ELSEVIER

Influence of atomic-scale irregularities in fractal analysis of electrode surfaces

Ali Eftekhari[*], Mahmood Kazemzad, Mansoor Keyanpour-Rad

Department of Energy, Materials & Energy Research Center, P.O. Box 14155-4777, Tehran, Iran

Abstract

To clarify the vague points appeared in the literature, it was discussed that fractal analysis of electrode surfaces based on the concept of 'diffusion toward electrode surfaces' is only able to monitor surface roughness in scales larger than 10 nm. When inspecting fractality in atomic scale (and even up to 10 nm), electrochemical measurements are not reliable due to the presence of surface defects, which affect the electrochemical reaction. In other words, for fractal analysis of electrode surfaces, the diffusion layer width which acts as yardstick length, should be sufficiently large, incomparable to the scale of atomic inhomogeneities. To this aim, the experiment time should be sufficiently long or the diffusion coefficient should be sufficiently large.

© 2004 Elsevier B.V. All rights reserved.

1. Introduction

Investigation of surface roughness is an important issue in surface science. There are various methods to monitor and compare structural roughness of surfaces. Fractal geometry provides a powerful opportunity to investigate surface roughness via geometrical models [1,2]. The main parameters of fractal geometry are fractal dimension, fractality scale, and fractality factor. The latter one, which states how much a real object can be defined by fractal patterns, falls out of the scope of the present work, and has been extensively described elsewhere for electrode surfaces

[3]. However, it is aimed to clarify the physical meaning of the values reported in the literature for fractal dimension and particularly fractality scale of electrode surfaces.

Since fractal modeling of rough surfaces is a new and interesting tool, it has been widely used by various researchers (an extensive list of such papers published in the literature seems too long to be reported here). Unfortunately, in the absence of appropriate strategy, such studies are usually restricted to report of some values for fractal dimension and fractality scale, which sometimes the values reported have not physical meaning. For instance, Gobal et al. [4] have claimed that a typical conductive polymer has fractal structure in angstromic scale. In spite of the fact that this claim suffers from physical reality (since this is even smaller than the size of individual elements (ions) formed the

* Corresponding author. Tel.: +98 261 620 4136;
fax: +98 261 620 1888.
E-mail address: eftekhari@elchem.org (A. Eftekhari).

surface) [5], it is of interest to investigate the possibility of fractal analysis of electrode surfaces at atomic-scale. In general, surface irregularities can be divided into two different types (i.e. at different scales): the surface roughness corresponding to the geometrical irregularities at scales larger than 10 nm and atomic-scale inhomogeneities. The latter one is not necessarily at atomic-scale, and indeed this term was used to categorize irregularities at scales smaller than 10 nm. The atomic-scale inhomogeneities includes surface defects which have atomic scale, but they can be as large as few nanometers. Of course, atomic-scale inhomogeneities not only represent surface non-uniformities but also energetic inhomogeneities along the surface.

Very recently, powerfulness and limitations of electrochemical methods for fractal analysis of electrode surfaces and also non-conducting surfaces have been discussed [6]. The common approaches are based on the concept of 'diffusion toward electrode surfaces'. To this aim, a sufficiently fast redox system is needed to have an ideal diffusion process. The preliminary investigations in this context were performed using the fast redox of ferricyanide/ferrocyanide system at gold surface [7–10]. Since, such fast redox system is not available for all electrodes, the own redox of electroactive films has been widely used in the literature for fractal analysis; however, it has been described that structural changes of the electrode surface in the course of insertion/extraction process might be a source of significant errors [11]. Thus, gold masking approach was introduced, which has been successfully used for various cases including metallic surfaces [12], non-conducting dental surfaces [13], liquid–liquid and liquid–gas interfaces [14], etc.

Cyclic voltammetry is a common electrochemical method, which has been widely used for fractal analysis of electrode surfaces. According to the approach proposed by Stromme et al. [15,16], fractal analysis of electrode surface can be easily performed from cyclic voltammetric measurements as:

$$I_p \propto v^{\alpha} \tag{1}$$

where I_p is the peak current recorded from CV, v the scan rate, and α the fractal parameter which can be transformed to the fractal dimension as $\alpha = (D_f - 1)/2$. Thus, the fractal parameter can be easily estimated by plotting the peak current versus the scan rate in a log–log scale. Although this is a simple and efficient approach for fractal analysis of electrode surface, a careful attention should be paid on validity of this approach at different experimental conditions.

2. Experimental

The process of 'diffusion toward electrode surface' was provided for surface analysis of typical roughened Pt electrode via well-known redox of the ferricyanide/ferrocyanide system. The electrolyte solution was an aqueous solution of 5 mM $K_4Fe(CN)_6$ in 1.0 M NaCl as supporting electrolyte. In cyclic voltammetric experiments, electrochemical oxidation of ferrocyanide in the course of forward scan provides diffusion of electroactive species toward the Pt surface, and electrochemical reduction of ferricyanide during the reverse scan.

The electrochemical experiments were carried out with a convectional three-electrode cell employing an Ag/AgCl reference electrode. The working electrode was a small Pt plate. Cyclic voltammetric measurements were performed using a Metrohm 746VA potentiostat. X-ray diffraction (XRD) and small-angle X-ray scattering (SAXS) measurements were performed using a Philips PW3710 system with rotating mode X-ray generator under appropriate conditions.

A smooth Pt electrode was carefully polished mechanically and electrochemically. The Pt surface was first degreased by washing in acetone. Then, the Pt electrode was subject of thermal treatment to heal any possible defects on its surface. The procedure of cleaning and polishing of the Pt surface is of great importance, since existence of any organic contaminations or surface defects is the source of error in our study. In fact, a clean and smooth Pt should be used for the fabrication of working electrodes to assure that the only surface defects and roughness are those generated in the following process.

The Pt electrode with surface defects was prepared by mechanical roughening of the electrode surface with an emery paper of grit 80 randomly. By this action, the Pt surface is roughened and also some surface defects form. To prepare a defect-free Pt electrode, the same electrode was used. In fact, a single electrode was used to assure that the surface roughness in both cases (in the presence and absence

of surface defects) are exactly the same. For this purpose, the surface defects generated during the mechanical polishing was healed by thermal treatment. The best method for surface defect healing of the Pt electrode is flame-annealing. The roughened Pt electrode was placed on a Bunsen flame for 30 s. The surface roughness of the roughened Pt surface before and after thermal treatment was checked by means of optical microscope and also technique of scanning electron microscopy (SEM). No structural change in the surface roughness of the Pt surface was observed. Since such weak thermal treatment (the temperature is not higher than 500 °C) just heals atomic-scale imperfections, i.e. surface defects formed during mechanical polishing.

3. Results and discussion

3.1. Electrochemical methods for fractal analysis

Three common electrochemical techniques for fractal analysis are cyclic voltammetry, chronoamperometry, and impedance spectroscopy. The two former ones are based on the concept of 'diffusion toward electrode surfaces' and the latter one is based on 'frequency dispersion of capacitance'. Pajkossy as one of the founders of this approach in 1980s [17,18], have discussed that impedance spectroscopy is not a reliable technique for fractal analysis of electrode surfaces, since the calculated frequency dispersion caused by the surface roughness appears at frequencies in the kHz range or higher while the experimental results pertain to much lower frequencies [19], and indeed impedance spectroscopic results are related to atomic inhomogeneities instead of surface structural roughness [20]. However, many papers in the literature have reported agreement of the results obtained from this technique and those using the concept of 'diffusion towards electrode surfaces'. The possible source of error for the observation of such apparent agreement will be discussed below typically for the report of Gobal et al. [4]. Fractal analysis by impedance spectroscopy was always subject of controversy. For instance, Sadkowski has pointed out the problem of time domain response of constant phase electrodes [21–23]. However, less attention has been paid to the limitations of cyclic

voltammetry for fractal analysis from methodology point of view.

Since the thickness of diffusion layer varies by time in electrochemical measurements, the diffusion layer width can be considered as the yardstick length. Thus, the fractal dimension can be simply estimated from power-law behavior of data recorded in electrochemical experiments. To detect fractal structure, the electrochemical data should obey from the power-law when the diffusion layer width is in the range of fractality scale, which is defined by two boundaries namely inner and outer cutoffs. Since the aim of the present work is to investigate fractality at low scales, the discussion is mainly on the inner cutoff, i.e. the nearest points sensed. To sense fractality at atomic scale, it is necessary to have a yardstick with such length. It is obvious that this case cannot be achieved because of the importance of Helmholtz double layer. However, since this issue has been extensively discussed elsewhere [5], we neglect the importance of Helmholtz double layer in the present study. We come to conclusion that we should deal with the diffusion layer width to inspect the fractality scale.

In chronoamperometric measurements, the diffusion layer width or indeed the yardstick length is expressed as: $\delta = \sqrt{Dt}$ [24], where D is the diffusion coefficient. This means that the diffusion layer width increases by the experiment time, and since the diffusion coefficient is constant during the experiment; thus for a specified experiment time, the smaller the diffusion coefficient the wider the diffusion layer. Since cyclic voltammetry has been widely used in the literature for fractal analysis of electrode surfaces, it is necessary to obtain similar relation for scan rate dependency of the diffusion layer width. It is well-known that the diffusion layer width in cyclic voltammetric measurements is expressed by:

$$\delta = \frac{nFADC}{I_p} \qquad (2)$$

where n is the number of electrons involved, F Faraday constant, A the surface area, D the diffusion coefficient, C the concentration term, and I_p the peak current. The value of I_p can be incorporated from the famous Randles–Sevcik equation [24]:

$$I_p = -0.4463nFA\left(\frac{nF}{RT}\right)^{1/2}CD^{1/2}v^{1/2} \qquad (3)$$

From Eqs. (2) and (3), one obtains the scan rate dependency of the diffusion layer width as:

$$\delta = 2.24 \left(\frac{RT}{nF} \right)^{1/2} D^{1/2} v^{-1/2} \tag{4}$$

In addition to the numerical importance of this equation, it is of interest to see that $\delta = \sigma \sqrt{D/v}$, where σ is a proportionality factor depending on the experiment temperature and the number of electrons involved (e.g. has a value of 0.359 for one-electron system at room temperature). This relation is similar to that mentioned above for chronoamperometry. As expected, t in $\delta = \sqrt{Dt}$ was replaced by v in $\delta = \sigma \sqrt{D/v}$, since the experiment time is reciprocal to the scan rate. However, this suggests that to detect fractality at small scales, it is needed to perform cyclic voltammetry with high scan rates or using redox systems with small diffusion coefficients.

3.2. The role of surface defects

The appearance of surface defects is a common problem for electrodes. The significant effects of surface defects on electrochemical processes occurring at electrode surfaces have been widely studied in the literature [25–28]. To investigate the role of surface defects on fractal analysis of electrode surfaces, it is needed to prepare a typical electrode with both types of geometrical irregularities (i.e. surface defects and roughness). Such electrode can be simply prepared by mechanical roughening of a Pt electrode. The Pt electrode was roughened by emery paper to generate surface roughness on microscopic scale while some surface defects are formed on atomic scale.

The fractal analysis of the Pt electrode surface was performed using the most reliable case viz. fast redox of the ferricyanide/ferrocyanide system [7]. To sense fractality at small scales, the experiments were performed at relatively high scan rates where the diffusion layer thickness is very thin. It is obvious that the cyclic voltammograms (Fig. 1a) have not a well-defined shape of the ferricyanide/ferrocyanide system, particularly at fast scan rates where the diffusion layer thickness is comparable with scale of the surface defects. By plotting the peak current versus the scan rate in a logarithmic scale (Fig. 1b) to use Eq. (1), the fractal dimension of the Pt electrode surface can be obtained. For the system under investigation both
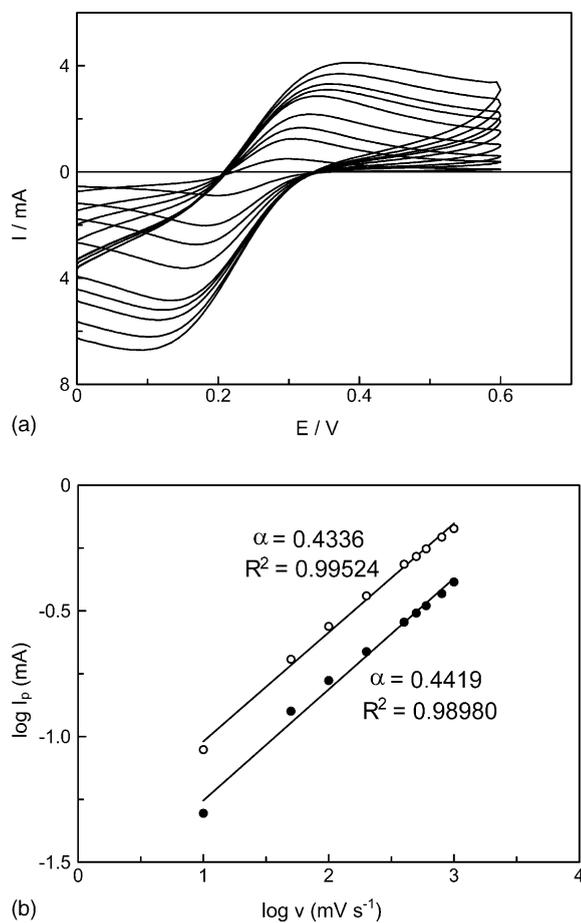
Fig. 1. (a) A set of cyclic voltammograms of the defect-included Pt electrode (prepared by mechanical roughening) in an aqueous solution of 5 mM $K_4Fe(CN)_6$ in 1.0 M NaCl. Scan rates: 10, 50, 100, 200, 400, 500, 600, 800, and 1000 mV/s. (b) The peak currents plotted vs. scan rate: (●) anodic peaks; (○) cathodic peaks.

anodic and cathodic peak currents can be used for the calculation of the fractal dimension, since both of them represent diffusion of electroactive species (ferricyanide or ferrocyanide ions) toward the electrode surface. The results obtained from scan dependency of anodic and cathodic peak currents suggest values of 1.88 and 1.87 for the fractal dimension of the roughened Pt electrode, respectively. Surprisingly, both of these sets of data suggest a fractal dimension lower than 2. From fractal geometry point of view, such data do not represent the fractal dimension of the Pt electrode surface, since a rough surface should have a fractal dimension larger than the dimension of ideal

smooth surface, i.e. 2. This failure is due to the fact that some parts of the roughened Pt surface are electrochemically inactive and do not participate in the electrochemical reaction. This case is known as partly active surfaces, and its diffusion model has been described in the literature (cf. Fig. 1 in [10]). As will be shown below high peak separation of the CVs also provides a strong evidence for this fact.

By omitting the point related to the scan rate 10 mV/s in Fig. 1(b), better fitting curves can be obtained with smaller fractal dimensions ($\alpha = 0.3899$ and $R^2 = 0.99974$ for the anodic peak; $\alpha = 0.4001$ and $R^2 = 0.99893$ for the cathodic peak). Better correlation coefficient is a measure of higher fractality factor [3]. The smaller fractal dimensions at smaller scales indicate that the blocking fractal structure is more significant at smaller scales. When the scan rate is sufficiently low, the diffusion layer width is significantly high to not sense the blocking fractality provided by the surface defects.

To prove that this failure is exclusively related to the existence of surface defects, it is needed to inspect the fractal structure of an electrode surface with microscopic roughness but without surface defects (i.e. representative of atomic-scale inhomogeneities). Instead of fabricating another rough surface, we used the same Pt electrode by healing the surface defects. Simple thermal treatment of the electrode can heal the surface defects. Keeping the Pt electrode at Bunsen flame for 30 s will heal the surface defects (generated during mechanical roughening) without any change on the structural roughness in microscopic scale. By this action, we have opportunity to compare two electrodes with exactly the same surface roughness but with and without surface defects.

A set of cyclic voltammograms of the defect-free Pt electrode is illustrated in Fig. 2(a). As expected, the CVs have a well-defined shape of the ferricyanide/ferrocyanide redox system. This obviously shows that deviation from well-defined CV of the system (as illustrated in Fig. 1a) is exclusively related to the existence of surface defects. The fractal analysis based on the data recorded suggests a fractal dimension of 2.15, which is the dimension expected for such rough Pt surface. This fractal dimension can be verified by fractal analysis of Pt surface image obtained from SEM or other imaging techniques. However, the aim of the present study is not to estimate the exact fractal
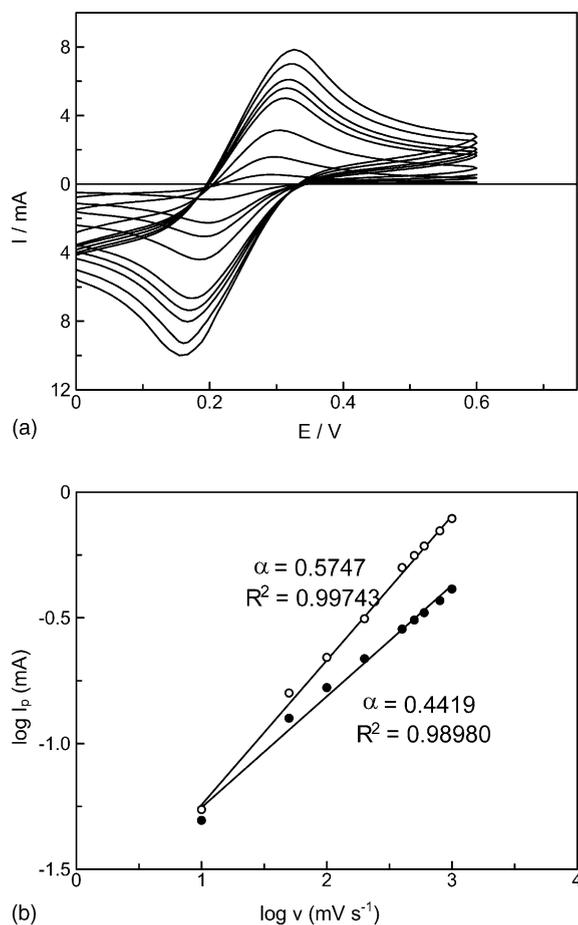

Fig. 2. (a) A set of cyclic voltammograms of the defect-free Pt electrode (prepared by thermal healing of the surface defects for the electrode used in Fig. 1) in an aqueous solution of 5 mM $K_4Fe(CN)_6$ in 1.0 M NaCl. Scan rates: 10, 50, 100, 200, 400, 500, 600, 800, and 1000 mV/s. (b) The anodic peak currents plotted vs. scan rate for the defect-included (●) and defect-free (○) Pt electrodes.

dimension of such randomly roughened Pt surface, and we come to an important conclusion based on a solid argument. Comparison of the results reported in Figs. 1 and 2 obviously indicates the significant role of the surface defects appeared on the electrode surface. Since the surface roughness for both cases was exactly the same, it can be concluded that the existence of surface defects is a severe problem for fractal analysis by means of electrochemical methods.

Contrary to the defect-included Pt electrode, both fractal dimension and correlation coefficient are

approximately independent of the scan rate range for the defect-free Pt electrode. Upon omitting the first and second points at the slowest scans (10 and 50 mV/s), no significant change of α and R^2 is observed. Since the fractality detected for the defect-free Pt electrode is due to its roughness, not surface defects, the electrode displays a uniform fractal structure in a broad range of scale. In other words, there is no difference between the fractal analysis of the defect-free Pt electrode in the 1–10 mV/s range or the 50–1000 mV/s, but there is a significant difference for the defect-included Pt electrode in these two ranges due to the scale of the surface defects.

The effect of surface defects on electrochemical processes is not well-understood, since the mechanisms of electrochemical reactions at surface are very complicated depending on various controllable parameters. Surface defects may act as inactive islands on the electrode surface to produce a partly active surface (like the case reported in Fig. 2), or contrarily can strengthen the electrochemical reaction via enhancing some required processes such as electron transfer at the electrode/electrolyte interface (for instance, see [20,28]).

Fig. 3 shows the peak-to-peak separation of anodic and cathodic peak potentials of the CVs. It is obvious that peak separation for the defect-included Pt electrode is significantly higher than that of the defect-free Pt electrode. According to the formalism made in [29] for the voltammetric behavior of rough electrodes,
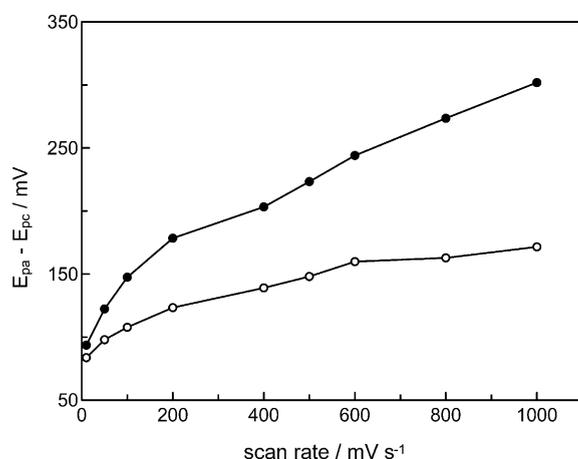

Fig. 3. Peak-to-peak separation of the CVs recorded for the defect-included (●) and defect-free (○) Pt electrodes.

such high peak separation is related to the case of partly blocked electrodes. Since the system under investigation is reversible (there is no preference for the oxidation or reduction process at the electrode surface), the peak separation changes is not representative of dynamical behavior of the system, and just originates from the geometrical factor of the surface.

3.3. Scale of surface defects

The results reported above suggest that there is a possible source of error in fractal analysis of electrode surfaces by means of electrochemical methods. It was demonstrated that the existence of surface defects was the reason for the appearance of such severe errors, and the methodology is efficient in the absence of surface defects. Although, formation of surface defects during mechanical roughening and defect healing during thermal treatment are well-known, it is of interest to inspect the existence of such surface defects with an efficient technique.

Among different physical techniques, small-angle X-ray scattering (SAXS) is known as the most reliable technique for the investigation of surface irregularities at small scales [30]. SAXS has also been successfully used for fractal analysis of different surfaces [31–34].

It is well-known that scattering intensity mainly includes [35]: the diffuse scattering, and the Porod term. The diffuse intensity originates from atomic-scale density fluctuations: Compton scattering, thermal diffuse scattering, static disorder, etc., which are all essentially angle-independent, and is mainly related to wide-angle X-ray scattering (WAXS). The last term represents 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 β depends on the material form (e.g. mass or surface), and for fractal surfaces is equal to $6 - D$ [34]. However, this relation is only valid when the scattering intensity is mainly due to the Porod term. As Ruland [36] 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.

To inspect the Porod term for both cases, the SAXS intensity was plotted as a function of the modulus of the scattering vector (not shown). In spite of similarity of two scattering patterns of the Pt electrode before and after thermal treatment through both SAXS and WAXS, a significant difference was just observed in a narrow range of q (0.7–1.3 nm^{-1}), corresponding to the scale range of 6–9 nm. This suggests that the surface defects formed on the Pt electrode surface are in this scale. Of course, surface defects generated during film growth are usually smaller, however, the present surface defects were formed during mechanical roughening in micro-scale.

The scattering intensity recorded at smaller angles corresponds to large scales and is independent of the existence of surface defects (i.e. in the scale <10 nm). By calculating the fractal dimensions of the Pt electrode before and after thermal treatment from the data collected in the q range of 0.7–1.3 nm^{-1}, the values of the fractal dimension are different, since the surface defects affect the fractal structure in this specified fractality scale, however, beyond this range, the fractal structure of the Pt surface is the same contributing the surface roughness. However, a wider range of data should be collected for fractal analysis by SAXS, as this approach has been employed by researchers in the literature to assure about the accuracy of the fractal dimension estimated. When comparing the log $I(q)$ − log q plots of the Pt electrode before and after thermal treatment in a wide q range, the tiny difference in the 0.7–1.3 nm^{-1} (i.e. corresponding to the surface defects) is not distinguishable. In other words, fractal analysis of surfaces by SAXS, as reported in the literature, also neglect the role of surface defects. However, inappropriate choice of the experiment range may result in errors due to the existence of atomic-scale imperfections.

It should be noted that surface defects are usually smaller than those in the present case (large surface defects were formed as result of micro-scale mechanical roughening), and indeed such atomic-scale inhomogeneities falls out of the range of SAXS. In other words, SAXS usually does not sense atomic-scale inhomogeneities of surface, and this is an advantage of this method for fractal analysis, since fractal structure of surface roughness (>10 nm) should be detected. However, we disregard fractal analysis by means of SAXS here, since the aim of the present

work is to inspect capability of electrochemical methods for this purpose.

3.4. Reliability of electrochemical methods

As demonstrated above, the electrochemical methods are reliable for fractal analysis of electrode surfaces in the absence of surface defects. However, this conclusion is not of interest from applied point of view, since most of real surfaces have some defects. Moreover, a great part of fractal analysis of surfaces is related to deposited films. Whereas, film growth is usually accompanied by the formation of defects. On the other hand, it is not possible to heal surface defects by thermal treatment for all cases. Thus, it is very important to find how electrochemical methods can be used for fractal analysis of real electrodes with possible surface defects.

As stated above, the deviation from the well-defined CV of the ferricyanide/ferrocyanide redox system in the presence of surface defects appears at high scan rates (Fig. 1a). In this case, the diffusion layer thickness is very thin, and comparable with the scale of surface defects. On contrary, at low scan rates, where the diffusion layer is sufficiently wide and its thickness is incomparable with the scale of surface defects, the electrochemical reaction is independent of the presence or absence of the surface defects. Fig. 4 displays CVs of the ferricyanide/ferrocyanide redox system at
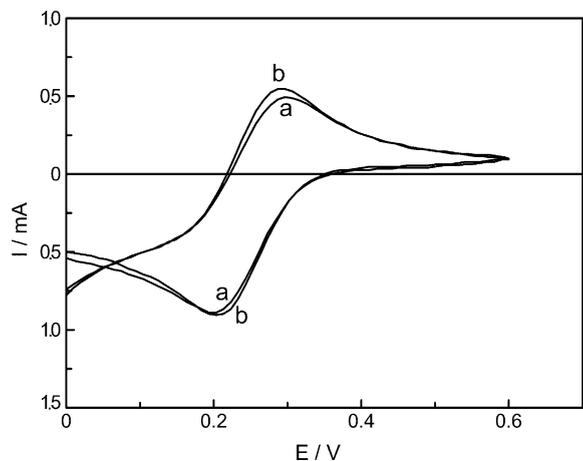

Fig. 4. Typical cyclic voltammogram of (a) the defect-included and (b) the defect-free Pt electrodes in an aqueous solution of 5 mM K$_4$Fe(CN)$_6$ in 1.0 M NaCl. Scan rates: 10 mV/s.

defect-included and defect-free Pt electrodes recorded with slow scan. It is obvious that CVs are similar with well-defined shape of the ferricyanide/ferrocyanide redox system, since the surface defects are not sensed under this experimental condition. In other words, the CV of defect-included Pt electrode does not show the existence of surface defects when recorded with small scan rates. This is in agreement with the results reported in Fig. 3, as the difference of peak separation is more significant at higher scan rates, where the surface defects (i.e. blocking parts or electro-inactive islands for the system under investigation) are effectively sensed by the electrochemical process.

Fractal analysis of the defect-included Pt electrode by means of cyclic voltammetry with a set of data recorded in the scan rate range of 1–50 mV/s suggested a fractal dimension of 2.13, which satisfactorily close to the fractal dimension of 2.15 obtained after defect healing. This means that electrochemical methods can be used for fractal analysis of real surfaces with defects, but when the experimental conditions exclude the scale of possible defects.

One may conclude that by excluding the high scan rates, the range of 50–500 mV/s, which is common in the literature (cf. [4]) is satisfactory to eliminate the role of surface defects in fractal analysis of electrode surfaces based on electrochemical methods. However, this is just a misunderstanding based on comparison of the experiment time. It is correct that at low scan rates (e.g. lower than 500 mV/s) the diffusion layer thickness is incomparable with the scale of the surface defects, but this numerical conclusion is applicable for the system under investigation. In other words, according to Eq. (3), the role of the diffusion coefficient should also be taken into account to estimate the diffusion layer width. In the system under investigation with a fast redox having a diffusion coefficient of the order of 10^{-5} cm^2/s, the experiments can be performed at such relatively high scan rates while the diffusion layer thickness is still incomparable with the scale of the surface defects. However, for the case reported in [4] with a diffusion coefficient of the order of 10^{-13} cm^2/s, cyclic voltammetric measurements should be performed at significantly slower scans (i.e. longer experiment times) to increase the yardstick length (i.e. diffusion layer width) beyond the scale of the surface defects. According to Eq. (4), at the

same experimental condition, the diffusion layer widths for different redox systems with various diffusion coefficients (e.g. 10^{-5} to 10^{-13} cm^2/s) have significant differences (few orders of magnitude).

It is a false conclusion that when the diffusion layer width is very thin, the yardstick can sense the atomic-scale irregularities of the surface. It should be emphasized that at very thin diffusion layer, the basic assumptions of electrochemistry are no longer fulfilled and the electrochemical signal recorded is not exclusively related to the faradaic current representing the process of 'diffusion toward the electrode surface'. As presented above, possible side-processes are source of error in the electrochemical signal recorded. Thus, there is no physical reality for fractal analysis in this condition (e.g. the results reported in Fig. 1b).

Kerner and Pajkossy discussed that fractal analysis of electrode surfaces by means of impedance spectroscopy is highly dependent on the atomic-scale structure of the surface [20]. Thus, impedance spectroscopy is not a reliable technique for the determination of fractal dimensions of electrode surface, since the value estimated depends on the defect density on the surface. According to Gobal et al. [4] (and other reports in the literature), there is no problem for impedance spectroscopy, since the fractal dimension determined by this technique is in agreement with that obtained from a "vastly different method" namely cyclic voltammetry. However, this apparent agreement does not prove efficiency of impedance spectroscopy. If the surface defects exist, according to Kerner and Pajkossy [20], the impedance spectroscopic results are accompanied by errors. Based on the results reported above, the presence of such surface defects also makes error in cyclic voltammetric measurements.

As the final words, if, for instance, atomic-scale inhomogeneities such as surface defects are source of error, they should be excluded in the experimental range of different methods, since inspecting irregularities is not the aim of surface analysis. Although, electrochemical methods such as cyclic voltammetry and non-electrochemical methods such as SAXS can sense such surface defects, it should be taken into account that fractal analysis of surface defects at small scales by SAXS has physical meaning, but surface defects have a significant effect on electrochemical processes to deviate from ideal faradaic process representing ideal diffusion. In fact, this is a major

disadvantage, or in better sentence, limitation of electrochemical methods for fractal analysis of electrode surfaces: electrochemical methods under no circumstance can be used for fractal analysis of electrode surface at scales smaller than 10 nm, at least due to the presence of surface defects.

4. Conclusion

Based on obvious experimental results and solid arguments, it was demonstrated that the existence of atomic-scale irregularities such as surface defects might be source of error in fractal analysis by means of electrochemical techniques, since such surface defects result in side-processes. To overcome this problem, the diffusion layer width, which acts as yardstick length, should be sufficiently larger than the atomic-scale irregularities of the surface. This situation can be achieved by performing electrochemical measurements at longer experiment times (e.g. slower scans in cyclic voltammetry). On the other hand, the role of the diffusion coefficient should be taken into account, because diffusion coefficients of electrochemical redox systems are significantly different. When the diffusion coefficient is small, the experiment times should be longer to assure that the diffusion layer thickness is significantly larger than the atomic-scale irregularities.

As a general conclusion, electrochemical methods cannot be used to inspect surface fractality at atomic scale. On the other hand, surface roughness is of interest for surface scientists rather than atomic inhomogeneities. From methodology point of view, since fractal analysis can be performed in a certain scale, the scale of investigation should be defined. For this purpose, the experiment time in accordance with the diffusion coefficient should be chosen. Upon inappropriate choice when the diffusion layer width is comparable with the atomic-scale irregularities of the surface, the results are not reliable and suffer from the lack of physical reality.

Acknowledgements

References

[1] B.B. Mandelbrot, Fractal Geometry of Nature, Freeman, San Francisco, 1983.
[2] F. Family, T. Vicsek, Dynamics of Fractal Surfaces, World Scientific, 1991.
[3] A. Eftekhari, J. Electrochem. Soc. doi: 10.1149/1.1773583.
[4] F. Gobal, K. Malek, M.G. Mahjani, M. Jafarian, V. Safarnavadeh, Synth. Met. 108 (2000) 15.
[5] A. Eftekhari, M. Kazemzad, M. Keyanpour-Rad, Electrochim. Acta, submitted for publication.
[6] A. Eftekhari, Phil. Mag. Lett., in press.
[7] T. Pajkossy, L. Nyikos, Electrochim. Acta 34 (1989) 171.
[8] T. Pajkossy, L. Nyikos, Electrochim. Acta 34 (1989) 181.
[9] A. Imre, T. Pajkossy, L. Nyikos, Acta Metall. Mater. 40 (1992) 1819.
[10] T. Pajkossy, J. Electroanal. Chem. 300 (1991) 1.
[11] A. Eftekhari, Electrochim. Acta 48 (2003) 2831.
[12] A. Eftekhari, Appl. Surf. Sci. 220 (2003) 346.
[13] A. Eftekhari, Colloids Surf. B: Biointerfaces 32 (2003) 375.
[14] A. Eftekhari, Appl. Surf. Sci. 227 (2004) 331.
[15] M. Stromme, G.A. Niklasson, C.G. Granqvist, Solid State Commun. 96 (1995) 151.
[16] M. Stromme, G.A. Niklasson, C.G. Granqvist, Phys. Rev. B 52 (1995) 14192.
[17] L. Nyikos, T. Pajkossy, Electrochim. Acta 30 (1985) 1533.
[18] L. Nyikos, T. Pajkossy, Electrochim. Acta 31 (1986) 1347.
[19] T. Pajkossy, J. Electroanal. Chem. 364 (1994) 111.
[20] Z. Kerner, T. Pajkossy, Electrochim. Acta 46 (2000) 207.
[21] A. Sadkowski, Electrochim. Acta 38 (1993) 2051.
[22] A.J. Motheo, J.R. Santos Jr., A. Sadkowski, A. Hamelin, J. Electroanal. Chem. 397 (1995) 331.
[23] A. Sadkowski, A.J. Motheo, R.S. Neves, J. Electroanal. Chem. 455 (1998) 107.
[24] A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, Wiley, New York, 1980.
[25] J.O'M. Bockris, S.U.M. Khan, Surface Electrochemistry, Plenum Press, New York, 1993.
[26] K.Z. Brainina, M.Y. Khodos, G.M. Belisheva, M.B. Vidrevich, Z. Phys. Chem. (Neue Folge) 168 (1990) 65.
[27] M.Y. Hodos, E.V. Bazarova, A.P. Palkin, K.Z. Brainina, J. Electroanal. Chem. 164 (1984) 121.
[28] F. Scholz, U. Schroder, S. Meyer, K.Z. Brainina, N.F. Zakhachuk, N.V. Sobolev, O.A. Kozmenko, J. Electroanal. Chem. 385 (1995) 139.
[29] X. Zuo, C. Xu, H. Xin, Electrochim. Acta 42 (1997) 2555.
[30] C.E. Williams, R.P. May, A. Guinier, in: E. Lifshin (Ed.), X-ray Characterization of Materials, Wiley/VCH, Weinheim, 1999, Chapter 4.
[31] M. Campos, B. Bello Jr., Synth. Met. 60 (1993) 1.
[32] S. Neves, C.P. Fonseca, Electrochem. Commun. 3 (2001) 36.
[33] C.-Q. Jin, S.-M. Park, Synth. Met. 124 (2001) 443.
[34] K. Tanaka, A. Ito, T. Yoshii, S. Suehiro, S. Nagura, N. Ando, Y. Hato, Carbon 39 (2001) 1599.
[35] D.L. Williamson, Mater. Res. Soc. Symp. Proc. 377 (1995) 251.
[36] W. Ruland, Carbon 39 (2001) 323.