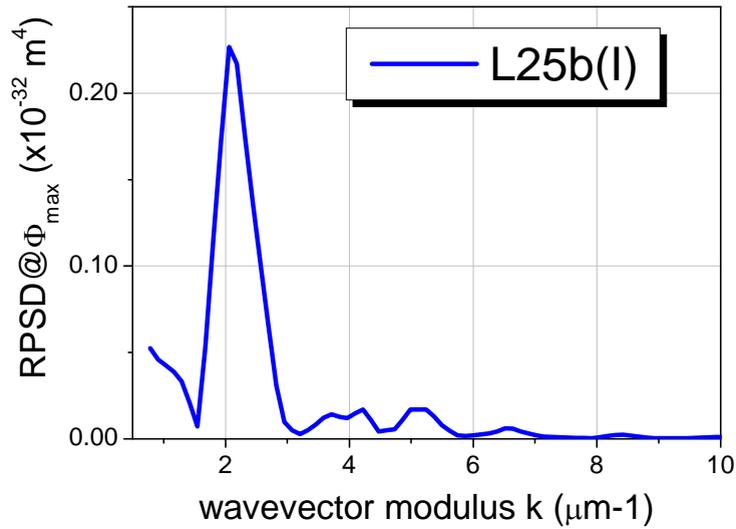
Figure 9. Power Spectral Density (PSD) function of sample L25 producing excess power
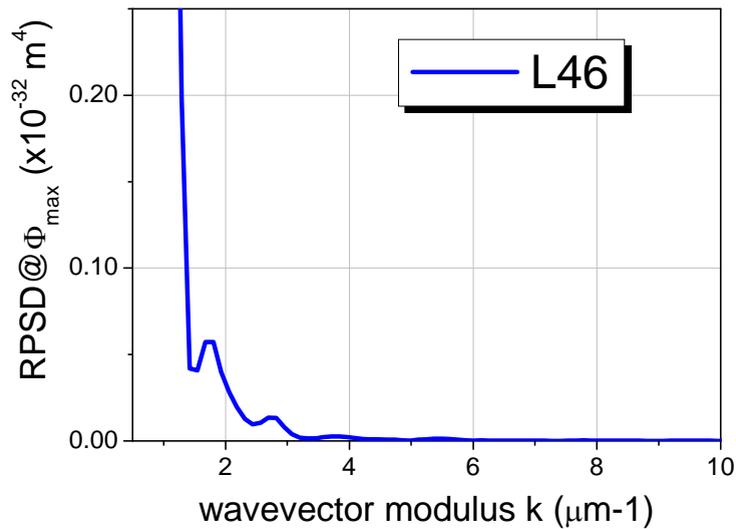
Figure 10. PSD of sample L46, peaks in the identified region are revealed
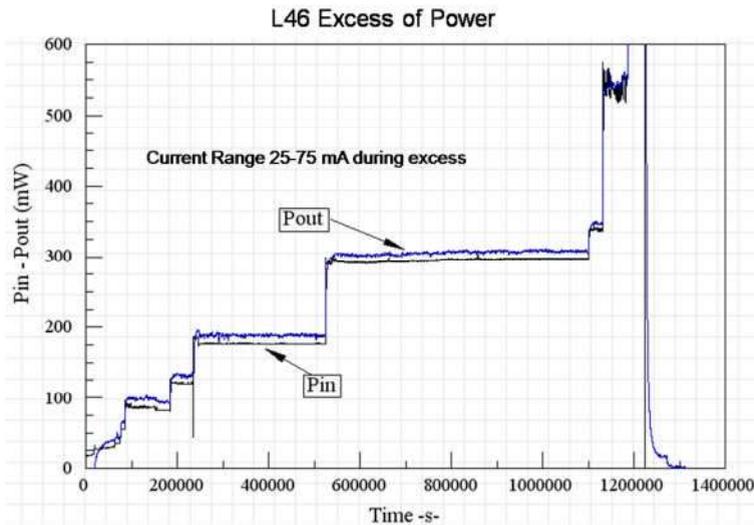
Figure 11. Evolution of the input and output power during experiment L-46: Excess up to 12% was observed and the amplitude results to be proportional to the PSD peaks amplitude

These characteristics were achieved with sample L46, and this sample underwent a calorimetric test with heavy water. Figure 10 shows the PSD of sample L46. We observe that the amplitude of the peaks is lower than given by sample L25, which produced excess power up to 250%. As shown in Fig. 8 the loading of sample L46 was satisfactory. The calorimetric result for this sample is shown in Fig. 11. We observed excess power up to 12% that disappeared completely when the input power exceeded 300 mW.

This result is not extraordinary in terms of power gain, but has a non-negligible value since it represents the first reproduced excess power based on a "designed" material. Furthermore, it provides additional evidence that proper surface morphology, combined with appropriate metallurgy for loading, and with <100> crystal orientation is a third condition for producing excess power. Obviously statistics confirming the result is required, and an enhanced surface analysis study should investigate a wider region of the wave vector range.

Conclusions

Characteristics have been identified that cause different cathode behavior. The probability of excess heat is enhanced when three conditions are met:

(1) Loading is easy at a relatively low current density due to proper metallurgy.
(2) <100> Crystal orientation.
(3) Identified surface morphology by PSD.

A sample demonstrating the three conditions was made, and production of excess heat was observed. Work is in progress to identify other correlations and, on the basis of the material characteristics, the mechanisms producing the effect.

435

Patent

The work is the object of a Joint Patent by ENEA, NRL, SRI and Energetics Technology.

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