# Microscopic characterization of palladium electrodes for cold fusion experiments

F. Sarto, E. Castagna and V. Violante
ENEA, Frascati, Italy

## ABSTRACT

Recent results [1] highlighted that material science is one of the more critical issues in condensed matter nuclear science. In the last years, the experimental results have given a clear indication that a relevant role within this task is played by the material properties of the cathodes.

In order to improve the characterization of the materials, an approach based on the atomic force microscopy is proposed in this paper.

The preliminary study is mainly oriented to identify, by means of the AFM results, parameters suitable for screening the materials.

## Introduction

The interaction of hydrogen with metal involves primarily the metallic surface. Therefore it is reasonably to assume that the surface morphology of the cathodes play a role in the metal-hydride formation. In fact, the hydrogen (deuterium) diffusion/adsorption mechanisms at the metal/electrolyte interface are primarily controlled by the surface activation energy and the effective surface area, which, in turn, strongly depend on the surface morphology.

Accurate images of the surface features can nowadays be obtained by different microscopic techniques. Between these, atomic force microscopy (AFM) is able to reproduce the surface topography in all three spatial dimensions.

However, microscopic analysis is limited to a very small area of the surface, which cannot be representative of the whole sample, mainly because of the random character of surface profiles.

Statistical analysis is usually applied in surface science to process AFM profiles, in order to extract information about the random or periodic properties of the surface, not just isolated features.

In this work, a preliminary study of the morphology of palladium cathodes is performed by AFM, mainly oriented to identify parameters suitable for a screening of the materials.

## Experimental

Atomic force microscopy [2] is the profiling technique with the highest lateral resolution. Similar to a stylus-based profiler, the atomic force microscope contacts the surface by means of a probe tip mounted on a cantilever. While the tip scans the surface, the cantilever deflects or changes its mechanical vibration characteristics due to interaction with the surface peaks and valleys. A laser beam measures this deflection and feedback mechanisms drives the piezo-electric scanners to keep the tip-surface force constant, thus reproducing the surface topography. The very high lateral resolution (down to 1 Å) of AFM depends on the fact that the probe/surface interaction forces are much smaller than in any other stylus-based profiler (down to $10^{-11}$ N) due to the extreme sharpness of the tip.

The AFM instrument used in this work (Assing S.p.A., Perception, installed at the ENEA Lab at the research center in Frascati) is shown in Fig. 1. The head was equipped with triangular SiN probes (MLCTAU by Veeco). A detail of the tip is shown in Fig. 2. The tip worked in contact mode. The piezo-electric scanners have a maximum scale of 40 μm (in the x and y coordinates) and 5.3 μm (along the z axis, normal to the sample surface). The analyzed samples consisted of palladium sheets of about 50 μm thickness.

Fig. 1. Measuring unit of the AFM microscope Perception (by Assing).

Fig. 2. SiN probe - side angle 35°, tip height 3μm.

The images were taken at different points in each sample, but within the same crystal grain, in order to get average statistical information without losing the information about the presence of different crystal orientations in the sample.

For each sample zone, several images (see Fig. 3) have been acquired at different magnifications, the length scale ranging from 30 μm to 500 nm.

**Results and Discussion**

Typical AFM image numerical processing methods have been employed to describe the observed morphologies in terms of statistical function (power spectral density) and parameters (surface roughness, correlation length, fractal grain dimension).

The power spectral density (PSD) provides a decomposition of the surface profile into its component spatial wavelengths. For a periodic surface, the PSD function consists of only fundamental peak and harmonics; for a random surface, the PSD function occupies a range of spatial frequencies. In analysing the frequency characteristics of surface profiles, care must be taken in considering the frequency limits dictated by the instrument setup and the measurement parameters. The more important factors affecting the AFM frequency limits are the sampling distance and the profile length, determining respectively the high and low frequency cut-offs. The tip geometry can also affect the high frequency limit, but, in our case, the tighter limit is that defined by the sampling distance. In order to extend the pass-band of the measurements, for each sample point, the PSD curves have been computed from images taken at different sampling distance and scale length values, and then they have been merged together.

In order to extract numerical parameters able to characterize the surface morphology, the PSD curves can be fitted by different models. Non-engineered surfaces are typically well modeled by random processes, whose squared fluctuations are correlated on length scale shorter than the transverse correlation length (Lc), and have a mean value whose square is defined as the “root mean squared roughness (RMS). Actually, the RMS and Lc are not intrinsic properties of the surface, as according to the random model described above, but they depend on the length scale of the measurement. Such a scaling (self-affine) behavior of non-engineered surfaces is typically described by fractal statistics, by using an inverse power law function to fit the PSD curve. The power exponent (n) and coefficient (Kn) are intrinsic parameters of the surface; they do not depend on the measurement details and they are connected with the self-affine behavior of the surface.

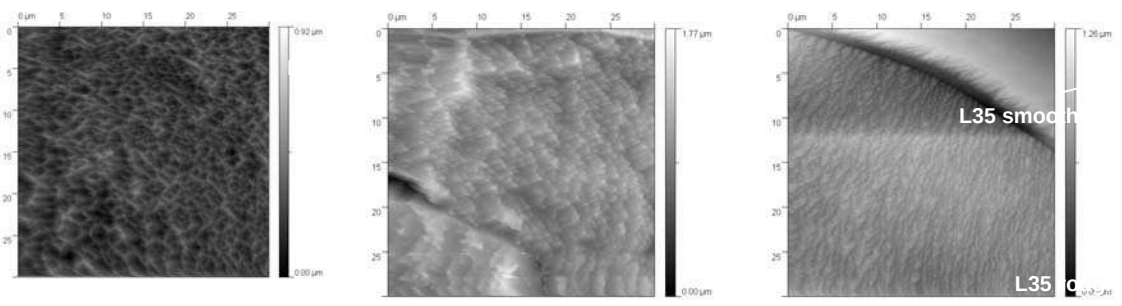


Fig. 3. AFM images of samples L25b (left), L40 (middle) and L35 (right).

In Fig. 4 the PSD curves computed from the AFM images of our samples are shown as a function of the spatial wavelength. Note that the AFM images shown in Fig. 3 are only a limited set of those used to compute the PSD spectra, and the frequency limits are not linked to the length scales shown here.

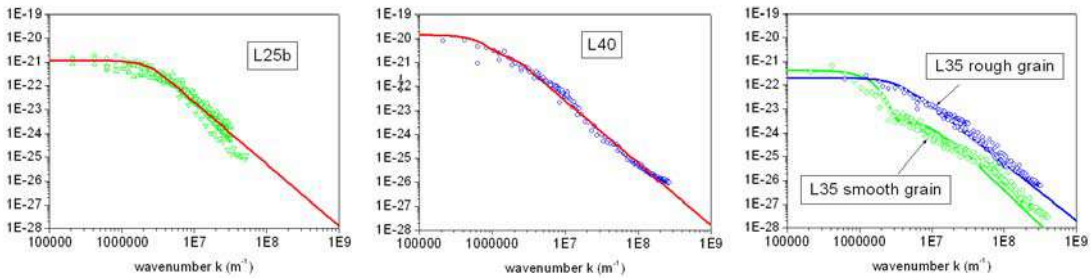


Fig. 4. Power Spectral Density curves of samples L25b (left), L35 (middle) and L40 (right). The data points represent data retrieved from experimental AFM row profiles, the lines represent the best fit to the models described in the text.

The PSD curves numerically retrieved from the digitized AFM images have been divided into two frequency ranges. In the low frequency range, the PSD curves have been well fitted by Gaussian functions, and the root mean squared roughness and the correlation length have been retrieved as best fit parameters and they have been reported in the first section of Table I. In the high frequency range, the PSD curves have been fitted by a power law function, and the power exponent and the coefficient have been derived as best fit parameters (see the second section of Table I).

Table I. Best fitting parameters retrieved by the PSD spectra of sample L25b, L40 and L35.

| SAMPLE | L25B | L40 | L35 rough | L35 smooth |
|---|---|---|---|---|
| *Gaussian Statistics* | | | | |
| **roughness (nm)** | 45 | 55 | 19 | 16 |
| **correlation length (μm)** | 0.73 | 3.32 | 0.81 | 3.12 |
| *Fractal Statistics* | | | | |
| **fractal index** | 2.99 | 2.6 | 2.2 | 2.3 |
| **fractal coefficient** | 0.016- | 1.072e-5 | 2.71e-8 | 1.52e-8 |

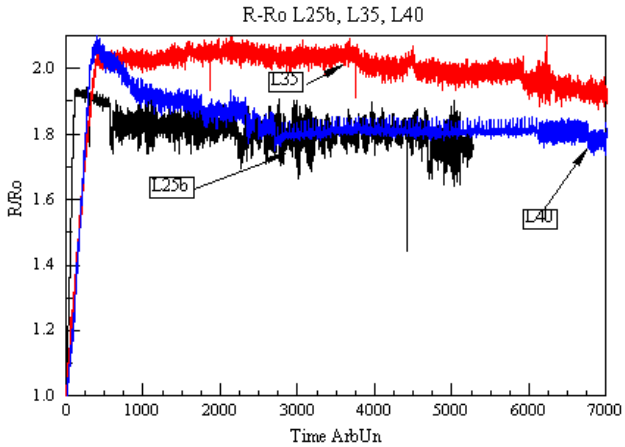


Fig. 5. Deuterium loading curves of the cathodes during electrolysis. The deuterium concentration is deduced by the resistivity ratio of the loaded to the unloaded sample.

In the case of sample L35, the surface analysis has been performed on two different crystal grains (indicated in Figs. 3 and 4. and in Table I as “rough” and “smooth”), which were found in about equal amounts on sample surface.

The results from Table I have been compared with the deuterium loading capability of the investigated samples. Fig. 5 shows the resistivity of the samples during deuterium loading with electrolysis. To monitor the deuterium concentration dissolved into the samples, the resistivity values were measured *in situ* with the 4-probe Van der Paul technique, and they have nrrn normalized to the initial value of the unloaded cathodes. As can be seen from the graph, the characteristic drop in the resistivity versus time curve, which corresponds to a D-to-Pd ratio higher than 0.9, occurs after a short time in the case

of sample L25b and L40, but much later in the case of sample L35. The comparison of these results with those of table I suggest that, between the investigated surface morphology parameters, the roughness and the fractal index could correlate with the deuterium loading behaviour. Of course, this observation must be considered tentative, because of the limited statistics. Work is in progress to extend the analysis to a larger ensemble of samples and to look for possible correlations of the surface parameters with the heat production experiments.

## Conclusions

A preliminary study of the surface topography has been performed on palladium cathodes by AFM. The profiles have been analyzed by using both conventional and self-affine statistics, each of them described by a limited set of parameters.

The preliminary results are indicative of a correlation between the hydrogen loading capability and the surface roughness.

## Acknowledgments

The authors acknowledge Assing S.p.A. for the technical support given in the development and customization of the AFM facility installed in ENEA Frascati.

## References

[1] V. Violante, F. Sarto, E.Castagna, C. Sibilia, M.Bertolotti, R. Li Voti, G.Leahu, M. McKubre, F. Tanzella, K.Grabowski, G.Hubler, D. Knies, T. Zilov, and I. Dardik, "Calorimetric Results of ENEA Cooperative Experiments", Proceedings of the *13th International Conference on Condensed Matter Nuclear Science (ICCF13)*, Dagomys, Sochi, Russia June 25 - July 1, 2007

[2] See, for example "Introduction to Atomic Force Microscopy: Theory, Practice, Applications", by Paul West, Pacific Nanotechnology, freely available online: http://www.afmuniversity.org/