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Research Article

Correlation Between Surface Properties and Anomalous Effects in F&P Experiments

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Abstract

The reproducibility of anomalous excess heat production during electro-chemical deuterium permeation of Pd cathodes has been recently observed[1] to be strongly correlated with the palladium surface properties (easy loading at low current, crystal grain distribution, crystallographic orientation, and surface morphology). The understanding of the physical mechanism that is responsible for such observed correlation is very challenging and it is complicated further by the fact that the different features are not, in principle, independent each from the other. In this work, the experimental results concerning the correlation of the excess heat production with the cathode surface properties are reviewed and some possible connections of the observed effects with the deuterium kinetics inside the palladium and the electromagnetic interactions at the metal/electrolyte interface are discussed.

Keywords: Atomic force microscopes, Electron states at surfaces and interfaces, Optical properties of surfaces

1. Introduction

The reproducibility of excess heat production in palladium/deuterium systems is a critical problem that, more than any other issue, has been feeding the criticisms against the reliability of the experimental evidences of this effect. In order to evaluate correctly the reproducibility of any experiment, it is necessary to define the system under study, as well as possible, getting the control over those experimental parameters which are expected to mainly affect it. In the case of anomalous excess heat production, being still lacking an exhaustive theoretical frame, the definition of these parameters is very difficult and it risks to be incomplete.

In the last years, an increasing amount of experimental evidence has been reported, pointing out the correlation between the material properties of the palladium cathodes used in the 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.

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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 [2]. The results support 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 the metallurgical properties, their correlation with the excess heat production can be partially adduced to their effect on the maximum hydrogen/palladium ratio achievable during the experiment, which is well known to correlate with the heat production through a threshold behavior [4]. Actually, the crystal grain size distribution and grain boundary shape can strongly affect the deuterium/hydrogen solubility in palladium, by controlling the diffusion processes and stress fields developed during hydrogenation [5].

The crystal orientation as well as the presence of impurities can strongly affect the result of chemical etching on the surface morphology of polycrystalline materials [6]. Both these material properties may have also a non-negligible role on electrode kinetics during electrolysis [7,8], then influencing the deposition/dissolution processes of the cathode surface, and, consequently, its local morphology.

Cathode's surface morphology seems to be a crucial parameter in controlling the excess heat reproducibility. In this article, we investigate some possible effects, through which surface features and the excess heat production could be related. Before going through the discussion, we briefly review the experimental results and setup concerning the surface characterization of the cathodes.

2. Experimental Results

2.1. Cathode manufacturing

The Pd samples used as cathodes in 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 [2], 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 μm; (2) annealing at temperatures ranging from 800 to 900°C for about 1 h, 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.

2.2. Characterization of cathodes' surface

The samples were analyzed by different microscopic technique before and after being electrolyzed. Scanning electron microscopy and electron backscattered diffraction spectroscopy were used to inspect crystal grain distribution and orientation.

Surface morphology was better investigated also by Atomic Force Microscopy (AFM). AFM gives a direct measurement of the tri-dimensional (3-D) surface height profile. This is different from images acquired by other microscopic techniques, such as scanning electron microscopy or optical microscopy, in which the contrast is not directly related to the changes in height profile, and 3-D profile reconstruction requires stereoscopic methods or numerical elaboration. 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 [3]. 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.

Table 1. Summary of max PSD intensity in the range 1–4 μm^{-1} and excess heat data. The second column indicates the excess to input power ratio, the third column indicates the ratio between the number of samples giving excess heat and the total number of experimented samples of the same lot.

Sample	Excess heat (%)	Reproducibility	Max PSD intensity ($\times 10^{-32}$ m^4)
#64	80–100	2/2	9.5
L5	25–60	2/4	0.7
ET-US3	25	1/1	0.6
L46	12	1/1	0.06

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 [3].

In Figs. 1–4, the PSD spectra of samples giving or not anomalous excess heat production were compared; the results showed the maximum intensity of the spectra is quite correlated with the percentage of heat in excess and its reproducibility (see Table 1), but it is much lower in the spectra of samples which did not produce excess heat.

A similar correlation does not appear to be evident in the specific surface area values, which are shown in Table 2I and which are scattered less than 10% around the same mean value.

3. Electromagnetic Field Enhancement at PD/Electrolyte Cathode Interface

It is well known that nano-metric surface features of a metal/dielectric interface can induce local oscillations of the electronic charge (surface plasmons), which can be associated to strong amplification of the local electromagnetic field [9].

It has been suggested that the presence of oscillating electromagnetic (EM) field of suitable frequency and intensity may affect the collision dynamics of two deuterons moving in a PdD lattice [10]. In that theoretical investigation, the bulk collective oscillation of the conduction electron was considered as the EM field source. Based on these premises, it could make sense to argue that the observed correlation between the surface morphology of Pd cathodes and the reproducibility of anomalous excess heat production may involve such surface plasmon oscillations and electromagnetic field enhancement effect. In order to explore this hypothesis, we try to get an estimate of the contribution of such a mechanism to the local EM field which is expected to build up at the cathode/electrolyte interface. In particular, we focalize on the role played by the surface morphology in the effect of EM field enhancement.

Table 2. Effective surface area of the studied samples, computed from the AFM 24×24 μm^2 images by the free GNU GPL software Gwyddion.

Sample	L46	ET-US3	L5	#64	L47	L51	L53
Effective area (μm^2)	588	634	653	684	631	640	602

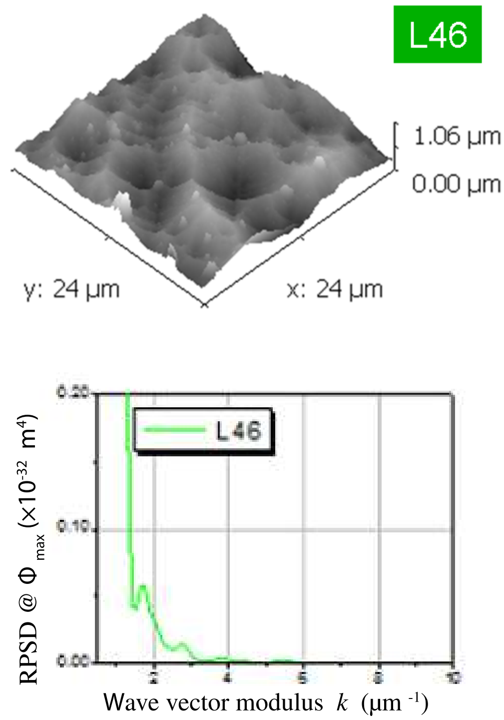


Figure 1. Top: 3-D AFM images of samples L46, which gave excess heat during electrochemical deuterium loading; Bottom: Maximum Power Spectral Density curves computed from the AFM images shown on the bottom.

3.1. Theoretical approach to EM field enhancement calculations

The theory of EM field enhancement at metallic interfaces has been developed deeply in connection with the study of surface enhanced Raman spectroscopy since about forty years [11] and it is based on the application of Maxwell's equations and linear material dispersion assumptions.

Surface plasmons polaritons (SPP) are eigen-states of the *conducting electron* gas, consisting in collective oscillations of the electronic charge at a metal/dielectric interface. These excited modes can be activated by an external EM field impinging on the interface, under some conditions specified below. In practice, the metal electron charge respond to the external excitation by such collective fluctuations, which induce in turn an EM field; the resulting total EM field distribution is spatially localized around the interface and its amplitude is strongly enhanced accordingly to energy conservation.

Depending on the particular geometry of the interface, the SPP may be characterized by different spatial EM distribution and amplitude amplification.

Although the rigorous calculation in the case of a "*real*" surface is a very complicate task, depending on the model adopted to describe the surface profile, some particular ideal cases have been extensively studied and analytically approached, from which physical insight can be extracted. Numerical simulations may also be a powerful tool in such a kind of calculations, but their results are hardly extendable to real physical situations because of the complexity of the real surface profile in the direct space. Parametric studies could be instructive, although time consuming.

A widely studied configuration, which could resemble our experimental case of not- engineered polycrystalline Pd surfaces such as those shown in Figs. 1–4, is that of a randomly rough metallic surface. Under the assumption that the average amplitude of the height profile fluctuation (roughness, σ) is small respect to the wavelength of the EM field, the linear theoretical approach can provide a very simple picture of the SPP effect [12,13]. In this scheme, the surface profile ($z(x, y)$) scanned by AFM is described as the superposition of several sinusoidal diffraction gratings; because of the linear hypothesis described above, the interaction of the EM field with the metallic surface is reduced to the superposition of the single interactions from each single sinusoidal grating. This interaction can produce the excitation of a SPP mode, that consists of in a longitudinal oscillation of the electronic charge confined close to the metal/dielectric interface, whose amplitude depends on the height of the grating, if the wave-vector of the incident field and the pace of the grating satisfy a proper matching condition [14].

The result of such theoretical formulation is an analytical expression describing the EM field enhancement due to SPP excitation, in which the effect of the metal surface properties is expressed only through the power spectral density of

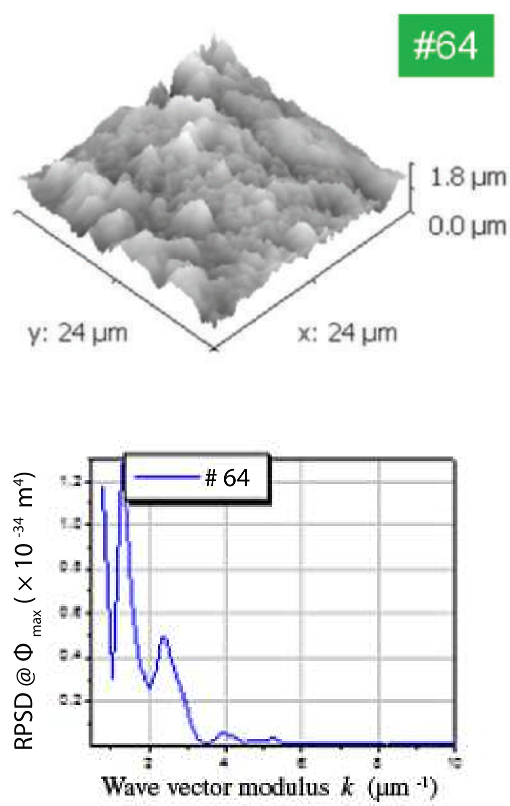


Figure 2. Top: 3-D AFM images of samples #64, which gave excess heat during electrochemical deuterium loading; Bottom: Maximum Power Spectral Density curves computed from the AFM images shown on the bottom.

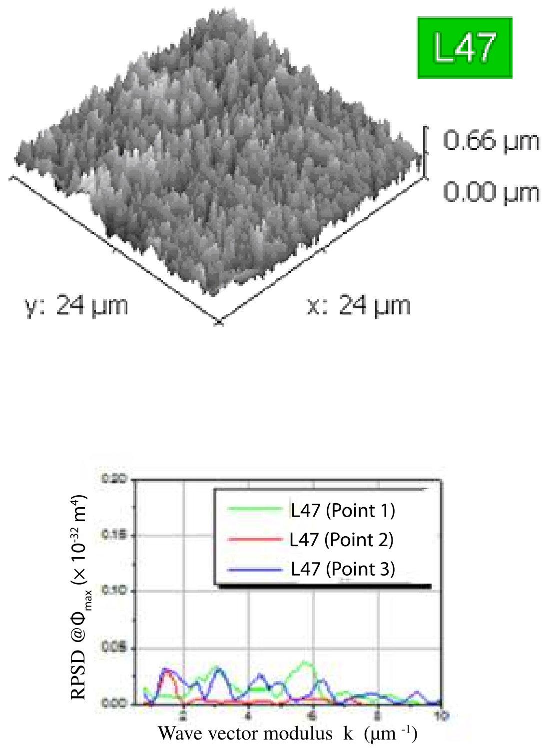


Figure 3. Top: 3-D AFM images of samples L47, which did not give excess heat during electrochemical deuterium loading; Bottom: Maximum Power Spectral Density curves computed from the AFM images shown on the top; in case of sample L47 the curves obtained by the analysis of three different sample points are also shown.

the surface profile and the dielectric constant of the metal. In particular, this model, describing the interaction between an electromagnetic field and a corrugated metal surface, finds out that the local amplification of the electromagnetic field, due to the presence of a particular surface morphology, is dependent on the intensity of the PSD spectrum of the considered surface profile.

This dependence of the field enhancement on the PSD profile, together with the experimentally observed correlation between the PSD profile of the cathode surface and the anomalous excess heat production, supports the idea that *this effect* may involve surface plasmon oscillations and electromagnetic field enhancement phenomena.

3.2. Predictions of the linear theory

To get a more quantitative feeling of how much such effects may be relevant, we have evaluated the ratio between the maximum amplitude of the SPP electric field and that of the incident one, by following the analytic approach of the linear theory described above, starting from the PSD spectra of the surface profiles of some PdH cathodes.

In Fig. 5, we have reported the results of the calculation of some samples used in excess heat experiment, but each

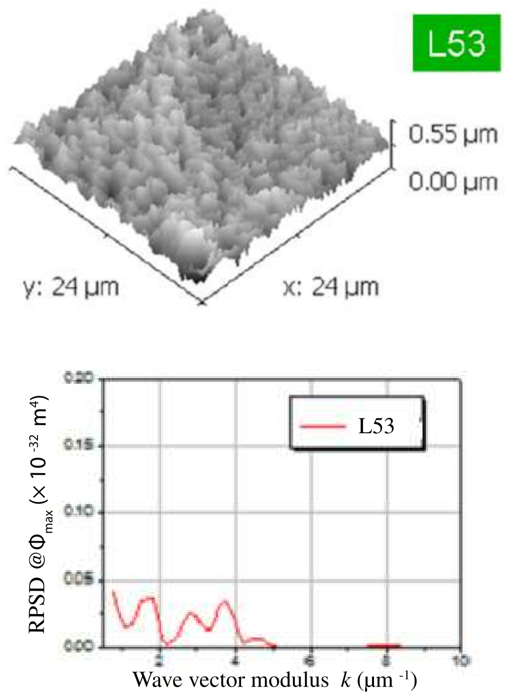


Figure 4. Top: 3-D AFM images of samples L53, which did not give excess heat during electrochemical deuterium loading; Bottom: Maximum Power Spectral Density curves computed from the AFM images shown on the top.

giving a different amount of heat as reported in Table 1. The pictures show a quite good correlation between the two effects, although the maximum values of the enhancement factor are not extraordinary high. Note that the results have to be considered as an upper limit of what can be obtained by a more accurate calculation, because of the approximations made in the computation. In particular, the imaginary part of the dielectric constant of palladium hydride has been assumed negligible; this implies that the damping of the electromagnetic field due to the absorption of the material has been neglected; the effect of neglecting the damping is the reduction of the maximum intensity of the amplified electromagnetic field. The other working hypothesis of the used theoretical approach consist in neglecting nonlinear interactions between the surface profile corrugation and the electromagnetic field; this hypothesis is valid for samples having a small roughness. If the sample roughness is not so small to satisfy the requirement of the linear approximation, the nonlinear contributions to the interactions between the surface profile corrugation and the electromagnetic field should be considered into the computation; the effect of these nonlinear contributions is to decrease the maximum intensity of the amplified electromagnetic field, as in the case of the first approximation mentioned above. Then, both the assumptions made lead to over-estimate in the simulation the effect of the electromagnetic field enhancement, so that the reported results should be considered as an upper limit of what can be obtained by a more accurate calculation [15].

3.3. The modification of the dielectric constant of PdH

We have already mentioned above that, beside the surface morphology, the other surface property of the cathode on which the SPP field enhancement depends is the dielectric constant of the metallic material. This property is strongly modified during the electrolysis, because of the chemical modification of the material due to the hydride formation and also because of the electric charging of the metal surface, produced by the building up of the electrolysis double layer. Calculations of the electronic density of states of palladium hydride at different H/Pd ratios have been performed by *ab-initio* methods [16]; comparison with experimental data is available in the literature only in the case of thin films of PdH, up to a loading ratio of 0.82 [17], showing the reduction of the modulus of both the real and imaginary part of the dielectric constant, in agreement with the lower electron density at the Fermi level induced by hydrogen. The measurement of the dielectric constant in bulk (i.e. some microns thick) samples at high loading ratios is difficult because of the high optical absorption of the metal, which prevents the use of plasmonic methods based on the attenuated total reflection configuration, and of the instability of the stoichiometric hydride at room temperature.

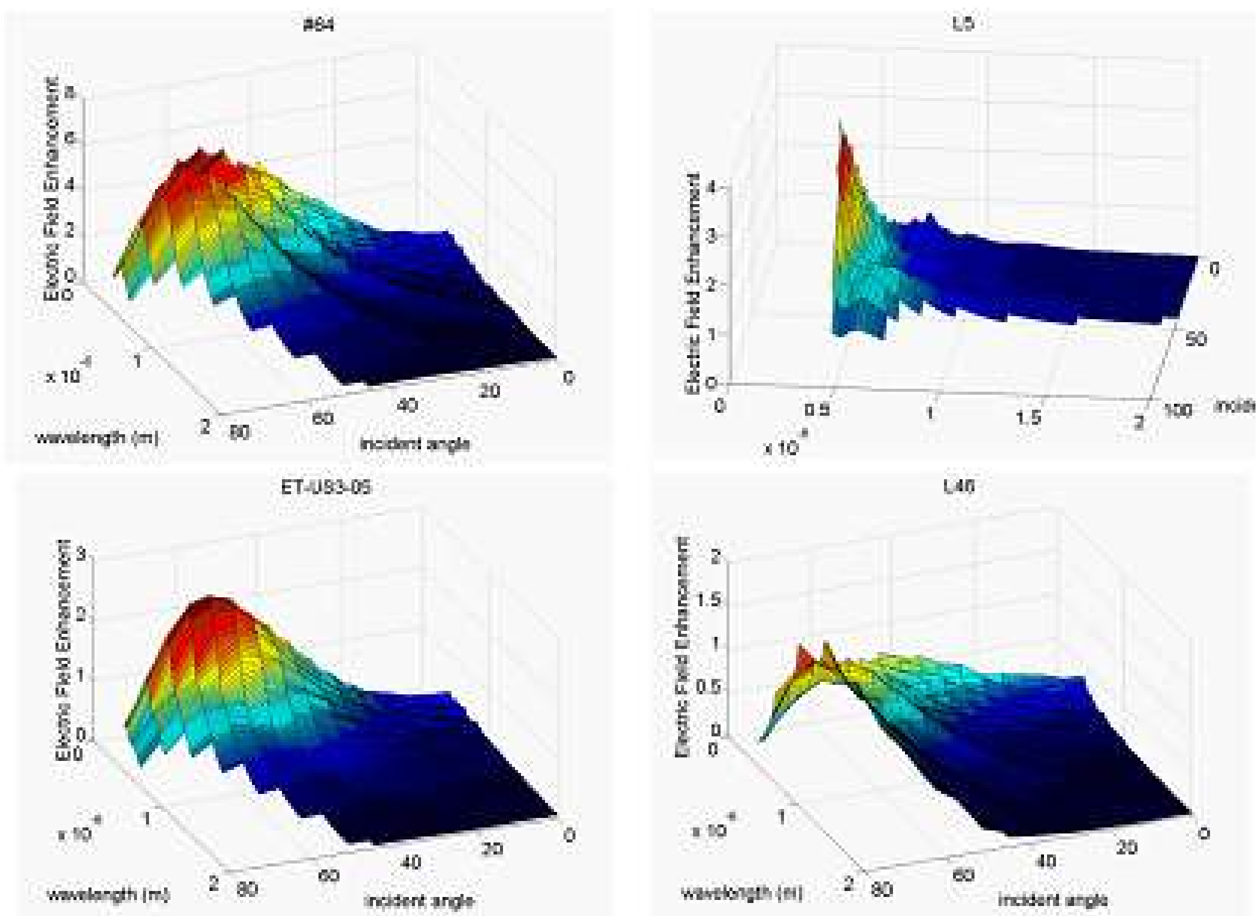
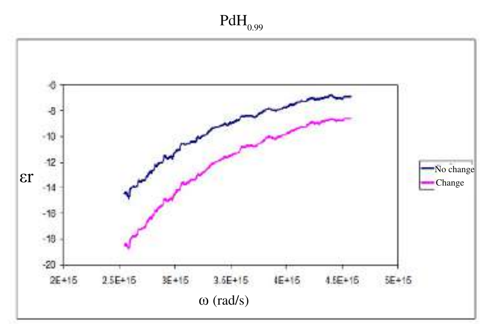


Figure 5. Calculation of the electric field enhancement factor of samples #64, L5, #ET-US3-05 and L46, according to the theoretical approach described in text.

As concerning the effect of the electrolysis double layer, in Ref. 17 the authors have applied to PdH the theoretical approach used in the literature to model surface plasmon polariton resonance sensing experiments with gold electrodes [18]. In this theoretical frame, the dielectric constant of the electrode material is assumed to be determined by the electronic charge density (Drude model). Because of the charging of the electrode due to the electrolysis, the electronic charge density of the electrode is modified, producing, consequently, the change of the dielectric constant of the electrode material [19]. The change of the electron density due to this mechanism depends on the electric charge accumulated at the electrode surface, which can be estimated by the Stern model of the double layer and depends on the electrolysis parameters [20]. Figure 6 shows the results of the calculation of the dielectric constant of the PdH electrode, with and without the application of the additional electric charge due to the building –up of the electrolysis double layer, according to the model described above. The results indicate that, the real part of the dielectric constant (see Fig. 6, top) moves towards more negative values, which are typical of the metallic behavior, while the imaginary part of the dielectric constant, that is indicative of the optical absorption of the material, remains quite un-changed (see Fig. 6, bottom).



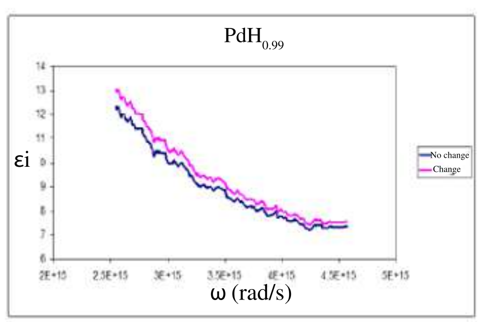


Figure 6. Real (Top) and imaginary (bottom) parts of the dielectric constant of palladium hydride cathode with and without cathodic polarization.

3.4. The effect of a dynamic interface

The analysis performed is for a static case but the electrochemical loading condition with electrons going to the surface and D atoms moving in (and out) through the surface is highly dynamic. Treating this mathematically is well beyond the scope of this paper. However, we try in this paragraph to speculate on how this dynamic might affect the above scenario.

The change in time regarding the metal-electrolyte interface system mostly concerns the variation of:

(1) double layer charge, whose time scale is the related to the rate of the external charge fluctuation and its screening by the metal free electrons;
(2) hydrogen/deuterium concentration inside the metal lattice, which follows the local dynamic of hydrogen/deuterium ions across the metal interface;
(3) surface morphology, which depends on mechanisms of corrosion and deposition at the metal surface.

In the proposed scenario of SPP excitation, both the double layer charge and the deuterium/hydrogen concentration enter into the process through their effect on the dielectric constant of the metal, while the surface morphology directly affects the power spectral density of the surface profile.

Given τ_ω the time period of the electromagnetic incident radiation and τ_{change} the time period relative to the system modification rate, if $\tau_{\text{change}} \gg \tau_\omega$ then we can assume to be valid the adiabatic approximation in which the external electromagnetic field and the system are mostly independent and the interaction scheme developed for the static condition still holds. Then, the effect of such a "slow" variation of the interface on the total field distribution will result in a corresponding "slow" change of the parameters entering the SPP resonance matching condition, i.e. the wavelength and incidence angle of the external radiation respect to the metal surface. Anyway, it's worth noting that, in the case in which the main source of interface variation is due to points 1 and 2, the expected modifications are quite small, as computation showed that there are not huge changing in the dielectric function with the double layer charge (see Fig. 6 in the paper). On the other hand, the effect of the changing of the surface morphology (point 3) can result in a change of the SPP resonance wave vector that can be also quite different from which found for the static case, according to the shape and size of the modified surface shape.

The condition $\tau_{\text{change}} \ll \tau_\omega$ is quite far from our experimental conditions, as the frequency of the incident radiation is quite high, typically in the range of the visible electromagnetic spectrum. However, in such a condition, a linear approximation vs. time, similar to the one applied vs. space in this paper to treat the interaction of the radiation with the "rough" surface, can be applied, under the hypothesis that the amplitude of the time variations was not to high. Within such a frame, the system could be considered to be as static, by considering the time average value of the dielectric function instead of the time varying one, and including as a new variable the time autocorrelation function of the surface fluctuations, with a role similar to that played by the power spectral density function within the static scenario.

Finally, if $\tau_\omega \sim \tau_{\text{change}}$, the linear response assumptions break down, since the time response of the system is no more linearly related to the external electric field. The system can still be described by the Maxwell's equations, but the time-harmonic solution will be no more valid because of the time dependence of the dielectric constant. Such a time dependence can be interpreted, in the frequency domain, as being responsible for the generation of additional frequency components of the total electromagnetic field, giving rise to a "multi-harmonic" nonlinear system.

4. Conclusions

The cathode's surface morphology seems to be a crucial parameter in controlling the anomalous excess heat reproducibility. Different mechanisms can be imagined to explain the experimentally observed dependence of the excess heat results on the cathode surface status. The possible effect of local electro-magnetic field enhancement at the metal/dielectric interface has been investigated. First order electromagnetic theory has been applied to simulate the enhancement of the EM field, starting by the experimental surface profile data acquired by AFM microscopy. The results support the idea that this effect can be involved in the correlation between the surface morphology and the excess heat production, although the expected maximum enhancement is not very high. This mechanism should be taken into account when the electrochemical kinetics at the cathode is considered, in particular in the case of nano-structured cathode surfaces.

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