

Electrode Surface Morphology Characterization by Atomic Force Microscopy

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Abstract

The introduction of hydrogen into a metal during electrolysis of water involves primarily the metallic surface. The effect of surface morphology on electrochemical reaction kinetics is well described in the literature [1] therefore it seems to be reasonable to assume that the surface morphology of the cathodes could play a role in the electrochemical metal-hydride formation. Actually, a wide variety of surface features and profiles have been observed in the Pd cathodes typically employed in excess heat production experiments. These features are noted in both the as-prepared samples and the electrolyzed ones. In order to establish a correlation between the occurrence of a particular surface morphology and calorimetric results, it is necessary to identify a useful metric with which to describe and compare the different surface morphologies. In this work an approach based on Atomic Force Microscopy (AFM) has been investigated. The method is oriented toward the identification of parameters suitable for a pre-screening of the materials.

Introduction

In recent years we have begun a research project focused on the study of the material science aspects of cold fusion. In particular, the preliminary results have pointed out a strong correlation existing between the metallurgical and surface properties of the Pd cathodes used in electrochemical experiments, and the occurrence of excess heat production [2]. We investigated cathode features including both bulk features (crystallography, deuterium loading, electrochemical behavior, hardness) and surface characteristics.

In this paper, we concentrate on the study of the surface morphology of the Pd electrodes, leaving the other aspects of material science to other papers [3],[4]. In particular, we limit our analysis to the length scale of a few micrometers, which characterizes the surface morphology “inside” each crystal grain. Grain boundary features fall outside this range, and they have been considered elsewhere [3],[4].

The experimental analysis has been carried out by Atomic Force Microscopy (AFM). This technique [5] is able to collect tri-dimensional surface morphology maps, with spatial resolution up to a fraction of a nanometer. The digitized images have been elaborated to extract numerical parameters and parametric functions, which could make the comparison between the various samples easier and more objective. The numerical procedure, based on the computation of Fourier transforms, aims to define a surface status function that can describe and compare the

surface morphology of different samples, and also to outline correlations between the surface morphology and the excess heat production.

Experimental

The Pd samples investigated in this work 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 described elsewhere [2], in order to reduce foil thickness to about 50 μm , and to improve metallurgical properties and surface morphology. Most of the samples were mapped by AFM before being electrolyzed, to avoid measurement problems caused by dirt on the surface. Actually, surface morphology changes have to be expected during the electrochemical process and, obviously, this modified morphology plays a role in the excess heat mechanism. By measuring the samples before electrolysis instead of after it, we are mainly interested in establishing a correlation between the initial cathode characteristics and the occurrence of excess heat, with the aim of developing instructions for “good” cathode manufacturing.

For each sample, several images have been taken at different points on the surface, excluding zones close to grain boundaries. The AFM instrument (Assing Corp., “Perception” model) is installed at the ENEA laboratory at the Frascati research centre. The instrument is equipped with a pyramidal silicon nitride probe (Veeco, MLCTAU) and is operated in contact mode. Comparison between samples has been performed by using images that were acquired on the same length scale (typically $24 \times 24 \mu\text{m}^2$) and with the same number of pixels (typically 257×257), to avoid experimental and/or numerical artifacts that could affect different samples to varying extents.

Image analysis

The AFM directly measures the 3-D surface height profile of the sample surface. 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. The height profiles of non-engineered surfaces, as those of the samples investigated in our study, are 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 (k_x, k_y), by computing the Power Spectral Density (PSD) of the height profile. The PSD function provides a decomposition of the surface profile into its spatial wavelength components. Mathematically, the PSD (that we indicate in the following as $PSD_{2D}(k_x, k_y)$) is defined as the squared modulus of the Fourier transform of the 2-dimensional surface height profile (that we indicate as $h(x,y)$). Assuming the surface profile to be the result of the linear superposition of an infinite ensemble of sinusoidal profiles, each with a different periodicity along the x and y axis directions, the PSD indicates the weight of each sinusoidal component having a precise periodicity, as a function of the spatial frequencies, which correspond to the inverse of each period length. As an example, a surface characterized by an infinite sinusoidal profile has a PSD spectrum consisting of just one fundamental peak; on the other hand, a random surface has a PSD spectrum extending over a broad range of spatial frequencies.

Commercial software for image processing is commonly suited for computing the 1-dimensional PSD of isotropic and stationary random surfaces. In that case, the surface profile fluctuations measured along any straight path of the surface are assumed to be independent of both the path direction and origin, so that the 2-dimensional PSD reduces to a 1-dimensional function ($PSD_{1D}(|k|)$), which depends only on the modulus of the frequency vector k .

In the case of anisotropic and textured surfaces, the computation of the 1-dimensional isotropic PSD may wash out the information about embedded patterns and periodicities, if the computational path is not carefully chosen, and it also cannot outline the height profile anisotropy. This is indeed the case for the samples studied in our work, which are characterized by a strongly anisotropic texture, related to the crystalline structure of the grain. To solve this problem, we have developed software to compute, from the 2-dimensional PSD, a set of 1-dimensional PSD functions, which can give insight also in the anisotropy of the surface, extracting the more relevant patterns. These additional functions are defined below, starting from a representation of the 2-D PSD in polar coordinates ($PSD_{2D}(|k|, \phi)$), where $(|k|, \phi)$ are the polar coordinates of the reciprocal 2-D k -space instead of Cartesian coordinates ($PSD_{2D}(kx, ky)$):

- The Radial Power Spectral Density ($RPSD(|k|)$), is the average of the polar 2-D PSD ($PSD_{2D}(|k|, \phi)$) over all polar angles (ϕ);
- The Angular Power Spectral Density ($APSD(\phi)$), is the average of the 2-D $PSD_{2D}(|k|, \phi)$ over all k moduli, along the direction of each k polar angle ϕ .
- The Maximum Radial Power Spectral Density ($R@ \phi_{max}(|k|)$) is obtained by taking the values of the 2-D polar Power Spectral Density along the k vector direction identified by the polar angle ϕ_{max} , which is the abscissa for the maximum of the $APSD(\phi)$ curve.

In Fig. 1 the 2-D k vector space is represented in polar coordinates, and the domains involved in the computation of the Radial (Fig. 1a), Angular (Fig. 1b) and Maximum (Fig. 1c) PSD functions are indicated.

The numerical procedure developed to compute the above functions consists of the following steps:

1. The AFM 2-D digital image is converted to a matrix $N \times N$.
2. The $PSD_{2D}(kx, ky)$ matrix is calculated from the 2-D fast Fourier transform (FFT) of the digitized image.
3. The polar PSD matrix ($PSD_{2D}(|k|, \phi)$) is obtained from the $PSD_{2D}(kx, ky)$ matrix, by data interpolation.
4. The Radial, Angular and Maximum Power Spectral Density functions are computed according to the above definitions.

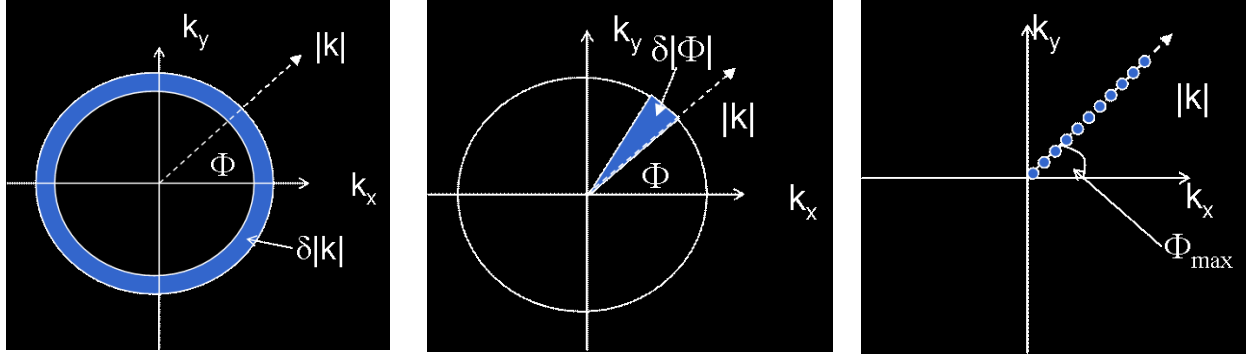


Figure 1. Polar representation of the 2-D reciprocal space in which the 2-D PSD is defined; the light blue areas indicate the domains on which the PSD_{2D} is averaged to compute the Radial Power Spectral Density (Fig. 1a), the Angular Power Spectral Density (Fig. 1b) and the Maximum Power Spectral Density (Fig. 1c).

The analysis has been repeated for different images taken on different sample points (within the same crystal grain), showing similar results within the same crystal grain.

Because of the finite sampling rate and limited scale length of the digital AFM images, the computed PSD functions are band-limited over the space of wave-vectors k . In particular, the low frequency cutoff is determined by the scan length, while the high frequency limit is determined by the sampling rate and by the tip geometry. In the present work, the typical wave-vector range is $0.2 - 30 \mu\text{m}^{-1}$.

Results and Discussion

The Power Spectral Density spectra of samples giving excess heat have been computed to look for common features. A preliminary screening of the data has outlined a particular “multi-peaked” structure in the Maximum Power Spectral Density function of the samples that gave excess heat (see Fig. 2 right), while this feature was not observed in the samples that did not give excess heat (see Fig. 3 right).

The peak intensities of the analyzed features scale with the peak wave number, which ranges from 1 to $4 \mu\text{m}^{-1}$. The similarity in the $R@ \phi_{max}(|k|)$ spectrum is indicative of the presence of a pseudo-periodic texture embedded in the surface morphology, with a period in the range of some tenths of microns. Furthermore, as can be seen in Table I, the maximum PSD peak intensity shows a good correlation with the excess heat percentage and reproducibility (when applicable), 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 II and which are scattered less than 10% around the same mean value.

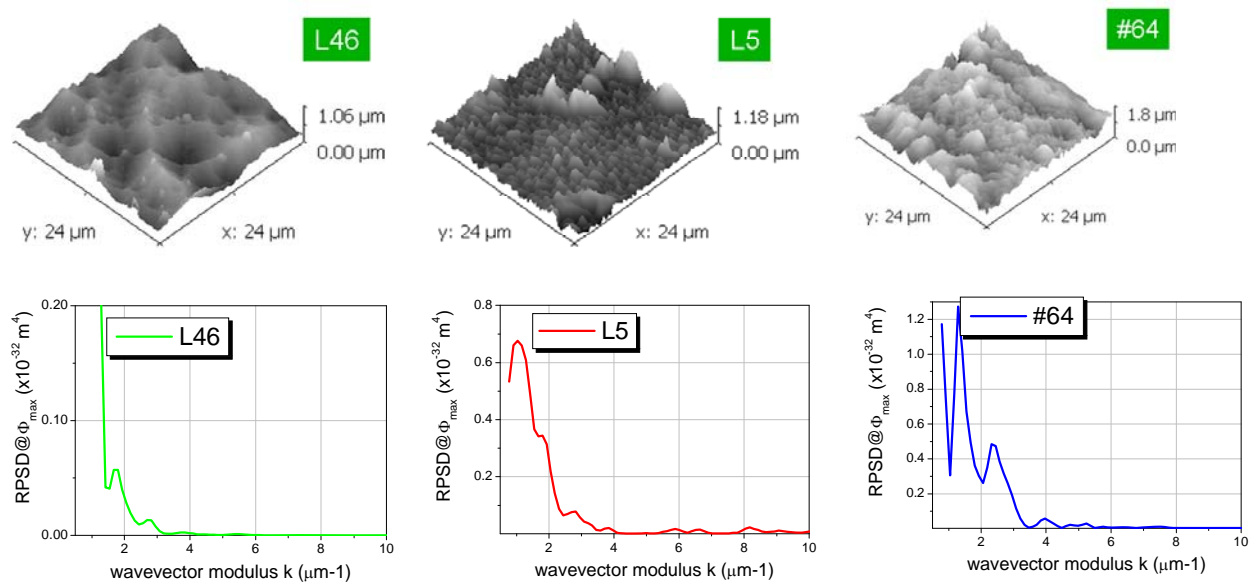


Figure 2. Top: 3-D AFM images of samples L46, L5 and #64, which gave excess heat during electrochemical deuterium loading; Bottom: Maximum Power Spectral Density curves computed from the AFM images shown on the top

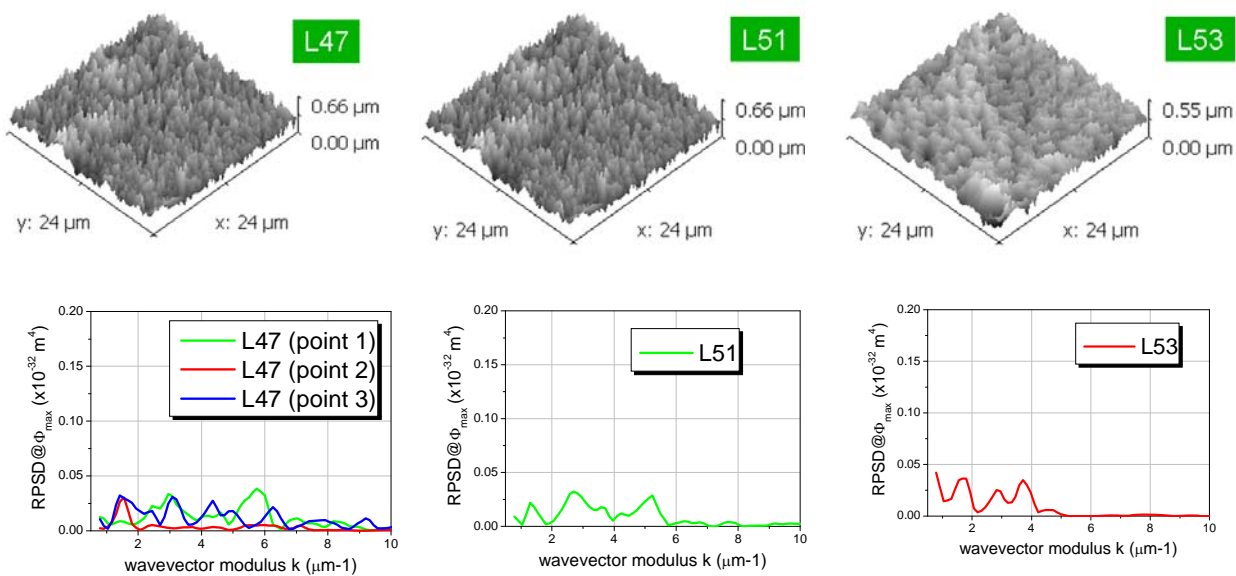


Figure 3. Top: 3-D AFM images of samples L47, L51 and L53, which did not give excess heat during electrochemical deuterium loading; Bottom: Maximum Power Spectral Density curves computed from the AFM images shown on the top; in case of sample L47 the curves obtained by the analysis of three different sample points are also shown.

Table I. Summary of max PSD intensity in the range 1 to 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 ($\times 10^{-32}$ m4)
#64	>1000	2/2	9.5
L5	25-60	2/4	0.7
L46	12	1/1	0.06

Table II. Effective surface area of the studied samples, computed from the AFM images by the free GNU GPL software Gwyddion.

Sample	L46	L5	#64	L47	L51	L53
Surface area (μm^2)	588	653	684	631	640	602

These results suggest that the surface morphology of the Pd cathodes itself plays a role in the excess heat production mechanism. We are not yet able to identify this role, but it cannot be simply reduced to the effect of the change in the specific surface. In this respect, the identified PSD function can be considered as a valid way to estimate the surface morphology.

However, a potential problem with the scale of this method should be noted. The analysis is limited to a small areas of the sample, which may not be representative of the entire specimen. To overcome this problem, a more extended and systematic mapping of the sample surface on different length scales should be done, aimed at eventually discovering scaling behaviors. This may show a relationship, for examples, between the local in-grain morphology and long scale crystal grain distribution. Anyway, even the small-scale investigation has proven to be a worthwhile method, and it has shown the occurrence of a particular PSD spectrum, which we have tentatively identified as a favorable condition for excess heat production, is just one of many other conditions, which involve metallurgical and electrochemical properties of the palladium cathodes⁴.

Conclusions

A method of characterizing the surface morphology of Pd cathodes, based on the spatial power spectrum, has been presented. A preliminary screening of the data showed some common features in the spectra of samples giving excess heat, which are not observed in samples not giving heat. The observed features indicate the presence of pseudo-periodic patterns in the surface morphology, whose period is in the range of some tenths of microns. The surface morphology requirement for excess heat is only a necessary condition, not sufficient: other criteria must also be satisfied.

References

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