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Research Article

The Study of the Fleischman and Pons Effect through the Materials Science Development

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Abstract

The state of the palladium metal has been identified on the basis of statistical data to play fundamental roles in producing the Fleischman–Pons excess heat effect. The deuterium loading dynamics and its equilibrium concentration are mostly controlled by the metallurgy; a minimum threshold loading (D/Pd $\sim$ 0.9) is necessary to observe the excess. The crystallographic orientation is also correlated with the phenomenon such that mainly $\langle 100 \rangle$ oriented samples gave the highest reproducibility. A specific cathode surface morphology, identified by means of the power spectral density function, represents an additional identified condition to observe the effect. Materials specimens respecting the characteristics described above have been used to obtain a transportable reproducibility. Designed materials giving excess power have been produced but the amplitude of the signals and full reproducibility are not yet achieved. Other features of the material such as the nature and content of impurities and defects seems to be crucial in obtaining the required palladium characteristics.
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Keywords: Calorimetry, Chemical potential, Diffusion coefficient, Dimensionless transport equation, Gorsky effect

1. Introduction

Since 1996 at ENEA, the metallurgy was identified to be responsible for the loading of hydrogen or deuterium into palladium cathodes [1]. Loading is, in general, not homogeneous and concentration gradients produce a stress field that modifies the chemical potential of hydrogen dissolving into the lattice, as a consequence the diffusion dynamics change and the hydrogen or deuterium equilibrium concentration may be reduced. A metallurgy able to minimize the concentration gradients is required in order to achieve the loading threshold considered to be a necessary condition to observe the production of excess heat.

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A process has been defined to have a metallurgy enhancing mass transfer by reducing the hydrogen (deuterium) concentration gradients and then the stress field into the sample.

The focus of our research activity was mainly on:

(1) Extended material science also involving the study of the surface and crystallography to increase both, reproducibility and signals.
(2) Calorimetric experiments conceived to have an appropriate signal/noise ratio.

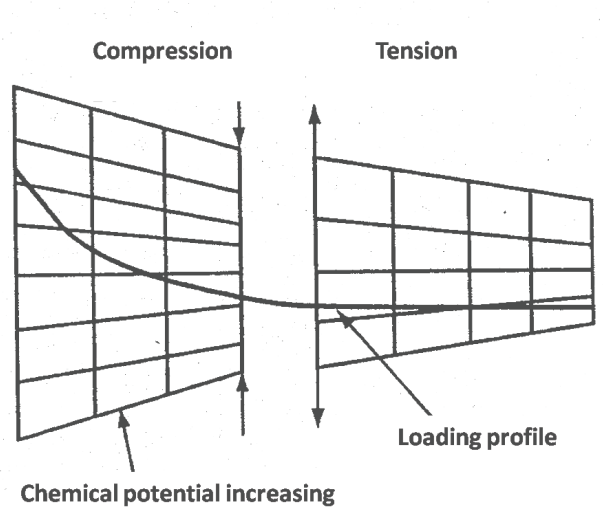

Figure 1. The effect of the hydrogen concentration profile on the stress field.

(3) Theoretical work to identify methods to trigger the effect.

2. Stress Field Limiting Hydrogen (Deuterium) Solubility in Palladium

The dissolution of hydrogen isotopes into a metal lattice is not only a problem of thermodynamic equilibrium between the hydrogen inside the lattice and the hydrogen in the external phase (gas or liquid) but is also a problem of disequilibrium because of the occurrence of a transport process. Both aspects of this phenomenon are correlated since the equilibrium concentration of the solute is achieved when the chemical potentials of the hydrogen in both phases are equal and because the transport process inside the metal lattice is driven by the gradient of the chemical potential.

The migration of interstitials in a metal under an applied external bending is well known as Gorsky effect [2]. The deformation field produces the defects migration toward the expanded areas. Lewis and co-workers [3–5] showed that internal stresses are generated during insertion and diffusion of interstitial hydrogen and that the resulting strain production represents an opposing force to the flux produced by the concentration gradient.

The study of the stress as limiting factor in achieving the deuterium loading threshold in palladium to generate excess power production is carried out in the following. The chemical potential of the hydrogen in solid solution in a metal lattice is strongly influenced by force fields, like the stress field, modifying the free energy of the system.

The hydrogen isotopes atoms dissolving into the metal (i.e. palladium) occupy interstitial sites, and thereby the lattice expands. This process generates a stress field when significant concentration differences (strong gradient or coexistence of different phases) are created.

The situation is quite similar to the stress produced by a temperature gradient as shown in Fig. 1.

In the following we show how to approach the solution to this problem in order to have an analytical tool to estimate the effect of the stress field on the loading and to identify the metallurgical conditions that can reduce this effect and hence allowing the increase of the amount of hydrogen dissolved in the metal.

Chemical potential of hydrogen diffusing into the metal lattice, in presence of a stress field, becomes [6]:

$$\mu_{\mathrm{s}} = \mu_{\mathrm{s}}^{*} - \frac{\bar{V}_{\mathrm{s}}}{3}\left(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}\right) = \mu_{\mathrm{s}}^{*} - \bar{V}_{\mathrm{s}}\ \mathrm{tr}\,\bar{\bar{\sigma}} \equiv \mu_{\mathrm{s}}^{*} - \bar{V}_{s}\sigma_{h}, \tag{1}$$

where μ_{s}^{*} is the chemical potential of hydrogen diffusing into the lattice without stress, $\bar{V}$ is the partial molar volume of the solute and σ_h the trace of the stress tensor.

2.1. Flux equation with a stress field

A diffusive flux of hydrogen within an homogeneous and solid media is created by a gradient of the chemical potential and by the field of the applied forces so that the expression for the flux is

$$\bar{J} = -Mc\frac{\partial\mu}{\partial c}\frac{\partial c}{\partial x} + Mc\bar{F}, \tag{2}$$

where M is the mobility, c the solute concentration, $\bar{F}$ the vector given by the sum of the applied forces acting on the hydrogen interstitially dissolved in the solid.

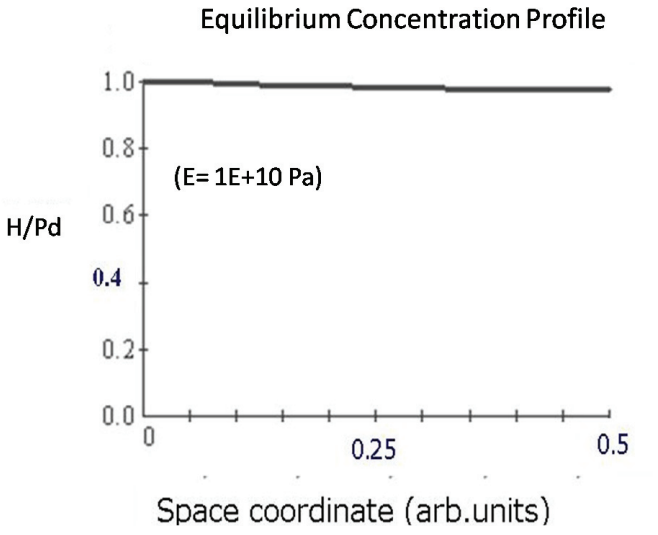

Figure 2. Equilibrium H concentration profile within a Pd foil with Young module = 1 E+10 Pa.

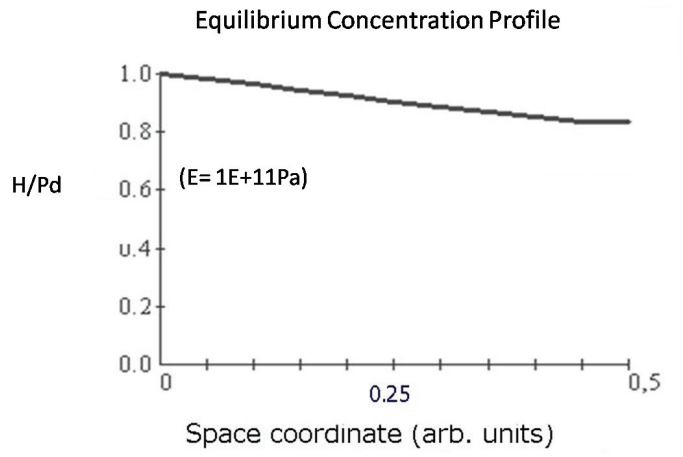

Figure 3. Equilibrium H concentration profile within a Pd foil with Young module = 1E+11 Pa.

By replacing the relationship between diffusion coefficient and chemical potential, $D = Mc(\partial\mu/\partial c)$, into Eq. (2) it follows:

$$\bar{J} = -D\nabla c + \frac{D\bar{F}c}{c(\partial\mu/\partial c)}. \tag{3}$$

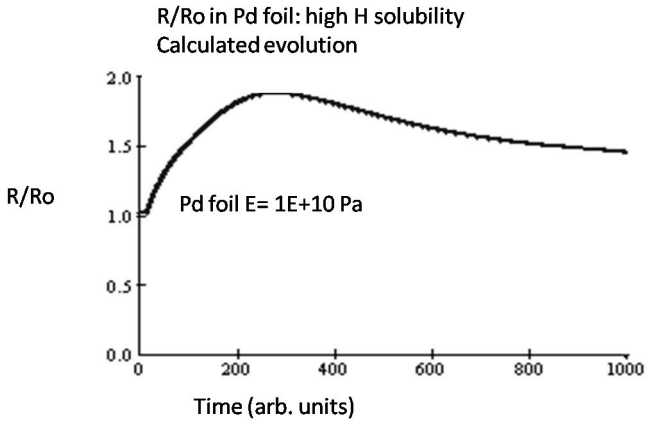

Figure 4. Calculated evolution of R/R_o for high solubility (reduced stress) material.

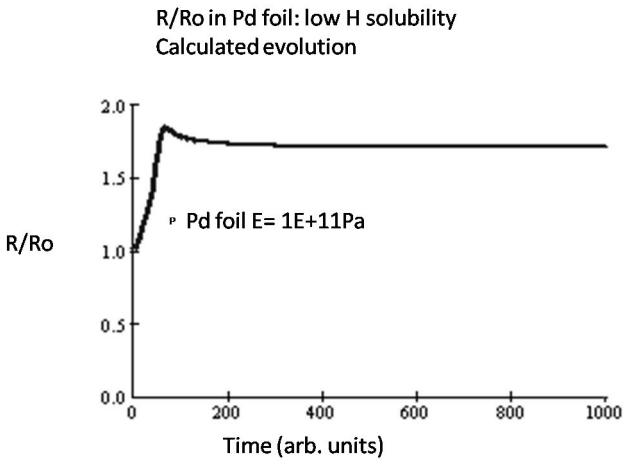

Figure 5. Calculated evolution of R/R_0 for low solubility (high stress) material.

A little of algebra leads to

$$\bar{J} = -D\nabla c + D\frac{\bar{F}}{RT}c. \tag{4}$$

For a stress field the flux equation becomes:

$$J = -D\left(\nabla c - \frac{c\bar{V}}{RT}\nabla\sigma_{\text{loc}}\right), \tag{5}$$

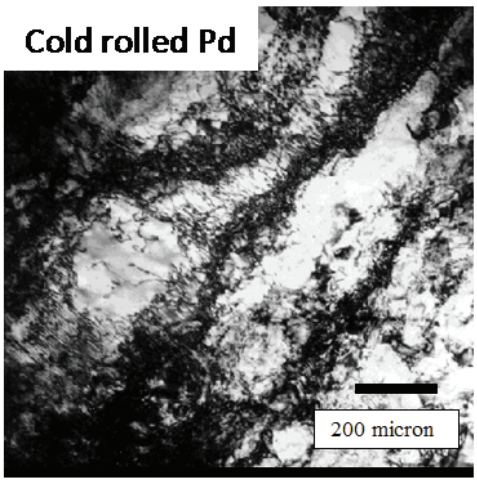

Figure 6. Cold rolled sample.

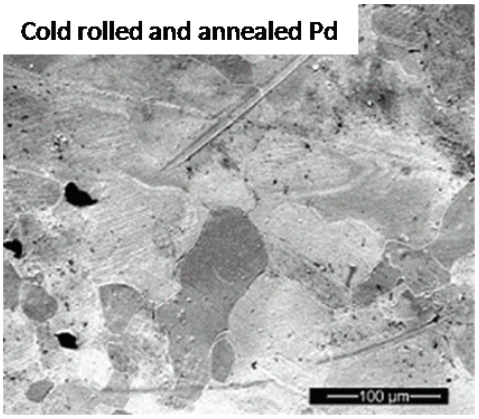

Figure 7. Cold rolled and annealed (850°C) sample.

where σ_{loc} is the local stress.

Equation (5) shows that a zero flux condition can be achieved even if a non-zero concentration gradient exists (i.e. when the two terms have the same value).

Therefore, the loading process may be inhibited by a stress gradient, for instance behind the external surface, where

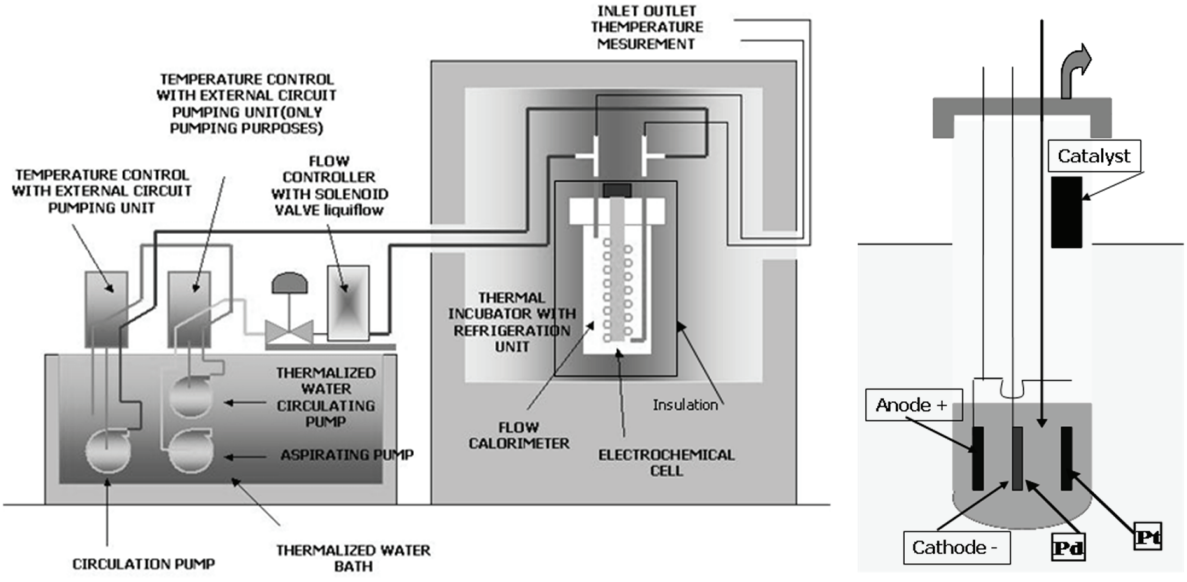

Figure 8. Schematic view of the flow calorimetric system and of the closed electrochemical cell.

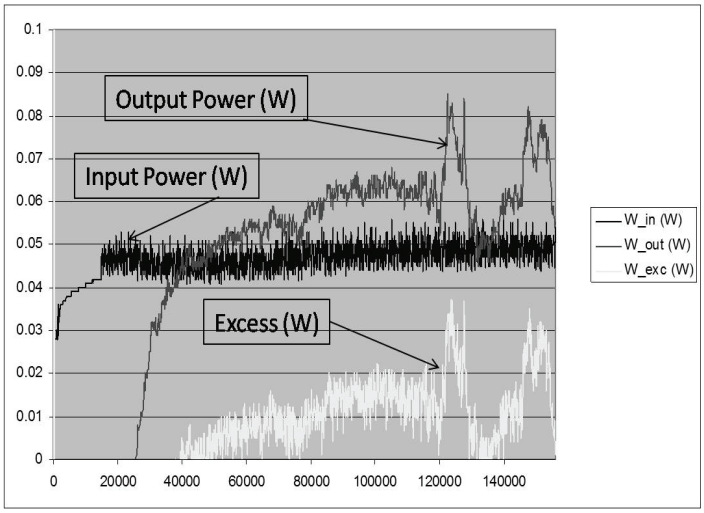

Figure 9. Input, output and excess power in experiment L14.

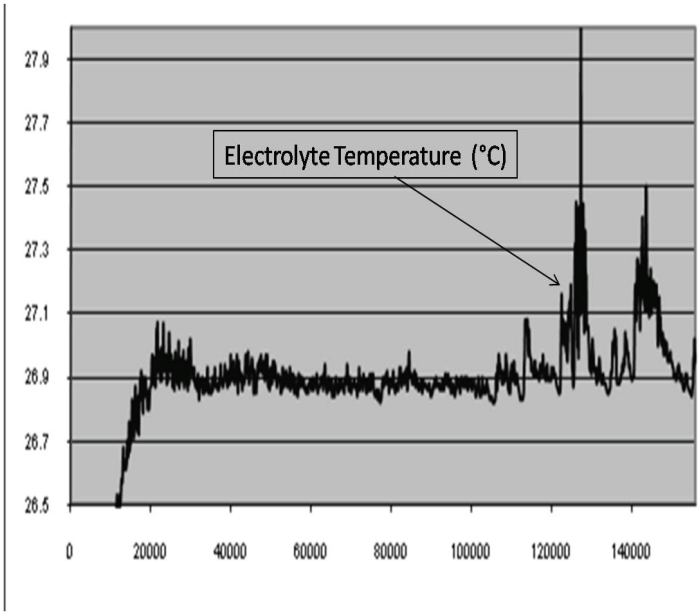

Figure 10. Increasing of the electrolyte temperature during the production of excess of power.

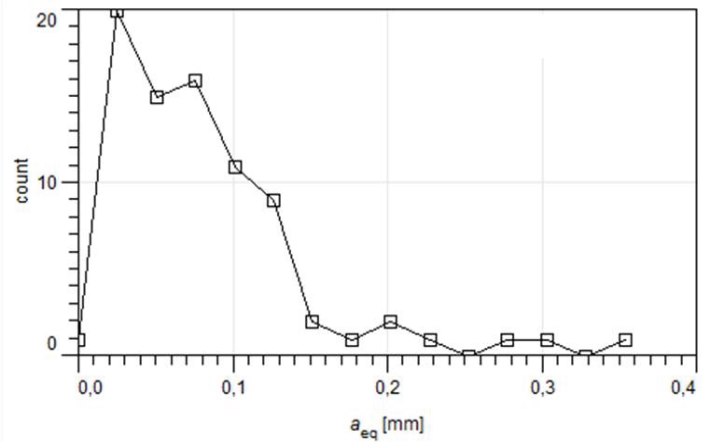

Figure 11. First lot grain-size distribution.

the effect is traceable to the effect of a strong temperature gradient. Thus, in the zone at high concentration, compressed by the zone at low concentration, the chemical potential of the solute increases and the loading can be inhibited.

The analysis allows us to study the mass transfer problem when the stress field is created during the loading. In the following, we consider a system where the diffusion is well described by one-dimensional time dependent model (foil, membrane or wire).

By introducing the fraction of relaxed stress *η(x)* into the flux equation it follows:

$$J^d = D\left(-\frac{\partial c}{\partial x} + (1-\eta)\frac{\bar{V}}{RT}c\frac{\partial \sigma}{\partial x}\right). \tag{6}$$

A mass balance on a foil leads to:

$$\frac{\partial c}{\partial t} = D\frac{\partial}{\partial x}\left(\frac{\partial c}{\partial x} - (1-\eta)\frac{\bar{V}}{RT}c\frac{\partial \sigma}{\partial x}\right). \tag{7}$$

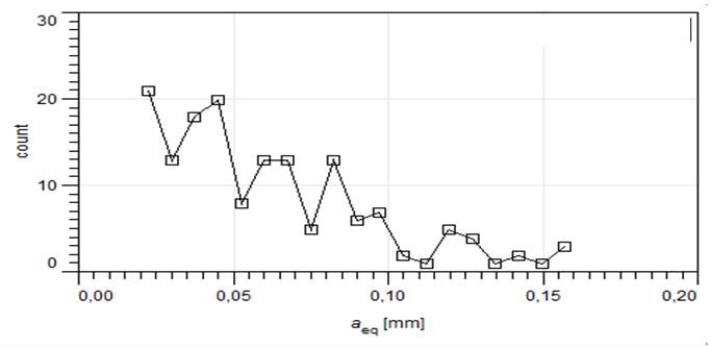

Figure 12. Second lot grain-size distribution.

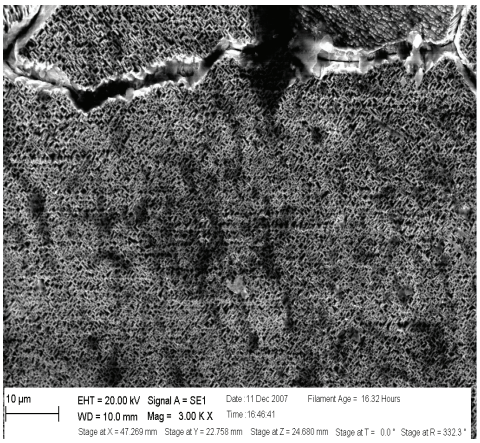

Figure 13. Microscopy of #64 sample surface.

Let us consider the well known stress (σ) strain (ε) relationship:

$$\sigma = E\varepsilon, \tag{8}$$

where E is the Young's modulus. The relationship between strain and concentration for the Pd beta phase (assuming that it may be extrapolated up to a loading atomic fraction close to one) can be expressed as

$$\varepsilon(\bar{c}) = [1 + b(\bar{c} - \bar{c}_{\beta\,\min})], \tag{9}$$

where $\bar{c}_{\beta\,\min}$ is the hydrogen concentration value for the $\alpha + \beta$ phases coexistence limit, $b = 0.044$ and $\bar{c} = c/c_0$ the dimensionless concentration (c_0 is the metal atoms concentration). Let us introduce the following dimensionless

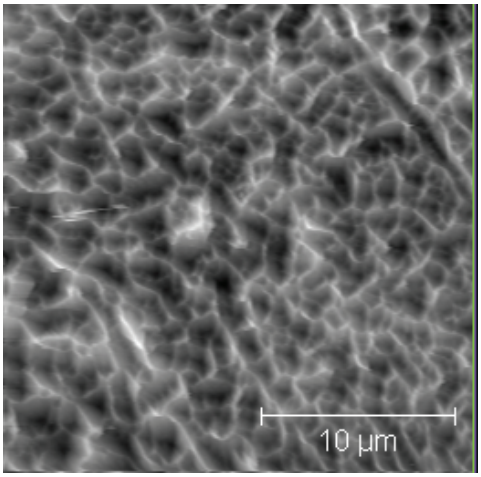

Figure 14. Microscopy of L25 sample surface.

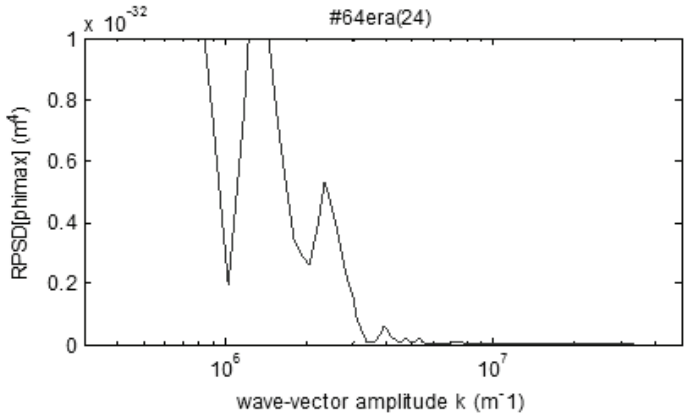

Figure 15. PSDF of #64 sample.

parameters

$$\bar{x} = {}^{x}\!/_{L}; \quad \tau = {}^{L^2}\!/_{D}, \tag{10}$$

L is the characteristic length of the system (typically the thickness or the radius).

A mass balance across a differential control volume leads to the following dimensionless transport equation:

$$\frac{\partial \bar{c}}{\partial \tau} = \frac{\partial^2 \bar{c}}{\partial \bar{x}^2} - (1-\eta) b \frac{\bar{V} E}{RT} \left(\frac{\partial \bar{c}}{\partial \bar{x}} \right)^2 - (1-\eta) b \frac{\bar{V} E}{RT} \bar{c} \frac{\partial^2 \bar{c}}{\partial \bar{x}^2} - b \frac{\bar{V} E}{RT} \frac{\partial \eta}{\partial \bar{x}} \bar{c} \left(\frac{\partial \bar{c}}{\partial \bar{x}} \right), \tag{11}$$

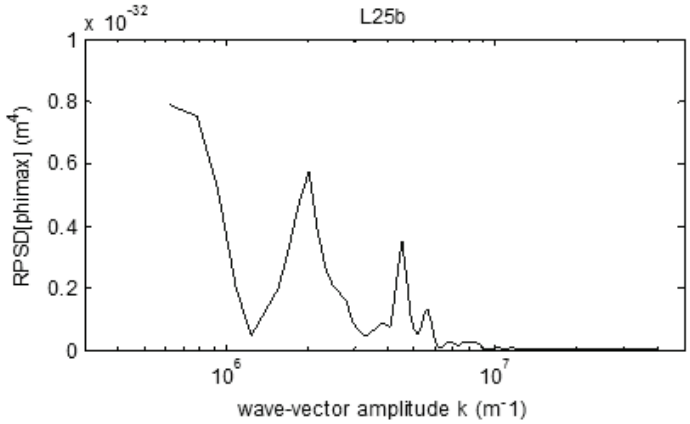

Figure 16. PSDF of L25 sample.

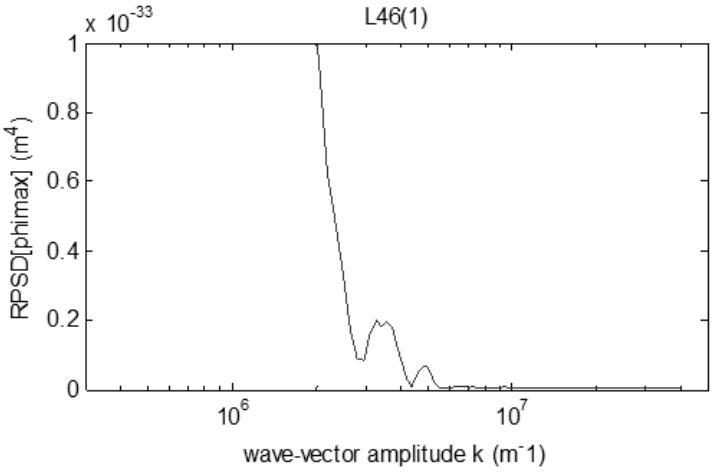

Figure 17. PSDF of a material designed to produce excess of power.

where we introduced above $\eta(x)$ as a parameter giving the percentage of stress that is released by plastic deformation or by dislocation slipping:

$$\eta = \frac{\sigma_{\text{loc}}}{\sigma_{sn}}$$

σ_{sn} yield strength.

When the release of the stress is complete ($\eta = 1$ and constant along the domain), Eq. (11) reduces to the Fick's law.

Equation (11) describes the interstitial diffusion of hydrogen into the metal (e.g. palladium) under a stress field. The effect of stress at steady state conditions results in a different concentration profile, hence in different loading characteristics that depend on the properties of the material such as the Young module.

The transport equation (11) is numerically solved with the boundary and initial conditions $\bar{c} = 1, \ \bar{x} = 0(\forall\, \text{t})$ and $\partial\bar{c}/\partial\bar{x} = 0, \quad \bar{x} = L/2, \ \bar{c} = 0, \ t = 0$ and includes the calculation of the relaxed stress on the basis of the mechanical properties of the material (σ_{r}). Some calculations have been done by using indicative values of the Young module in order to clearly show the effect. Figures 2 and 3 present the equilibrium concentration profile, from the external side up to the symmetry plane, for two palladium foils with different Young modules. In the first case the value of the Young module is 1.0×10^{10} Pa whereas in the second case the value is 1.0×10^{11} Pa (these values are chosen to better enforce this effect). It is clear that the loading reduces when the Young module increases. The calculation of the concentration profile evolved has been used to also calculate the evolution of the *R*/*R*o ratio by assuming the foil to be as a parallel of the electric resistance and by considering the well-known literature data on palladium hydride (deuteride) resistance. Figures 4 and 5 show the evolution of the R/R_0 ratio for the two considered loading conditions described above.

Figures 4 and 5 represent typical situations that one may observe experimentally.

(1) *High loading*: R/R_0 reduces to 1.4 and to 1.6, after achieving the maximum, for both H and D, respectively.
(2) *Low loading*: R/R_0 shows a small reduction, after achieving the maximum, since the dissolution of H or D stops because of the stress field (surface contaminants are in control at the same level during the loading process).

The model allows us to seek for a material that shows homogeneous loading characteristics able to minimize the concentration gradient and hence the stress field. Some treatment processes, based on cold rolling and annealing steps are shown to optimize the metallurgical structure of the materials in order to increase the H(D) loading. The raw material is a palladium foil (1 mm thick) able to reach a loading ratio of about 0.8 (hydrogen atomic ratio). The treatment has been done in two steps:

(1) Cold rolling of the raw material leading to a Pd foil of 50 μm thickness.
(2) Annealing at different temperatures (ranging from 700 and 1100°C) at different time intervals.

Figure 6 shows a simple cold worked sample. Figure 7 shows the effect of the annealing after the rolling treatment procedure.

A H/Pd ratio of 0.97 has been obtained in the sample, cold worked and annealed at 850°C for 1 h.

The tests described above have shown a satisfactory reproducibility.

3. Calorimetry: Experimental Results

The calorimetric set-up was conceived to directly measure the output power by means of a mass flow calorimeter. The electrochemical loading was performed in a closed electrochemical cell equipped with a catalytic fixed bed to recombine the gas produced during electrolysis. The mass flow calorimetric system is composed of 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 cm^3/s), read by the data acquisition system in order to precisely measure the output power. Inlet and outlet temperature of the coolant are measured using two Pt 100 thermometers (four wires measurement). The closed electrochemical cell is equipped with a recombiner (Sued-Chemie Pd on alumina catalyst). Cell power supply is provided by the AMEL galvanostat. Output power is measured by means of the mass flow rate and coolant temperature, R/R_0 measurement is done by means of an HP- 4284 (four wires measurement). Figure 8 shows a schematic view of the flow calorimetric system.

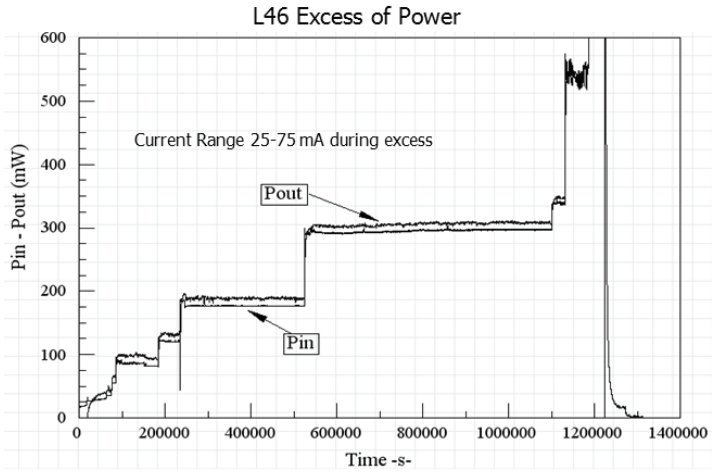

Figure 18. Excess of power produced by the designed material.

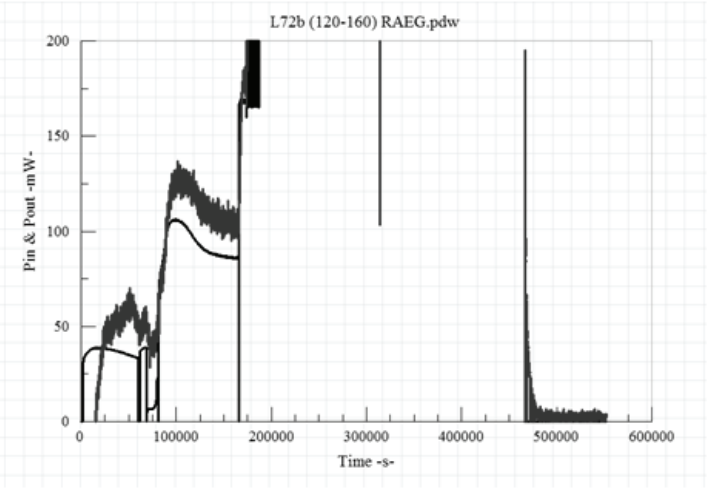

Figure 19. Excess of power produced by a designed sample.

Several (reference) experiments in light water (LiOH 0.1 M electrolyte) were carried out, and with this a calorimeter efficiency of 97.5% was obtained (the difference between input and output power is due to heat loss). Using light water during electrolysis, we did not observe any release of excess power, despite the fact that a very high loading ratio (H/Pd = 0.97) was always achieved.

Different behavior was observed using Pd cathodes loaded in deuterium containing solutions, concentration threshold (at. frac.) D/Pd of 0.9:

(1) High-power gain during the excess,
(2) low-power gain during excess,
(3) no excess.

Differences in two palladium lots received from the same producer have been identified, both lots were 99.95% pure Pd. The first lot gave a reproducibility larger than 60% with signal amplitudes well above 100%, Fig. 9 shows the input, output and excess power in the experiment L14, Fig. 10 shows the increasing of the electrolyte temperature in this experiment during the excess production. The reproducibility reduces under 20% with the second lot and the excess amplitude was always below 25% of the input power.

4. Material Characteristics

Such evidence led to a systematic effort to improve knowledge about the status of the material that is required to have the effect.

The experimental work 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 effect.

The first observation correlated to the different calorimetric behavior of 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:

Contaminants may act on: Grain size, Crystal orientation, Grain boundary.

The effect on grain size distribution can be seen in Figs. 11 and 12, where the typical grain size distribution of samples obtained from the first and second lot is shown. The microscopy images have been analyzed by using GWYDDION software.

Samples belonging to the first and the second lot showed a different crystallographic orientation: the first lot was mainly oriented ⟨100⟩ while the second lot was ⟨100⟩ and ⟨100⟩ 50% oriented. Excess of power was observed with samples having a dominant ⟨100⟩ 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. This may be explained as a micro-corrosion process. The consequence was a different surface morphology between samples belonging to the two lots.

The second lot required a current density higher than the one used for the first lot to achieve the same loading. This is indicative of a different mass transfer regime.

The Power spectral density was selected as merit figure to identify the status of the surface.

Figures 13 and 14 show the surface microscopy of samples #64 (experienced at Energetics) and L25 respectively; both gave a significant excess of power production but the effect was stronger for lot #64. Figures 15 and 16 show the power spectral density function for lot #64 and for lot L25 respectively.

One may observe that the structures of the Power Spectral Density Function (PSDF) are quite similar but the larger the amplitude of the PSDF peaks the larger the produced excess of power. This correlation was also found in other measurements.

5. A Designed Material

The experimental evidence led us to produce a material having characteristics close to the ones described.

A Pd lot having a spectrum of contaminants similar to lot 1 underwent treatment leading to a dominant ⟨100⟩ orientation and appropriate metallurgy.

We have identified some metallurgical differences between samples and we know from the physical metallurgy that these differences can be produced by contaminants. The preliminary analysis work [7] revealed a different spectrum of contaminants in the considered lots. The role of the individual contaminant is under study.

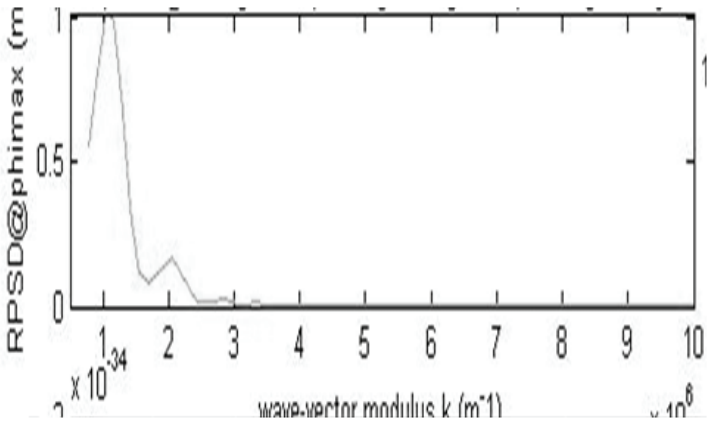

Figure 20. PSDF of a designed material.

The chemical etching treatment on the surface produced a morphology quite similar to the ones of #64 and L25. The PSDF for such a sample, shown in Fig. 17, reproduces the shape of samples #64 and L25 even if with peaks of lower amplitude. A small excess was expected from such a sample. The experimental behavior was in agreement with the expectation. Fig. 18 shows the produced excess of power up to 12% of the input.

This is giving an additional evidence that a proper surface morphology is an additional condition for having the excess of power. The rebuilding of a material designed to have excess of power production was replicated successfully by using the approach described above. Figures 19 and 20 show the excess of power and the PSDF for another designed sample.

The results show an increased control of the effect even if not yet satisfactory, in particular if one looks at the amplitude of the signals.

6. Conclusions

Some characteristics have been identified that give cathodes different behavior. Enhanced probability for having an excess of power is observed when:

Loading is easy at a relatively low current density due to proper metallurgy.

⟨100⟩ Crystal orientation.

Identified surface morphology.

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

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