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

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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.

Keywords: Surface disorder; Atomic imperfection; Fractality scale; Diffusion layer; Length scale; Surface defects; Cyclic voltammetry; SAXS

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

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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