

Evolution and Progress in Material Science for Studying the Fleischmann and Pons Effect (FPE)

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Abstract. Calorimetric experiments have revealed a crucial role of the metallurgy and surface characteristics for reproducing the FPE. A material status to have an improved probability to observe the effect under electrochemical loading of deuterium in palladium has been identified by means of statistical approach. The evolution of the research approach is described in this work.

1. Introduction

The threshold effect of the deuterium concentration into the palladium lattice was identified as condition for observing the excess of power during electrolysis of palladium cathodes with LiOD electrolyte [1-2], i.e. Fleischmann&Pons effect [3].

Such an experimental evidence created a broad interest in identifying the mechanisms controlling hydrogen isotope dissolution into the palladium lattice during the loading process.

A material science study allowed to define a metallurgical treatment to have the most appropriate metallurgy to facilitate absorption and hydrogen mass transfer into the palladium lattice [4].

The most significant out coming of the study was an increasing of the loading reproducibility, near 100%, in achieving a deuterium concentration larger than 0.9 (atomic fraction), that was considered to be the threshold value to observe the effect.

The high loading reproducibility was the condition to demonstrate that the loading threshold is a necessary condition but not sufficient to have the excess of power production [5].

A research effort was performed for identifying others necessary features of the material correlated with the excess of power production and, for such a reason, the focus of the research was mainly oriented on metallurgy, crystallography, triggering, and interface - surface physics.

2. Experimental results

A mass flow calorimeter and closed electrochemical cells equipped with a catalytic fixed bed to recombine the gas produced by the electrolysis have been conceived and operated to directly measure the output power.

The calorimetric system is composed by a Memmert thermostatic box (± 0.05 °C), Haake thermostatic bath for coolant water, Bronkhorst high precision mass flow meter and controller (0.3-0.1 cc/s), read by the data acquisition system in order to have a precise measurement of the output power. Inlet and outlet temperatures of the coolant are measured with two Pt 100 thermometers (four wires measurement). The closed electrochemical cell is equipped with a recombiner. Cell power supply is an AMEL galvanostat. Output power is measured by means of the mass flow rate and coolant temperatures, R/Ro measurement is done by means of an HP- 4284 (four wires measurement). The calorimeter efficiency is 97.5% and was estimated by using LiOH electrolyte in several experiments. No excess of power production has been observed by using H₂O despite a very high loading (H/Pd=0.97) was achieved.

Palladium cathodes, loaded above the deuterium concentration threshold (D/Pd =0.9: atom. frac.) gave a different behavior:

- 1) Excess of power larger than 100% of the input power.
- 2) Excess of power lower than 20% of the input power.
- 3) No excess.

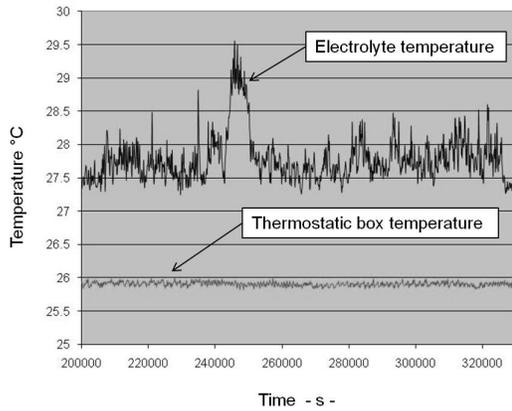


Fig. 1. – Input, output and excess power in the experiment L17.

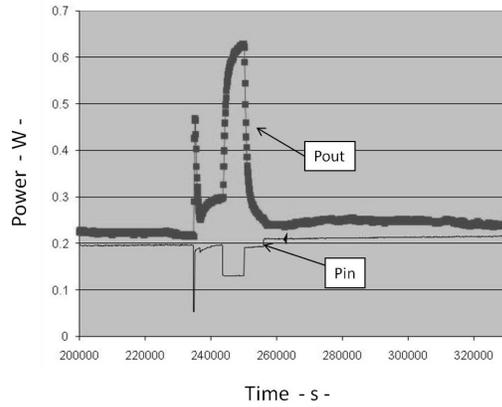


Fig. 2. – Increasing of the electrolyte temperature during the production of excess of power.

We identified some differences in two palladium lots received from the same producer. Both lots were 99.95% pure Pd. The first lot gave a reproducibility larger than 60% with signal amplitudes well above 100%. Fig.1 shows the input, output and excess power in the experiment L17 performed with a sample belonging to the first lot; Fig.2 shows the increasing of the electrolyte temperature in this experiment during the excess production. During the experimental campaign performed with the second palladium lot the reproducibility reduced below 20% and the excess amplitude was always below 20-25% of the input power.

A systematic work, to improve the knowledge about the status of the material that is required to have the effect, was conceived on the basis of such a different behavior of the two lots.

The experimental data highlighted that high loading is a necessary, but not sufficient condition to have the production of excess of heat, for such a reason the focus was moved on other features of the samples correlated with the occurrence of the excess of power production.

The most significant evidence, to be correlated to the different behavior in terms of excess of power production from these two lots, was the different spectrum of contaminants. It is well known from physics metallurgy that contaminants may have several effects on the metal characteristics; in fact, contaminants may act on grain size, crystal orientation and grain boundaries shape and depth.

The figures 3 and 4 show the typical grain size distribution of samples obtained from the first and second lot, undergone to the same metallurgical treatment. In addition samples belonging to the first and the second lot showed a different crystallographic orientation: the first lot was mainly oriented $\langle 100 \rangle$ while the second lot was $\langle 100 \rangle$ and $\langle 110 \rangle$ 50% oriented. Excess of power was mostly observed with samples having a dominant $\langle 100 \rangle$ orientation.

The difference in the spectrum of contaminants produced also a different effect of the chemical etching because of the different reactivity of the surface. The consequence was a different surface morphology between samples belonging to the two lots.

We selected the Power Spectral Density Function (PSD) as merit figure to identify the status of the surface.

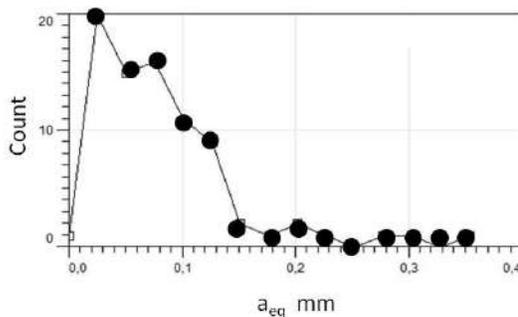


Fig. 3. – First lot grains size distribution.

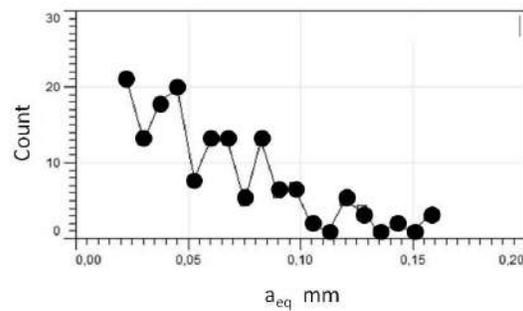


Fig. 4. – Second lot grains size distribution.

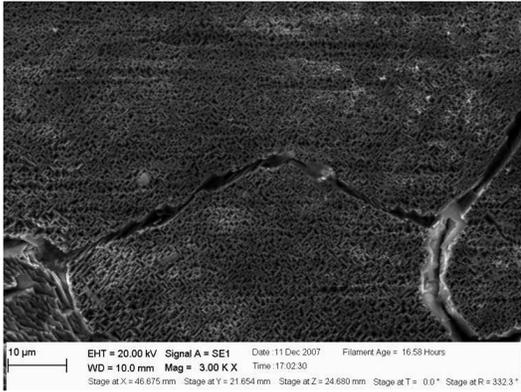


Fig. 5. - Microscopy of #64 sample surface.

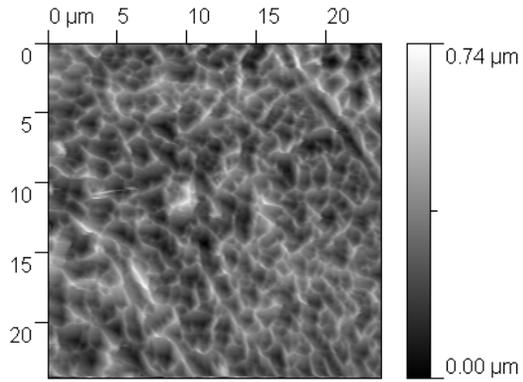


Fig. 6. - Microscopy of L25 sample surface.

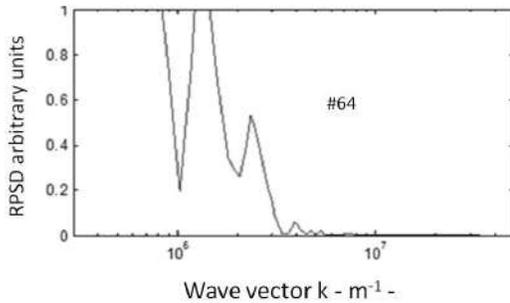


Fig. 7. - PSD of #64 sample.

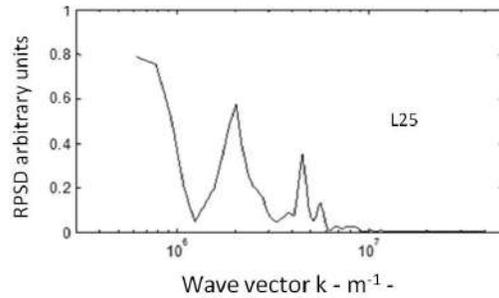


Fig. 8. - PSD of L25 sample.

Fig. 5 and Fig. 6 show the surface microscopy of samples #64 (sample #64 was produced at ENEA and experienced at Energetics) and L25 respectively; both gave a significant excess of power production but the effect was stronger for lot #64. Samples #64 and L25 gave an excess of power larger than 1000% and 200% respectively. Figures 7 and 8 show the power spectral density function for lot #64 and for lot L25 respectively. One may observe that the structure of the PSDF are quite similar but the larger the amplitude of the PSD peaks the larger the produced excess of power. This correlation, highlighting a significant role of the surface, was also found in other measurements.

3. A designed material

The experimental correlations presented in the previous paragraph led to produce a material having characteristics close to the ones described above.

A lot of Pd having a spectrum of contaminants approaching the one of lot 1 was undergone to the treatment leading to: dominant <100> orientation and an appropriate metallurgy.

A surface morphology quite similar to the labirintic one of sample #64 and L25 was produced by the chemical etching.

Fig. 9 shows the PSD for such a sample that results to be similar to the one of samples #64 and L25 even if the peaks amplitude is lower. A small excess was expected from such a sample. The experimental behavior gave a satisfactory agreement with the expectation. Fig. 10 show the produced excess of power up to 12% of the input.

A material designed to have excess of power production was replicated successfully by using the approach described above. Fig. 11 and 12 show the excess of power and the PSD for another designed sample.

An increased control of the effect is achieved even if not yet satisfactory, in particular if we compare the amplitude of the signals with the values observed experiencing the samples obtained from the first palladium lot. However a correlations between the amplitude of the power spectrum and the amplitude of the excess of heat turns out. This result is pointing into the direction of a crucial role of the surface status

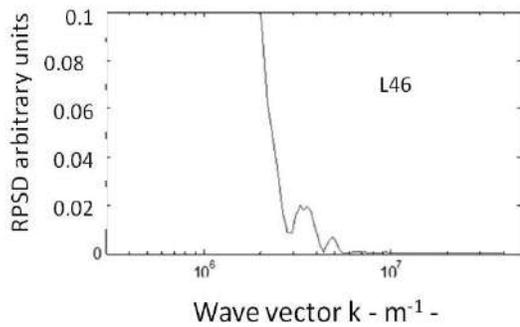


Fig. 9. – PSD of a material designed to produce excess of power.

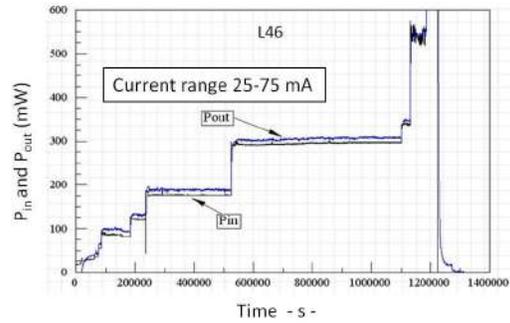


Fig. 10. – Excess of power produced by the designed material.

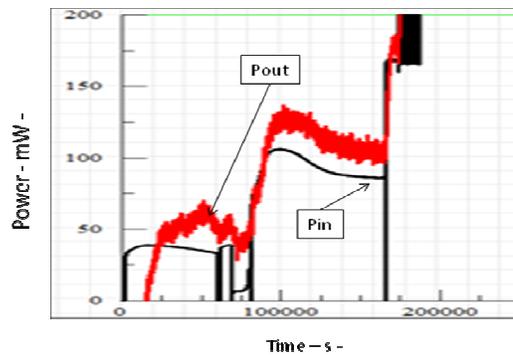


Fig. 11. – Excess of power produced by a designed sample.

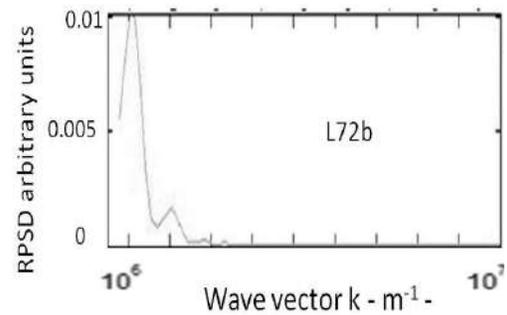


Fig. 12. – Designed material PSD.

to observe the effect; in other words an appropriate surface morphology is confirmed to be an additional condition to observe the effect. A certain reproducibility has been achieved in preparing “designed materials”; however the samples produced with the “designed material” and the ones obtained from the first lot are similar but not equal to each other. In other words the broad effort in the material science remains a crucial point for enhancing the level of knowledge in this field.

4. Conclusions

Reproducing the characteristics of the palladium cathodes that have been identified to be correlated with the excess of power production during electrochemical deuterium loading allowed to obtain the effect. This effect correlation was observed in several experiments performed with a designed material.

The enhancement of the probability to have excess of power is given by:

- 1) Easy loading at low current density due to proper metallurgy.
- 2) $\langle 100 \rangle$ mostly oriented material.
- 3) Labirintic surface giving a defined shape of the power spectral density function.

The correlation of the amplitude of the excess of power with the amplitude of the PSD is pointing in the direction of a crucial role of the surface under electrochemical conditions.

References

- [1] K. Kunimatsu, N. Hasegawa, A. Kubota, N. Imai, M. Ishikawa, H. Akita and Y. Tsuchida, Proc. Third Int. Conf on Cold Fusion, Nagoya (Japan) October 20-25, 1992, p.31.
- [2] M. C. H. McKubre, S. Crouch-Baker, A. M. Riley, S. I. Smedly, F. L. Tanzella, Proc. Third Int. Conf on Cold Fusion, Nagoya (Japan) October 20-25, (1992), p.5.
- [3] M. Fleishmann, S. Pons, J. Electroanal. Chem. Vol. 261, (1989) p. 301.
- [4] V. Violante et al., Phys. Rev. B, Vol. 56, (1997) pp. 2417-2420.
- [5] V. Violante et al., Proc. ICCF-14 Washington DC 10-15 August 2008, Vol. 2 p. 429.