



# Quantitative surface analysis of plastic deformation of Pd electrodes in nanoscale

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## Abstract

Small-angle X-ray scattering (SAXS) was employed as a powerful technique for quantitative surface analysis of Pd electrodes subjected to severe plastic deformation. The experimental data obtained from SAXS measurements were analyzed by means of fractal geometry, as so-called fractal dimensions can be used as a quantitative measure of surface roughness. The influence of the strength of plastic deformation induced to the Pd/H system (due to phase transformation) on the degree of surface roughness was inspected. The powerfulness of this approach is ability for inspecting surface roughness in nanoscale. The surface fractality at nanoscale is significantly different from that at microscale.

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## 1. Introduction

Pd/H systems are of great interest for practical applications due to possibility of hydrogen storage [1]. This is due to the fact that the adsorbed hydrogen atoms penetrate the Pd surface layer and moves into an internal bulk site [2]. However, this phenomenon is very complicated. Since the Pd/H systems are accompanied by the formation of different phases, occurrence of essential phase transformations are of particular

interest [3,4]. Such phase transformations causes the appearance of severe plastic deformations. Surface analysis of plastically deformed Pd electrodes is very useful for two reasons: (i) it can provide information about the plastic deformation occurred with the bulk; (ii) since diffusion of hydrogen occurs from the electrode surface, it is necessary to inspect surface structure from subsequent insertion/extraction process.

Pyun and his coworkers [5] have claimed usefulness of fractal analysis to inspect the strength of plastic deformation induced to the Pd electrode surface. Although, this is indeed a brilliant approach, they employed an inappropriate method for this purpose

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leading to serious experimental errors in the fractal dimensions estimated. It has been discussed that direct fractal analysis of electrode surfaces by means of electrochemical methods is not reliable due to the occurrence of side-processes [6,7]. Thus, electrochemical methods should only be used in company with gold-masking approach for fractal analysis of real electrode surfaces [8–10]. The possible chemical change of the surface is a source of error in the course of electrochemical measurement. For the system investigated in [5], it has been described that chemical activity of Pd surface to form palladium hexacyanoferrate [11] and its chemical inhomogeneities due to partially oxide formation are main reasons leading to unreal fractal dimensions [12]. Whereas, employing gold-masking approach results in the estimation of reasonable fractal dimensions [12].

In the present paper, we would like to emphasize that this issue deserves a more careful attention. In this direction, the importance of scale of fractal analysis and choice of appropriate tool for this purpose are mentioned. On the other hand, as a typical case, powerfulness and limitations of fractal geometry for quantitative surface analysis are also described.

## 2. Experimental

For the sake of similarity of the experimental results, the experiments were performed in accordance with the procedure reported in [5]. Briefly, different amounts of hydrogen were injected into Pd electrodes by applying a constant current of  $13.5 \text{ mA/cm}^2$  for various times under galvanostatic condition in a solution of  $0.1 \text{ M NaOH}$ . Then, the hydrogen injected into the Pd electrode was completely extracted. This process was carried out potentiostatically by jumping the electrode potential from  $0.5$  to  $0.9 \text{ V}$  versus SCE. Similar to [5], four different Pd electrodes were prepared by injection of various amounts of hydrogen during the preliminary charging process, as the galvanostatic current applied for different times:  $0$ ,  $0.9$ ,  $1.8$  and  $2.7 \text{ ks}$  ( $10^3 \text{ s}$ ). Thus, different Pd electrodes approximately with the states of  $\text{PdH}_0$ ,  $\text{PdH}_{0.23}$ ,  $\text{PdH}_{0.46}$  and  $\text{PdH}_{0.6}$  were obtained. Note these are just symbols employed to distinguish them, and indeed all of them were transformed to the state of Pd. The  $\text{PdH}_0$  is a Pd electrode without any plastic deformation, and  $\text{PdH}_{0.6}$

is considered as a Pd electrode with severe plastic deformation.

Small-angle X-ray scattering (SAXS) investigations were carried out using a Philips PW-3710 diffractometer employing a rotating X-ray source under appropriate conditions. Interestingly, SAXS measurements can be simply employed to inspect the nanoscale surface roughness generated as a result of plastic deformation, since their sizes are smaller than  $20 \text{ nm}$ . Whereas, the difficulties for performing SAXS experiments is related to larger scale where the scattering should be done at very small angles (which may be accompanied by severe errors depending on the apparatus sensitivity).

## 3. Results and discussion

Fig. 1 shows typical SEM images of a Pd electrode before and after severe plastic deformation. The

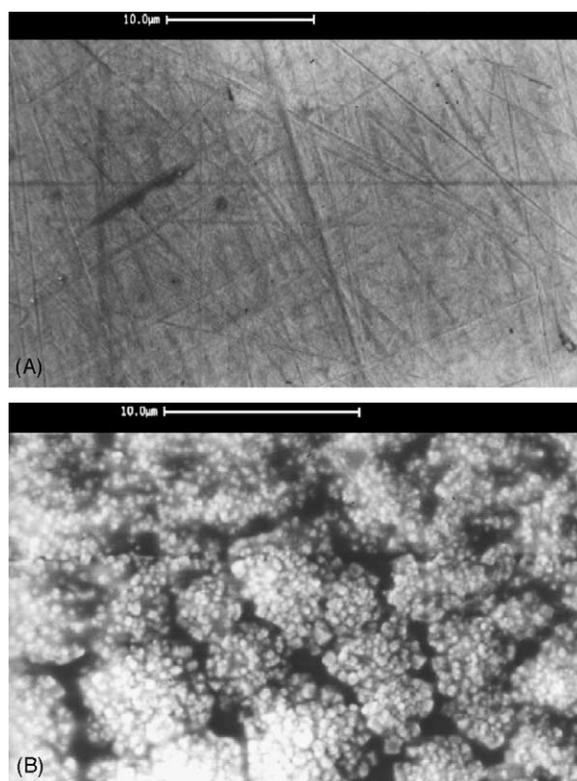


Fig. 1. SEM images of a Pd electrode surface (A) before and (B) after plastic deformation. Typically the plastic deformation corresponds to hydrogen insertion up to the  $\text{PdH}_{0.46}$  form.

appearance of surface roughness in microscale is obvious. Indeed, plastic deformation of Pd electrode is vivid in high scales, as surface roughness generated is even observable by the naked eye. However, due to the small size of hydrogen atoms, the most interesting feature of plastic deformation may be inspected in smaller scales.

Although, electrochemical methods has been successfully used to monitor the strength of plastic deformation by means of fractal geometry, unfortunately, electrochemical methods are not applicable for fractal analysis at nanoscale due to the methodology limitations [10]. Therefore, another technique capable of fractal analyzing at nanoscale is needed to inspect the plastic deformation of Pd electrode.

Small-angle X-ray scattering is an efficient tool in surface science. It is able to reveal surface structure in nanoscale (i.e. 0.5–200 nm) [13]. Another interesting feature of SAXS is its ability for fractal analysis. Determination of the fractal dimensions of various surfaces by this approach has been widely reported in the literature [14–21]. This provides reliable data for quantitative analysis of the Pd electrodes with different degrees of plastic deformation, and satisfies the requirement of our comparative study.

It is well known that scattering intensity mainly includes the diffuse scattering, and the Porod term [22]. The last term can represent the surface roughness. The Porod term is accompanied by a sharp rise of the intensity in the small-angle region, which is indicative of density fluctuations on nanoscale. The Porod term corresponds to the material structure on a scale from about 0.5 through 200 nm. In this region, the Porod power-law suggests:  $I(q) \propto q^{-\beta}$ , where  $\beta$  depends on the material form (e.g. mass or surface) and for fractal surfaces is equal to  $6 - D$  [21]. However, this relation is only valid when the scattering intensity is mainly due to the Porod term. As Ruland [23] pointed out the validity of Porod's law should be taken account for fractal analysis, and indeed an appropriate scale should be used for collecting the data.

Fig. 2(A) presents SAXS patterns of a typical Pd electrode before and after plastic deformation as a result of phase transformation in the course of hydrogen insertion/extraction. It is obvious that up to the  $d$  spacing of ca. 2.5 nm, the SAXS intensity is angle-independent corresponding to diffuse intensity.

This means that up to this scale, the surface structure is featureless. As the lower limit of SAXS technique is about 1 nm (depending on the case under investigation and apparatus capability), it can be assured that the value of 2.5 is the smallest size of surface roughness.

In the range of 2.5–6.5 nm, the SAXS patterns of the Pd electrode before and after the plastic deformation is approximately the same, suggesting that the plastic deformation does not affect the Pd structure in this scale. A significant difference between the SAXS patterns appears in the range of 6.5–18 nm. At higher scales (up to 150 nm), the SAXS patterns are once again similar (the curves of increasing intensities are parallel). In fact, the plastic deformation occurred as a result of phase transformation caused the generation of surface roughness at this scale (6.5–18 nm). This is indeed the original plastic

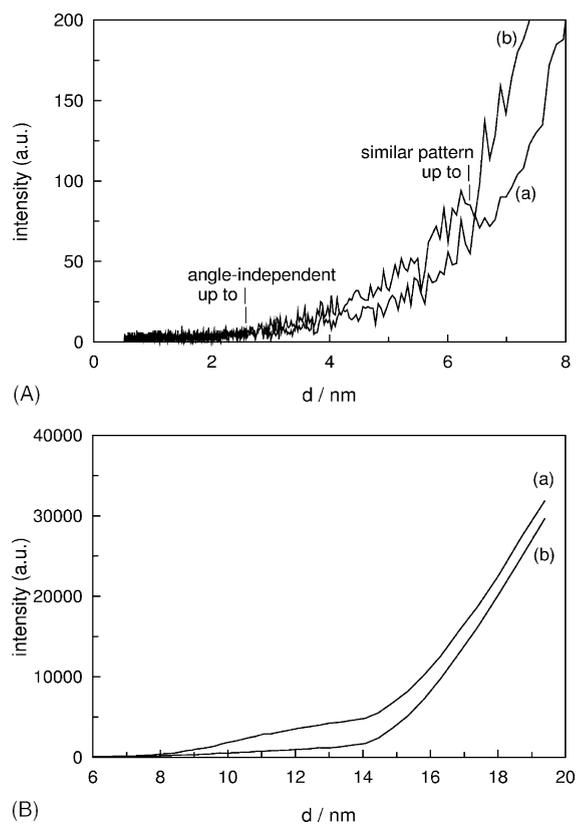


Fig. 2. Scattering patterns of a Pd electrode surface before (A) and after (B) plastic deformation. The SAXS intensities are plotted against  $d$  spacing value. The degree of plastic deformation was similar to that mentioned in Fig. 1.

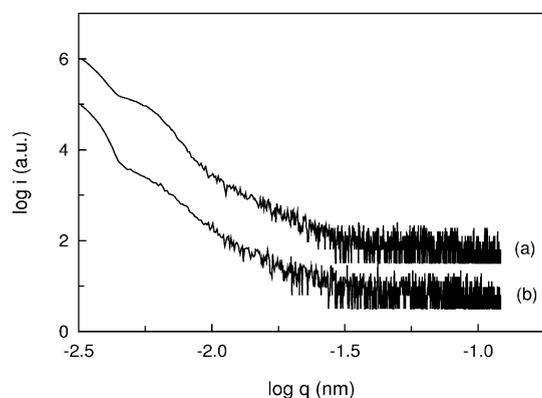


Fig. 3. SAXS intensities of a Pd electrode surface before (a) and after (b) plastic deformation as a function of  $q$  factor plotted in a log-log scale.

deformation appeared in the Pd lattice structure. In other words, the microscale surface roughness can be considered as secondary result of plastic deformation, since the surface roughness in microscale is consequence of the latter nanoscale surface roughness, which led to the formation of larger structures in microscale. Therefore, it is necessary to investigate such nanoscale surface roughness in order to inspect the plastic deformation induced to the system.

In addition to the success of distinguishing the scale range of plastic deformation in nanoscale by means of SAXS, this powerful technique can be used for fractal analysis to achieve quantitative results for comparison purpose. Fractal dimension is an efficient quantitative measure to compare roughness of different surfaces.

By plotting the intensity as a function of the  $q$  factor in logarithmic scale (Fig. 3), it is possible to calculate

the fractal dimensions of different Pd electrode subjected to different degrees of plastic deformation, as the slope is equal to  $6 - D$  [21]. For comparative purpose of this study, the original data were used without correction for the detector sensitivity, and the background scattering as well as transmission. The diffuse intensity originates from atomic-scale density fluctuations: Compton scattering, thermal diffuse scattering, static disorder, etc., which are all essentially angle-independent. Thus, it can be satisfactorily assumed that the scattering intensity recorded at smaller angles is mainly related to the Porod term. The results obtained from fractal analysis are summarized in Table 1. The results are indicative of a systematic increase of the fractal dimension in respect with the degrees of plastic deformation induced to the system, though this increase is not linear, like that reported for microscale fractal structure of Pd electrodes subjected to different degrees of plastic deformation [5,12].

There are stronger uncertainties for rougher surfaces. This comes from weaker correlation coefficient of the fractal power-law due to data dispersion. It has been described that this can be considered as a measure for degree of fractality [24]. Fortunately, this failure is ignorable for the results obtained, indicating an acceptable fractal behavior. Of course, this is stronger for the SAXS results in comparison with the electrochemical measurements, which is attributed to sensitivity of SAXS experiments. However, the results are satisfactory, particularly for comparative study.

Comparison of the data obtained from SAXS corresponding to fractal analysis at nanoscale with those reported in [12] corresponding to fractal analysis at microscale by means of electrochemical methods

Table 1  
Fractal dimensions of various electrode surfaces subjected to different degrees of plastic deformation.

Electrodes	Scale of fractal analysis	
	Microscale 1–100 $\mu\text{m}$ (by electrochemical method)	Nanoscale 1–100 nm (by SAXS)
Au <sup>a</sup>	$2.018 \pm 0.002$	$2.052 \pm 0.011$
Untreated Pd <sup>b</sup>	$2.092 \pm 0.002$	$2.103 \pm 0.018$
PdH <sub>0</sub> <sup>c</sup>	$2.216 \pm 0.004$	$2.112 \pm 0.019$
PdH <sub>0.23</sub> <sup>c</sup>	$2.260 \pm 0.004$	$2.335 \pm 0.025$
PdH <sub>0.46</sub> <sup>c</sup>	$2.346 \pm 0.006$	$2.473 \pm 0.028$
PdH <sub>0.6</sub> <sup>c</sup>	$2.464 \pm 0.006$	$2.498 \pm 0.028$

<sup>a</sup> Au-coated Au electrode. Au covered by gold-masking approach on a smooth Au surface (with a roughness factor lesser than 2).

<sup>b</sup> A polished Pd electrode, which was not subject of potentiostatic electrochemical treatment.

<sup>c</sup> The notations are related to the H-inserted states. All four electrodes were subject of potentiostatic condition to extract hydrogen.

leads to interesting conclusions. Two Pd electrodes were compared in [12] without plastic deformation: (1) the original Pd electrode, and (2) a Pd electrode which was subject of electrochemical treatments (as well as those were subject of plastic deformation) but without hydrogen insertion/extraction and subsequent plastic deformation. The surface roughness of the Pd electrode subjected to electrochemical treatments even without plastic deformation (denoted as PdH<sub>0</sub>) is significantly stronger than the original Pd electrode (denoted as untreated Pd electrode), as can be judged by comparison of their fractal dimensions. This leads to an important conclusion for surface analysis of plastic deformation: the surface structure of plastically deformed Pd electrodes is not exclusively due to the plastic deformation induced, but electrochemical treatments can also affect the surface structure in microscale. Thus, for inspecting plastic deformation by means of surface analysis, it is necessary to consider side-processes affecting the surface structure.

Electrochemical treatments have no significant influence on nanoscale structure of the Pd electrode, as the untreated Pd and PdH<sub>0</sub> electrodes have similar fractal dimensions (Table 1). In fact, nanoscale surface roughness of the Pd electrodes subjected to plastic deformation corresponds to hydrogen insertion/extraction process. When phase transformation occurs hydrogen extraction leads to irreversible solid-state structural changes of the Pd lattice structure. For this reason, the rate of hydrogen extraction has a significant influence on the strength of plastic deformation, and extremely severe plastic deformation may be generated upon fast hydrogen extraction.

According to the results reported in Table 1, the occurrence of even weak plastic deformation is accompanied by a significant increase of the fractal dimension in nanoscale. This is due to the above-mentioned irreversible solid-state structural changes, which are applicable for any phase transformation. On the other hand, there is a limit for this phenomenon, as the fractal dimensions of Pd electrodes subjected to strong plastic deformations (two upper cases) are approximately the same. In other words, the irreversible solid-state structural changes do not increase after reaching a limit, which is due to the Pd lattice structure (it can be considered as maximum disorder).

It is worth noting that morphological investigations of the Pd electrodes by means of electron microscopy

revealed that the surface structures for these two latter cases (PdH<sub>0.46</sub> and PdH<sub>0.6</sub>) are different (similar results corresponding to AFM investigations have also been reported in [5]). However, this difference is not considered in quantitative analysis of fractal geometry. In other words, this is a limitation of fractal geometry in studies of such complicated surfaces. It should also be emphasized that fractal dimension does not provide any useful distinction between such different surfaces, but geometrical modeling of them can be useful for comparative study.

#### 4. Conclusion

Fractal analysis of surface structure formed as a result of plastic deformation in Pd/H system was performed to investigate this important system and also to understand the vague features of fractal analysis for surface studies. It was shown that the scale of fractal analysis should be defined before such studies, and this should be chosen in accordance with the system under investigation. For instance, the plastic deformation originally provides surface roughness in nanoscale, though it is usually studied in microscale. SAXS is an efficient technique for fractal analysis at nanoscale. This strategy of research can provide an opportunity to reveal the mechanism of such complicated processes in surface science. It is also emphasized that fractal dimension is not always applicable for quantitative analysis. Although, two surfaces with the same fractal dimensions are similar from geometrical point of view, however, such judgment is not always satisfactory from phenomenological point of view. It should be taken into account that every surface structure is not just a geometrical model, but it corresponds to a complicated physical phenomenon led to its formation. The latter is of interest for surface scientists; despite they attempt to understand such complicated structure by simplified geometrical models.

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