The Role of Cathode's Surface Properties in the Electrochemical Deuterium Loading of Pd Foils

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Abstract. Recent experimental evidences clearly indicate that the reproducibility of excess heat production is correlated with the cathode surface properties. To support the results, a theoretical frame has been also developed, that suggests that a relevant role in the excess heat production is played by the electrodynamics processes at the cathode interface. In particular, one of the mechanisms involved is the enhancement and spatial localization of the electro-magnetic field at the metal/electrolyte interface, promoted by proper surface roughness and morphology.

A further point to be considered is the dynamic character of the metal/electrolyte interface during electrochemical deuterium loading, that derives from the coupling between the different interface characteristics. Surface reconstruction of the metallic cathode is expected to happen, due to corrosion-deposition mechanisms, D/H transport, stress relaxation and defect production, and so on. All these mechanisms both affect and are affected by the surface properties, such as the morphology of the metal/electrolyte interface, the metallurgical and crystal structure of the cathode and the presence of contaminants.

1. Introduction

In the last years, an increasing amount of experimental evidences has been reported, pointing out the correlation between the material properties of the palladium cathodes used in the Fleischmann and Pons (F&P) excess heat experiments and the reproducibility of the effect [1-3]. Replication of calorimetric results in different laboratories was achieved according to the fact that the cathodes had undergone the same manufacturing process and were belonging to the same commercial Pd lot [4]. Some cathodes features have been preliminarily identified to be relevant to the occurrence of the effect, in particular the polycrystalline structure and the surface morphology on micrometer scales.

Recently, a systematic study has been carried out by the authors, aimed to characterize the surface properties of the cathodes and to correlate them with the excess heat occurrence [3]. The results supported the preliminary observations, showing further evidence of the dependence of the anomalous heat effect on the crystallographic orientation, impurity contamination and microscopic features of the cathodes' surface. As concerning this last observation, an extended characterization of the surface morphology at the microscopic scale have been carried out by Atomic Force Microscopy (AFM) [2]. This study was also inspired by a theoretical frame suggesting that electro-dynamical effects (plasmons excitation) could be involved the excess heat production of F&P experiments [5,6].

Based on these recent experimental results and considerations, in this article we analyze some possible scenarios through which the microscopic surface morphology of the Pd cathodes could affect the electric filed distribution at the metal/electrolyte interface during the electrochemical deuteride formation.

2. Experimental methods

The Pd samples used as cathodes in the electrolysis experiments were obtained from different commercial lots of pure Pd, having nominal purity above 99.95%. They have been processed by mechanical, thermal and chemical treatments, well described elsewhere [3], in order to reduce foil thickness and to improve metallurgical properties and surface morphology. The typical manufacturing procedure consists in the following steps: 1) cold rolling of the raw 1 mm thick material to produce foils thinner than 50 microns; 2) annealing at temperatures ranging from 800 to 900°C for about 1 hour, to relax defects and induce re-crystallization into a proper polycrystalline structure, optimized for achieving maximum deuterium loading; wet chemical etching by nitric acid and aqua regia, to remove impurities and native oxide, and to produce a specific surface roughening.

Atomic Force Microscopy was used to investigate the surface morphology of the samples. AFM gives a direct measurement of the tri-dimensional (3-D) surface height profile. For each sample, several images have been taken at different points on the surface, excluding grain boundaries. Details of the AFM instrument used can be found elsewhere [2]. To make easier the comparison between different samples, the images were acquired on the same length scale (typically 24×24 μm^2) and with the same number of pixels (typically 257×257). Scanning of the same sample zone on different scale was also performed, in order to select the magnification factor more convenient to observe the surface features of typical samples.

The height profiles of the investigated samples were generally characterized by random fluctuations superimposed on periodic or quasi-periodic patterns. These surface features are hard to recognize in direct space, but can be effectively revealed in reciprocal space of the spatial frequencies *(kx, ky)*, by computing the Power Spectral Density (PSD) of the height profile, that provides a decomposition of the surface profile into its spatial wavelength. Although the computation of the PSD is a quite common practice in isotropic random surface characterization, because of the anisotropic texture of our samples, we have defined a dedicated set of (1-D) PSD functions, which were more appropriate to extract the more relevant patterns embedded in the surface profiles, without missing the information relative to surface anisotropy. Details of image processing and analysis can be found in previous publication [2].

3. Results and discussion

It's well known that nano-metric surface features of a metal/dielectric interface can induce collective oscillations of the free electron gas (surface plasmon polaritons (SPP) or localized surface plasmons (LSP)), which can be associated to strong amplification of the local electromagnetic field [7].

The electromagnetic (EM) field can be enhanced close to a metal-dielectric interface via the excitation of surface plasmon (SP) modes. Surface roughness and isolated surface features make it possible the coupling of a EM field source with the SP modes, because they provide additional wave-vector to the source EM field that is necessary to fulfill the required momentum conservation. Thus, the role of the surface morphology in the electric field enhancement is played by the wave-vector content of the surface morphology. The Power Spectral Density is just a tool to quantify such a "wave-vector content" of the height profile, since it represents the distribution of the intensity of the sinusoidal components of the surface morphology. The correlation between the shape and intensity of the PSD curves and the anomalous thermal behavior of the Pd cathodes, observed in ref. [2], supports this scenario.

SPP modes can be excited on rough metal surfaces by electromagnetic radiation of suitable frequency and polarization to fulfill simultaneously energy and momentum conservation laws. In the specific case of a plane wave of wavelength λ impinging on a sinusoidal corrugated metal surface of wave-vector $\boldsymbol{G}$, this condition implies that

$$\boldsymbol{G} = \boldsymbol{K}_{sp} - \boldsymbol{K}_i \qquad (1)$$

where $\boldsymbol{K}_{sp}$ is the wave-vector of the SP mode given by

$$\boldsymbol{K}_{sp} = (2\pi/\lambda)^2\ Real(\varepsilon_m / (\varepsilon_m + \varepsilon_d)) \qquad (2)$$

where $\boldsymbol{K}_i$ is the projection of the incident wave-vector into the surface plane, ε_m is the metal dielectric constant and ε_d is the dielectric constant of the adjacent dielectric medium (see for example, ref. [7] pag.8).

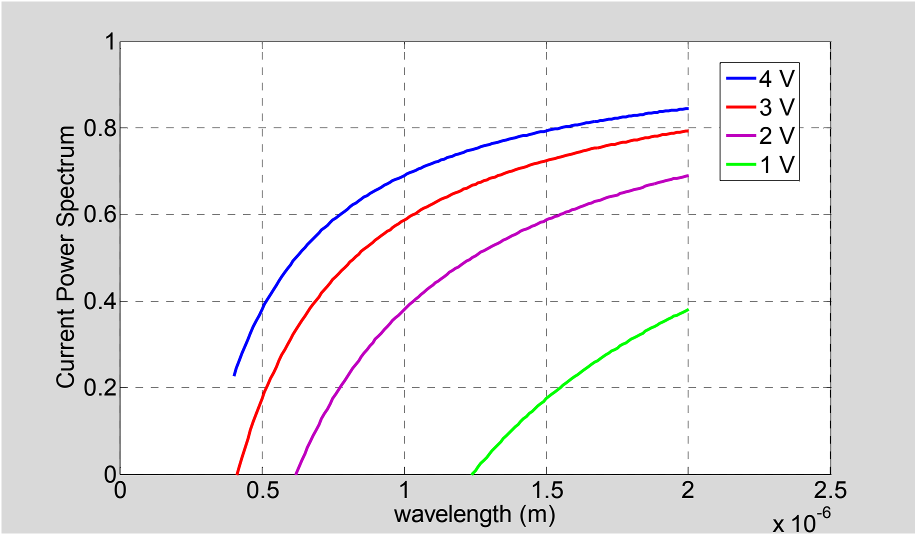

Fig. 1 Power Spectrum of the DC Current fluctuations at the interface of a DC polarized tunnel junction; different colored lines refers to different values of the DC polarizing voltage.

Typical experiments have been performed by using laser radiation to excite surface plasmons modes confined on the surface of thin metal films during electrolysis [8]. Electrochemical F&P experiments have been also carried out, in which laser irradiation of the metallic cathode was performed during deuterium loading [9]. Anyway, most of the F&P-type electrolytic experiments do not usually employ external sources of electromagnetic radiation, because they operate under direct current (DC) control.

An interesting case that presents some similarities with the typical situation occurring in the F&P experiments is the SPP excitation by microstructures on tunnel metal/insulator (or metal/semiconductor) rough junctions [10]. The effect was well know from the literature since more than 30 years ago and it consisted in the observation of light emission by tunnel junctions DC polarized, when the metal/dielectric interface presented a rough morphology. A DC bias voltage across a tunnel junction causes a DC tunnel current to flow across the dielectric barrier. Although this current is continuous, its time dependent fluctuations have a frequency spectrum ($C(\omega)$) extending from DC to a cutoff frequency (ω_c); then, such time fluctuations can drive SPP modes. In ref. [10] the tunnel current spectrum and cutoff frequency were reported:

$$C(\omega) = \frac{eV}{2\pi R_0}\left(1 - \frac{\hbar\omega}{eV}\right). \quad (3)$$

where e is the electron charge, R_o is the DC junction resistance, $\hbar$ is the Planck's constant V is the DC voltage across the junction and $\omega_c = eV/\hbar$.

In a typical F&P experiment we could depict the double layer zone at the metal/electrolyte interface as the equivalent of the metal/dielectric interface of a tunnel junction. Under the DC current flow across the junction, the SPP modes localized at the metal interface can be excited by the time dependent fluctuations of the electric current. The frequency spectrum of the fluctuations depends on the particular type of noise by which they are produced: in the case of the tunnel junctions described above it was assumed to be that typical of "shot" noise, due to the discrete nature of the electrons flow, which has been shown in fig. 1; in the case of an electrolysis experiment different sources of noise can be imagined to be involved, such as "thermal noise" or "bubble noise".

Once a driving EM field is available to excite SPP, the amplitude and frequency spectrum of the SPP field depends on the coupling between the source spectrum and the characteristic modes of the rough surface. The linear theory [11] offers a simple approach to compute the total field enhancement due to SPP.

We have followed this approach in order to get an approximate estimate of how much the SPP effect can be relevant to the surface morphology of our investigated samples.

In the following section, we briefly illustrate the linear method and its main assumptions and we report the results of the calculations of the electric field enhancement relative to the surface profiles of the cathodes measured by AFM technique.

3.1 The linear model

The surface profile *z* of the metallic cathode is described as the superposition of several sinusoidal diffraction gratings [11]:

$$z = \zeta(x, y) = \sum_{\vec{G}} \zeta_G e^{i\vec{G}\cdot\vec{R}} \tag{3}$$

where $\boldsymbol{R}$ is the position vector of Cartesian coordinates (x,y), the average value of the profile is zero (i.e. $<\zeta(x,y)>=0$), $\boldsymbol{G}$ is the wave vectors of the surface profile, belonging to the reciprocal space of the Cartesian plane.

Under the hypothesis of "small roughness", (i.e. $\sigma << \lambda$, where $\sigma = [<\zeta (x,y)^2>]^{1/2}$ is the surface roughness and λ is the wavelength of the electromagnetic field) the first order approximation can be assumed to be valid, in which the electromagnetic field scattered by a surface having the specific profile $\zeta(x,y)$ of eq. (1) is reduced to the linear superposition of many fields, each scattered by a sinusoidal diffraction grating characterized by an amplitude ζ_G of eq. (1).

Consequently, SPP modes can be excited on the rough metal surface if eq. (1) and eq. (2) are fulfilled, being $\boldsymbol{G}$ the wave vectors of the surface profile defined by eq. (3) and $|\boldsymbol{K_i}|=(2\pi/\lambda)\cos(\theta_i)$, where θ_i is the incidence angle of the electromagnetic radiation.

In the same hypothesis, it can be shown that the SPP excitation probability (ΔR_{sp}) is given by:

$$\Delta R_{sp}= (2\pi/\lambda)4\cos(\theta_i) \int PSD(\boldsymbol{G})\Phi(\boldsymbol{G}, \theta_i, \varepsilon_m, \varepsilon_d)\delta(|\boldsymbol{G}|^2-| \boldsymbol{K_{sp}}-\boldsymbol{K_i}|^2)\, d\boldsymbol{G} \tag{4}$$

where $PSD(\boldsymbol{G})$ is the power spectrum of the surface profile; $\Phi(\boldsymbol{G}, \theta_i, \varepsilon_m, \varepsilon_d)$ is a factor that does not depend on the surface profile; $\delta(x)$ is the Dirac δ function, whose effect in the integration of eq. (4) is to reduce the integration domain to the ensemble of wave-vectors $\boldsymbol{G}$ which fulfill the matching conditions stated by eq. (1) and (2).

The electric field associated to the SPP charge oscillation is enhanced because of its spatial confinement close to the interface. The enhancement ratio ($|E_{sp}|^2/|E_{inc}|^2$) is given by [12]

$$|E_{sp}|^2/|E_{inc}|^2 = \cos(\theta_i)\ \Psi(\lambda,\varepsilon_m, \varepsilon_d)\ \Delta R_{sp} \tag{5}$$

where $\Psi(\lambda,\varepsilon_m, \varepsilon_d)$ is a factor that does depend only on the dielectric constant of the metal and of the adjacent dielectric and on the wavelength.

3.2 Computation results

The surfaces of the Pd cathodes used in F&P experiments have been scanned by atomic force microscopy and the collected data have been numerically processed to compute the corresponding bi-dimensional PSD spectra. Such PSD spectra were used to calculate the enhancement ratio of the electric field,

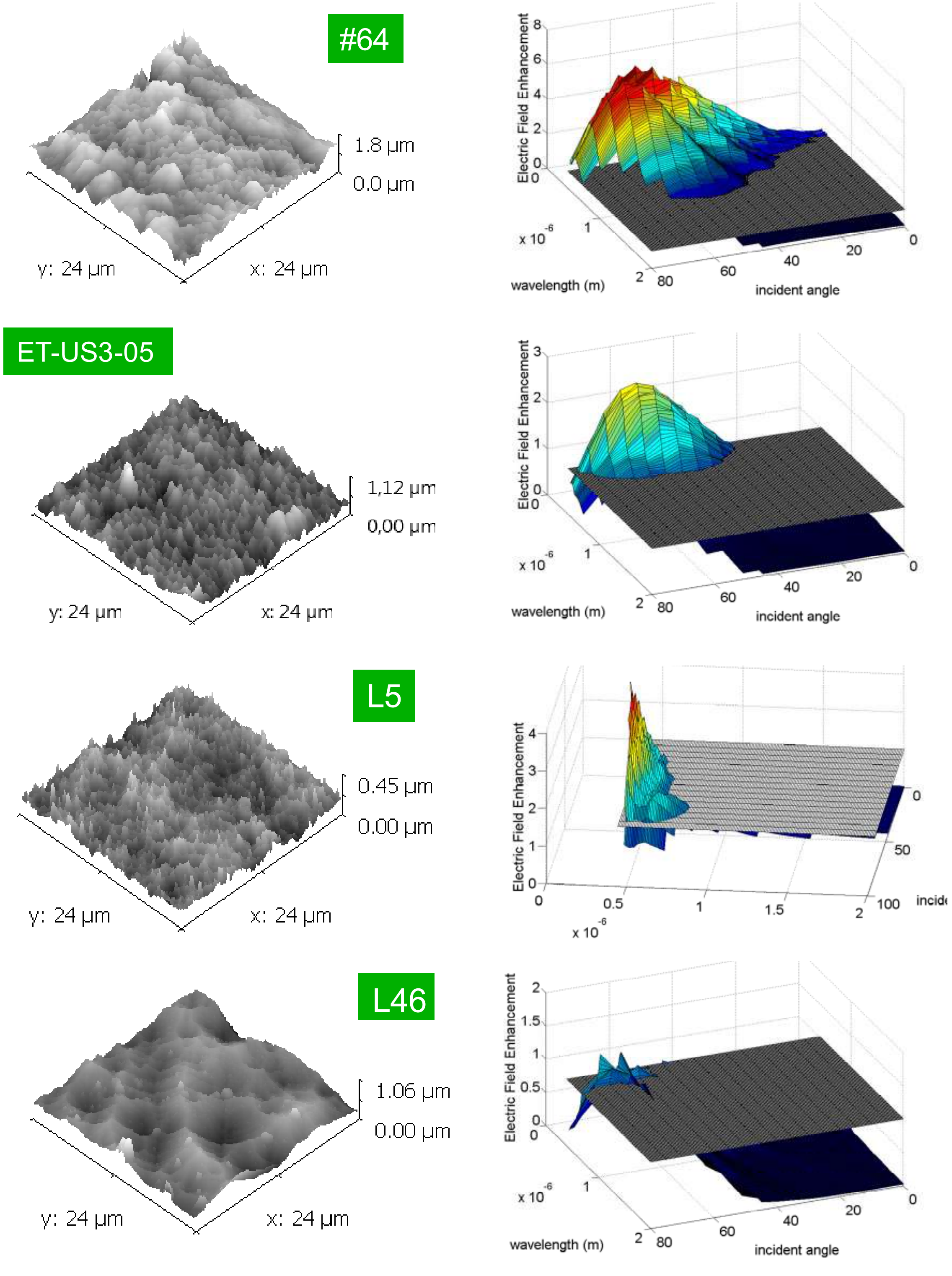

Fig. 2 AFM images (left) and corresponding electric field enhancement (right), computed according to the linear approach described in the text, of samples which gave anomalous excess heat production; the horizontal plane outlines the region in which the enhancement factor is higher than 1.

according to the linear theory described above, by means of eq. (4) and eq. (5), in which the values of the dielectric constants of the metal and the dielectric have been taken from ref. [13] and set to be 1, for the PdH and the electrolyte, respectively.

In fig. 2 the AFM images (left) and the results of the calculations of the enhancement ratio (right), relative to a set of samples which showed anomalous thermal behavior, have been reported; it can be observed that this ratio is higher than 1, in a selected domain of the incident electromagnetic radiation parameters (angle and wavelength). In particular, in going from the top to the bottom of the figure, the measured amount of excess heat produced by the corresponding samples decreased, as expected on the basis of the results reported in ref. [2], showing a correlation between the amount and reproducibility of excess heat and the maximum value of the PSD spectrum (see table I of ref. [2]). In addition, it can be noted that the max values of the field enhancement correspond to values of the incident wavelength in the range of a fraction of to a few microns.

4. Conclusions

The surface morphology of Pd cathodes used in electrochemical experiments has been characterized by atomic force microscopy, after electrochemical loading of deuterium. The electric field enhancement due to surface plasmons excitation has been estimated on the basis of the AFM images and the Power Spectral Density function, following the approach of the first order perturbation theory of the interaction of electromagnetic radiation with a random moderately rough metal surface. The results indicate that the surface morphology of the samples giving anomalous heat production can sustain SPP modes at wavelengths in the range of a fraction to some microns, thus enhancing the electric field at the metal/electrolyte interface up to a factor ten.

5. References

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