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Joint Scientific Advances in Condensed Matter Nuclear Science

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Abstract

A joint effort performed by ENEA, SRI, Energetics Technologies, NRL and the University of Rome La Sapienza allowed to obtain a remarkable level of sheared reproducibility both in high loading of palladium with deuterium and in observing excess power production during calorimetric experiments. The excess heat was observed with a signal well above the measurement uncertainty, with up to 70% of reproducibility.

The wide-ranging scientific work carried out in optimizing the palladium electrodes and the accuracy of the calorimetry are the reasons for the success of this project.

Introduction

In 1989 M. Fleishmann and S. Pons [1] discovered excess power production during electrochemical deuterium loading in palladium but at that time the reproducibility of this effect was very low. McKubre (SRI) [2] and Kunimatsu (IMRA Japan) [3], in 1992, discovered that the excess power production was a threshold effect occurring only (but not always) when the average deuterium concentration in the palladium lattice exceeded the atomic fraction value D/Pd ~0.9. After these results were reported, research activity moved to concentrate on the aspects of material science concerning the mechanisms controlling the hydrogen isotope mass transfer into metal lattices. Material thermodynamics and transport processes have been investigated to optimize the palladium to be tested into calorimetric experiments during electrochemical loading of deuterium. The goal was to increase the reproducibility of the excess power production by increasing the hydrogen isotopes solubility into the metal lattice.

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 non-equilibrium because of the occurrence of a transport process. The two aspects of the 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 since 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 [4]. The deformation field produces the defects migration toward the expanded areas. Lewis and co-workers [5, 6, 7] 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 fields of force, like the stress field, modifying the free energy of the system, modify the chemical potential of the hydrogen in solid solution in a metal lattice.

Hydrogen isotopes dissolving into a metal (i.e. palladium) occupy interstitial positions and expand the lattice. This process generates a stress field when extreme concentration differences such as strong gradients are created [8]. Metallurgy and the status of the interface have been studied to design a material to increase control of the loading [9]. The control of the deuterium concentration threshold leads to an increase in both the reproducibility of the excess heat and in the amplitude of the signal.

A flow calorimetric system, designed on the basis of detailed and accurate modeling, was developed for this study.

Materials

A material having a metallurgical structure able to ensure homogeneous loading makes it possible to minimize the stress field by minimizing the concentration gradients. Some treatments, based on cold and annealing steps followed by thermal processing, optimize the metallurgical structure increasing the H(D) loading. The row material was palladium foil 1 mm thick, which was able to reach a loading ratio of about 0.75 - 0.8 (hydrogen atomic ratio). The treatment was done in two steps:

1) Cold rolling of the raw material to produce a palladium foil 50 μm thick.
2) Annealing at temperatures around 900°C for one hour or more.

Figure 1 shows the effect of the treatment; that is, the metallurgical structure on the H (D) loading. H/Pd=0.97 has been obtained in the sample that was cold worked and annealed.

On the basis of the mechanisms considered above, a possible interpretation of such results is that in the sample the concentration profiles are maintained relatively flat because of the reduced size of the grains and because of proper boundary grain diffusion. Loading tests have shown satisfactory reproducibility.

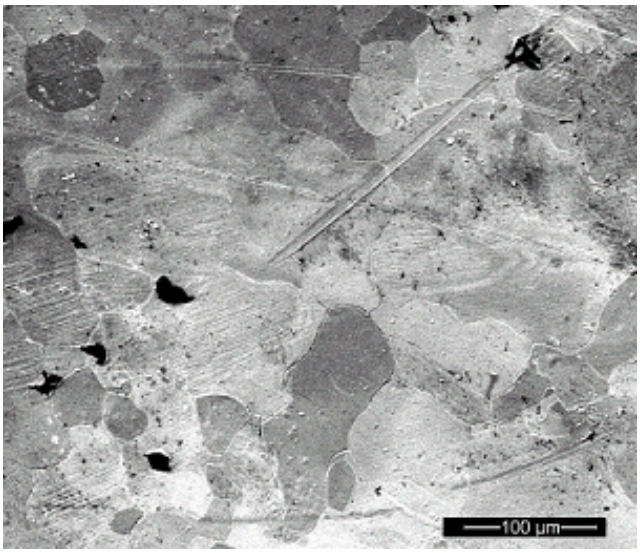

Fig. 1. Pd cold worked and annealed.

Calorimetric system

The experiment is carried out using flow calorimeters equipped with electrochemical cells in which pre-treated palladium cathodes have been electrochemically loaded by using LiOD 0.1 M electrolyte. Some experiments employ laser irradiation during the electrolysis. Figure 2 shows a schematic of the calorimeter.

The calorimetric cells have been modeled and designed to have the required sensitivity and measurement accuracy by using a three dimensional, time dependent, finite element approach.

Two methods have been adopted to cool the electrochemical cells. The first cell is working in a cooling water jacket, the second one employs a coolant pipe (steel covered by a thin Teflon layer) passing through the electrolyte and is equipped with two windows for the laser irradiation. Both are helium tight (He leakage < 1E-10 mbar l/s), and equipped with a catalyst that recombines the gas produced by the electrolysis. A pressure gauge is used to measure pressure in the cell during the experiment. The two cells have an electrolyte volume of 30 and 60 ml respectively.

The cells are enclosed in an insulator and operated in a thermostatically controlled constant temperature box (±0.05°C). The coolant coming from a thermostatic bath (Haake ±0.05°C), passes through a high precision flow meter and controller (Bronkhorst, 0.3 - 0.1 cc/s) and the input and output temperatures of the coolant are measured with PT-100 thermometers read by a temperature monitor (Lake Shore, model 218). Electrolyte temperature is also measured with PT-100 thermometers.

Cell power is supplied with a galvanostat modulated (AMEL, 555c), and sometimes equipped with a wave function generator (HP, 33120). Galvanostatic operation allows direct current power to be computed as a scalar product of current and voltage. Current and voltage are measured by means of two HP34401A 6.5 digit multimeters. Typically the cells operate with voltage and current ranging between 2.5 and 12 V and 5 - 300 mA. The constant temperature box, bath and

ambient temperatures as well as the cell pressure are read by an HP34970A. The data acquisition system uses GPIB connections and LabView.

Output power is measured by means of the mass flow rate and coolant temperatures. R/Ro four-wire loading measurement is done by means of an HP-4284.

Several experiments have been done using light water (LiOH 0.1 M electrolyte) obtaining calorimeter heat recovery efficiency of 97.5% (output=0.975 input, with 0.025 unaccounted for heat losses).

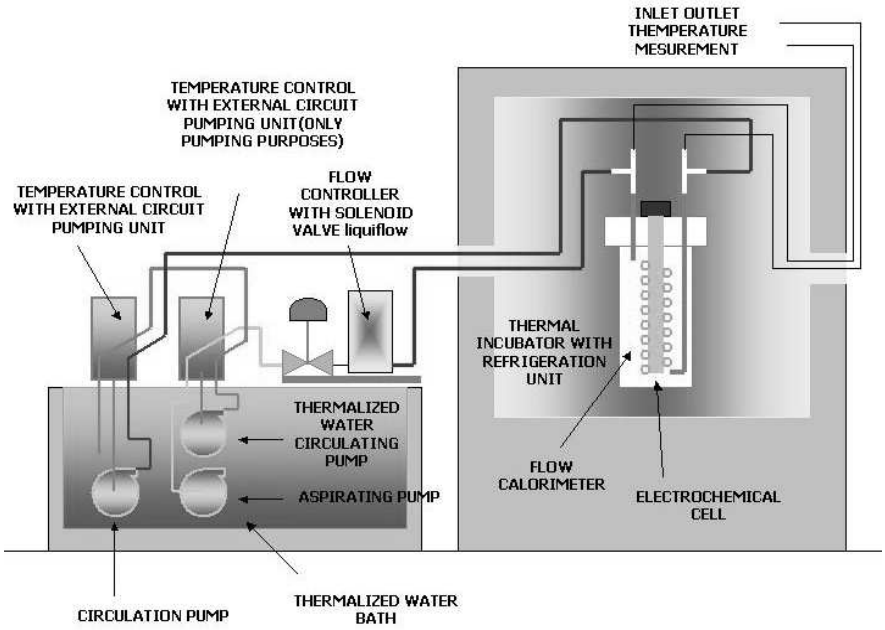

Fig. 2. Flow calorimeter system with electrochemical cell.

The cathode is a palladium foil (20 × 10 mm × 50 μm) between two platinum foils (symmetric 45 × 15 mm), the anode-cathode distance is 6 mm.

Figure 3 show the temperature field in the cells under typical operating conditions.

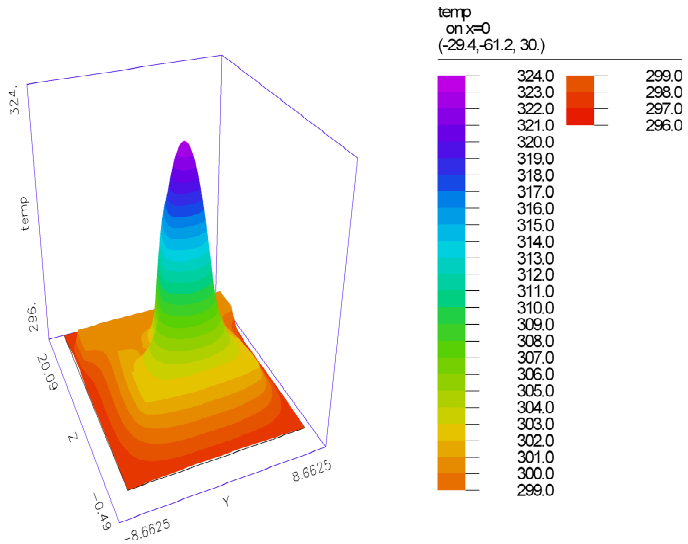

Fig. 3. Calculated 3-D Temperature distribution in the cell shown in Fig. 2.

Experimental activity

Several cells have been run with light water with two goals: to determine the efficiency of the calorimeters and to study if anomalous thermal behaviour occurs with palladium loaded with hydrogen.

No excess power production has been observed using H_2O despite the fact that very high loading (H/Pd=0.97) was always achieved.

The sensitivity of the calorimeter was estimated to be 50 mW ± 20 mW.

Excess power production has been observed only during electrochemical loading of deuterium in palladium, both with laser irradiation and without irradiation.

Although only a small number of tests with laser triggering have been done, preliminary results indicate that the laser has a stabilizing effect on excess power production.

This experimental campaign shows very high reproducibility (close to 100%) in loading above the threshold, and significant reproducibility in triggering excess heat. Excess heat appeared in around 60% of the tests at ENEA and up to 75% of the tests at SRI. It is clear that the loading above the threshold, to an average value estimated to be around D/Pd = 0.9, is a necessary condition to obtain the production of excess power.

The strategy leading to this improvement in results was extended research into material science. Metallurgy was integrated with a study of surface materials, the processes occurring at the interface, and with the electrochemical experimental conditions. This project was jointly performed by ENEA, SRI, NRL, the University of Rome and Energetics Technologies. A study oriented to correlate the surface morphology with the loading is presented by some of the authors in another paper [10].

Here are some of the experimental results obtained at ENEA:

Sample L14 was etched with and nitric acid for 60 sec and with 100% aqua regia for 60 s before electrolysis. During the experiment the current and voltage ranged between 10 to 15 mA and 2.4 to 3.5 V respectively. This sample showed good loading, up to D/Pd = 0.95. The maximum was achieved at very low current (13 mA on 6 cm^2 of cathode surface).

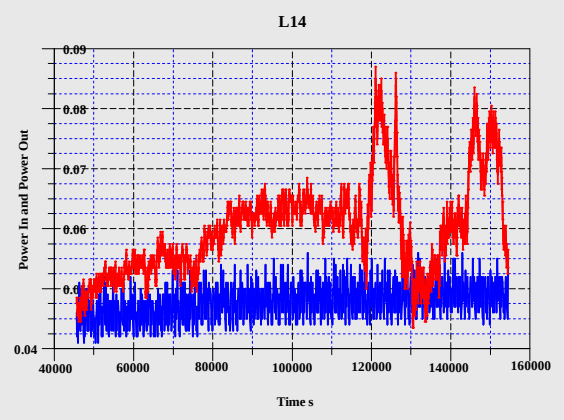

Fig. 4. Excess power (sample L14)

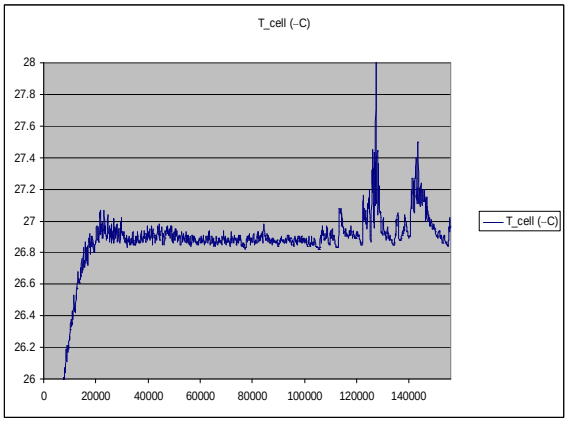

Fig. 5. Electrolyte temperature (sample L14)

Excess power occurred as shown in Fig. 3, where the measure of uncertainty is taken into account. Both heat bursts are very well correlated with the electrolyte temperature, as may be seen from Fig. 5. The temperature of the electrolyte was monitored with a PT100 thermometer as was the inlet and outlet coolant temperature. Notice that the electrolyte temperature was read with a different temperature reader, so that a malfunction of temperature reader can be excluded. The amplitude of the excess peaked at 80% of the input power.

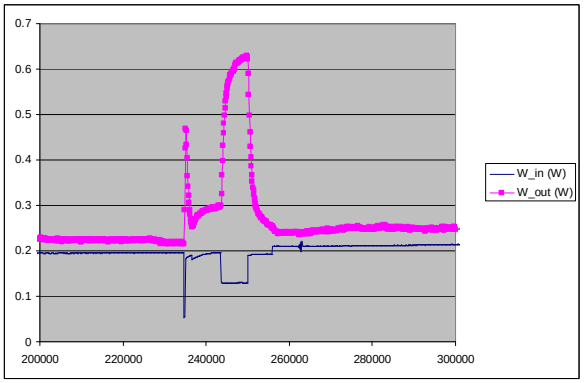

Fig. 6. Input and output (upper curve) power evolution in experiment L17.

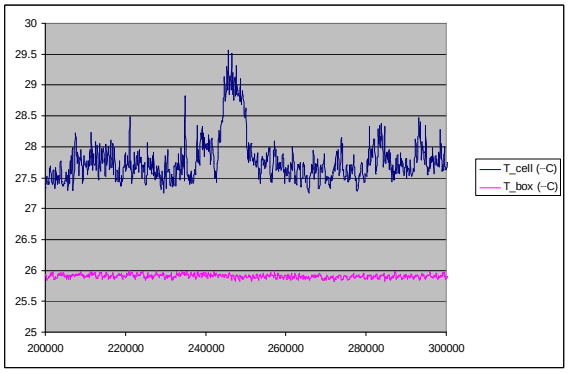

Fig. 7. Electrolyte temperature evolution: the temperature increase is well correlated with excess power.

Larger excess was obtained with sample L17. The input and output power are shown in Fig. 6. The second burst is long enough for the calorimeter to achieve a steady state. We can see in Fig. 6 that during the excess power event, the input power declines. This is due to the power supply operating in galvanostatic mode. The strong excess heat, up to 620 mW, produced a temperature increase of the electrolyte (Fig. 7) that reduced the electrolyte resistivity and the interface impedance, so that less voltage was required to maintain the set current, thus reducing input power.

In conclusion, input was 125 mW and output was 620 mW, so that the output gain was 500%. Specimen L17 was etched like L14. The current ranged from 10 to 65 mA and voltage ranged from 2.6 to 4.5 V. Figure 7 shows that the electrolyte temperature increase during excess power production in experiment L17 reproduced the behaviour observed during experiment L14.

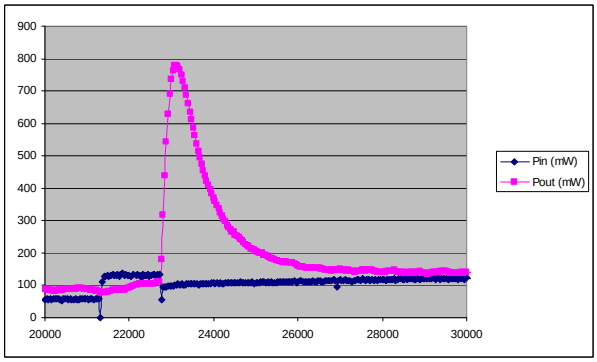

Fig. 8. Excess power during experiment L30.

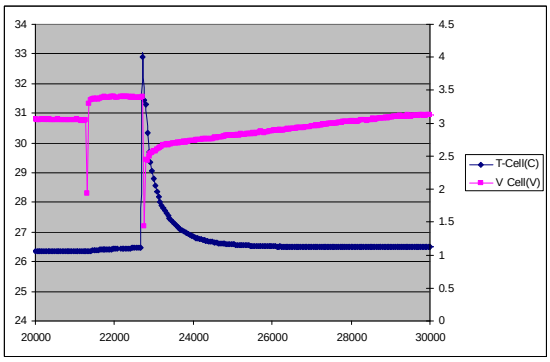

Fig. 9. Electrolyte temperature increasing and voltage evolution during excess power in experiment L30.

Figure 8 shows the excess power during experiment L30, and Fig. 9 shows the corresponding increase in the electrolyte temperature. In this case a steady state in the calorimeter was not achieved. Output power increased up to 800 mW with input power of 100 mW. But a calculation accounting for the transient temperature rise of the calorimeter shows that 7 W of additional power output occurred during the 600-second transient event. This result is quite astonishing since it indicates output power that is 7000% of input. The model accurately describes the evolution of the electrolyte temperature. The modeling tool developed to design calorimeters was used to estimate the excess in transient conditions.

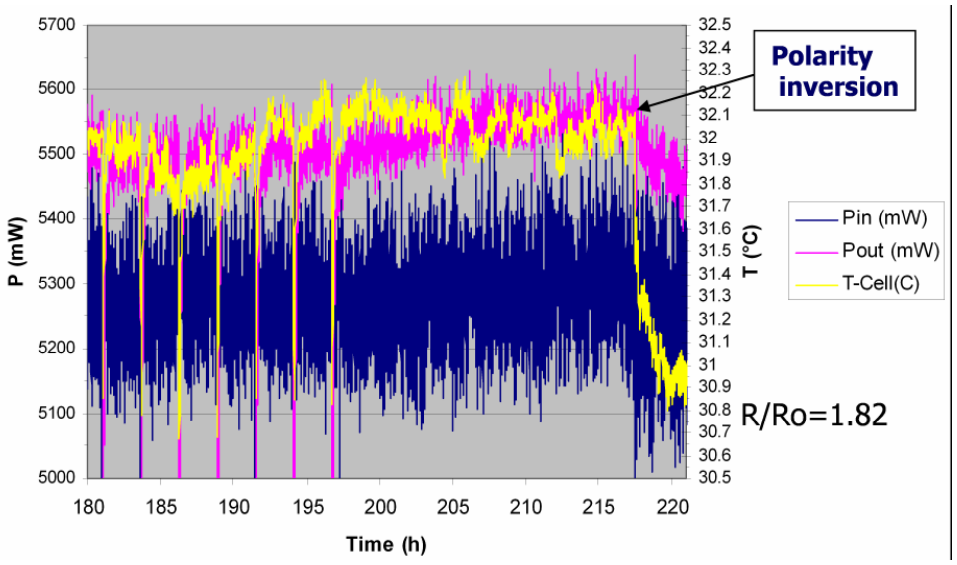

Fig. 8. Temperature and Output Power decreasing after changing electric polarity. Pin=constant

A very stable effect seems to be obtained with sample L35, under laser irradiation. Figure 8 shows the cell temperature and output power decreasing due to electric current polarity switching during sample L35 electrolysis. The two consistent effects prove the presence of an excess heat, switched off by a sharp de-loading produced by current inversion.

Conclusions

Research activity at ENEA in the field of Condensed Matter Nuclear Science has been oriented to material science in order to increase the reproducibility of excess power production during loading of palladium with deuterium.

A finite element model has been developed to simulate the calorimeter's thermal response. This simulation allowed us to obtain real heat recovery efficiency of 97.5%. The sensitivity of the calorimeter was estimated to be 50 mW ± 20 mW.

The palladium metallurgy was optimized to improve the loading of deuterium.

A preliminary study has been done to identify a correlation between the loading and the surface structure.

Even though the extended material science approach is still in progress, an improvement at experimental level was obtained leading to increased of the reproducibility at ENEA, SRI and Energetics Technologies to a level of 60% in ENEA, and up to 70% at SRI.

Some examples of the observed excesses power are presented. Sample L14 showed good loading up to D/Pd = 0.95, and amplitude of the excess power is 80% of the of the input at the peak.

Sample L17 gave a large excess gain of 500%.

Sample L30 gave the strongest excess power observed up to now in the ENEA Frascati Laboratory using electrochemical loading of palladium with deuterium.

Laser triggering seems to act as a stabilizer of the phenomenon: excess power usually does not show burst behaviour, but is quite stable over time, and of low amplitude. The low level of excess heat could be ascribed to the small spot size of the laser beam.

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