



Fractal Dimension of Electrochemical Reactions

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The reaction dimension of electrochemical processes was introduced as a quantitative factor for reactivity of catalysts. It is representative of the effective (reactive) surface area of the electrode for a catalytic reaction. Such a dimension can be estimated from the reaction efficiency at different particles sizes of the catalyst. The approach was proposed theoretically and was examined based on experimental results. For this purpose, three known electrochemical processes viz. electrochemical oxidation of methanol and of CO and electroreduction of O₂ at Pt particles were chosen as typical examples. The results obtained from experimental measurements showed the validity of the theory proposed. It was demonstrated that the approach proposed is not restricted to fractal surfaces and all catalysts with noninteger dimensions (due to the universal aspect of fractal geometry) can be considered. © 2004 The Electrochemical Society. [DOI: 10.1149/1.1773583] All rights reserved.

Manuscript received April 14, 2003. Available electronically August 9, 2004.

Since the revolutionary discovery of fractal geometry by Mandelbrot,¹ numerous efforts have been made by researchers in various branches of science and technology to find various examples of fractals.²⁻⁵ Although, statements of fractals being everywhere² and the fractal law of nature^{1,4} are not yet universally accepted, fractality of different objects has been described. Generally, two types of fractality have been developed (i) fractal structure of different objects and (ii) fractal aspects of different processes. The first type of fractals is well known, as fractal geometry has been introduced based on this type. This type of fractal has been described based on artificial models and even real complex objects such as those found in nature. However, the second type of fractal is not well understood, due to the strange physical meaning of the dimension of a process. Nevertheless, it has been described for different complex processes such as music.⁶

In pioneering studies of fractals in chemistry,⁷ both types of fractality have been described in the chemical literature. Several examples have been reported to show that the surfaces of most materials have fractal structure at the molecular scale^{8,9}. Chemical techniques have been successfully utilized to evaluate fractal structure (by determining their fractal dimensions), and demonstrate that fractal structure is a physical property of surfaces. Less attention has been paid to investigations of the second type of fractals in chemistry. However, it has great interest from a fundamental point of view, as it provides an opportunity for the investigation of chemical processes using fractal geometry. This feature has been elaborated by Farin and Avnir^{10,11}. In the present manuscript, we would like to extend their finding to electrochemical systems. To this end, the approach is described for electrochemical systems involving reaction at electrodes with solid particles to create a comparative study with the previous reports. It is a novel approach for electrochemical systems, as application of fractals in electrochemistry has been restricted to determination of the fractal dimension of electrode surfaces. Considerable attention has been paid to this subject during the past two decades.¹²⁻¹⁸ Electrochemical methods have even been successfully employed for the determination of fractal dimension of electrode surfaces in molten salt media¹⁹ and nonaqueous media of lithium secondary batteries.²⁰

Theory

It has been proposed that the real surface area of a particle-based fractal surface is dependent on the particle radius by the following relationship¹⁰

$$A \propto R^{D_f-3} \quad [1]$$

where D_f is the fractal dimension. It is well known that effective surface of a solid catalyst is not as certain as its real surface area.

Thus, if we consider the value of the surface area, which is effective in a catalysis process, the following relationship can be obtained

$$S \propto R^{D_R-3} \quad [2]$$

where D_R refers to the dimension of the reaction which takes place at the effective part of the catalyst surface. On the other hand, it has been well known for two centuries, based on a classical laws of physical chemistry proposed by Wenzel,²¹ that the initial rate of a reaction is directly proportional to the reactive surface area of the catalyst ($\nu \propto S$).²² As stated above, the reactive surface area of a catalyst is different from its real surface area. The reactive surface area depends on the surface morphology, which is related to different factors including particle size. Farin and Avnir have used the $\log \nu$ - $\log R$ plot to determine the value of D_R of different reactions from the data.¹⁰ To simplify the measurements, the efficiency of the chemical reaction in a certain period of time can be used as a measure of the reaction rate for different particle sizes. Therefore, it is possible to choose an appropriate experimental time and measure the amount of the products (or any other species of which the concentration change is directly proportional to the reaction rate), E . If all of the experimental conditions are the same for measurements using the catalysts with different particle sizes, D_R can be estimated from the slope of the $\log E$ - $\log R$ curve.

Let us turn our attention to electrochemical processes. In an electrochemical reaction, the total amount of the reaction can be expressed with the Faraday's law, and the reaction rate is related to the current.²³ As we wish to create a comparative study, the parameter of time simply can be eliminated by choosing a certain experiment time for all measurements. For example, the parameter of time can be eliminated by choosing a constant scan rate in cyclic voltammetric (CV) measurements. Therefore, we can conclude that

$$\begin{aligned} I(\text{at constant scan rate}) &\propto P(\text{at constant experiment time}) \\ &\propto \nu \\ &\propto S \end{aligned} \quad [3]$$

This suggests that the value of D_R can be estimated for an electrochemical reaction by plotting the dependence of the peak current recorded from voltammetric measurements using a catalyst with different particle sizes. It is of importance to note that mass-specific current should be used for this purpose. This comes from the fact that ν is defined as moles·time⁻¹·gram⁻¹. We used the current in electrochemical systems instead of moles, in accordance with fundamentals of electrochemistry. The parameter of time was eliminated by assigning a unity value for that. Similarly, we should calculate the current for every gram (generally mass unit) of the catalyst for the comparative study. It is important to note the increase of the particle size of particle-based electrodes is accompanied by an increase of the amount of the catalyst attached. Also, the specific current density of the electrochemical reaction per real surface area of the catalysts is used in the electrochemical literature, not

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mass-specific current per gram of the deposited catalyst. It should also be emphasized that the activity of the electrochemical process is dependent on the reactive (effective) surface area of the catalyst, not its real surface area. The only debate on the approach proposed is whether the current recorded from electrochemical measurement can be considered as a factor of reaction progress? It should be emphasized that the current measured in an electrochemical system can have capacitive and faradaic contributions. The faradaic current can also be under diffusion-controlled or mass transfer-controlled conditions.²³ The above assumption for estimating the progress of an electrochemical reaction by the current measured is only valid for the case of diffusion-controlled conditions. Let us review this problem in chronoamperometric measurements. In $I-t$ transition, the current measured at short times is related to capacitive current due to double layer charging and at long times is due to mass transfer processes where planar diffusion is perturbed. Thus, only moderate times can be considered to show well-defined diffusion behavior. This is the base for estimating the methodology limitation for the determination of the fractal dimension of electrode surfaces based on the concept of diffusion towards electrode surfaces.¹²⁻¹⁵ Indeed, it is a common limitation widely used in the literature devoted to fractal studies of electrode surfaces, as only a certain region of chronoamperograms at moderate times are selected.¹²⁻²⁰ This is also true for the CV measurements, as only a certain range of scan rate can be used for the determination of fractal dimensions. According to such statements, moderate scan rates in CV measurements can be employed to gain kinetically controlled reactions, and consequently, it is proper to use the above-mentioned hypothesis for the determination of fractal dimension of electrochemical reactions.

It is proposed that the well-known concept of diffusion toward electrode surfaces, which has been widely used in the literature for the determination of fractal dimension of electrode surfaces, can also be used for the calculation of the fractal dimension of electrochemical reactions. The difference of these two approaches is that in the former, the diffusion process is studied for a given surface structure but under different conditions such as different times (in chronoamperometric measurements) or scan rates (in CV measurements), whereas in the latter the diffusion process is investigated at a constant condition such as a fixed scan rate in CV measurements but with different surface structures (by varying the particle size). From the fundamental concepts of fractal geometry¹⁻³ and extensive studies of fractal in chemistry,⁷⁻¹¹ we know that in a heterogeneous chemical process, both the catalyst surface and the catalytic reaction have fractal dimensions. In the approach proposed here, the fractal dimension of a given electrochemical reaction can be determined by varying the fractal dimension of the electrode surface in a known manner (changing the particle sizes). Indeed, the approach proposed here is similar to that widely employed in the literature for fractal studies of electrode surfaces and both of them use the same concepts.

Experimental

Experimental setup.—To support the proposed theory with experimental results, electrochemical oxidation of methanol and CO, and electrochemical reduction of O₂ were chosen as typical examples. The effects of catalyst particle sizes on both electrochemical oxidation of methanol and CO and electrochemical reduction of O₂ have been extensively studied in the literature.²⁴⁻²⁶ In the present research, we have used similar experiments to obtain the required data. The results obtained for different particle sizes are presented for comparison to find the relationship of the current to particle size. These electrochemical processes and their dependence on the particle size of the catalyst have been extensively studied.²⁷⁻²⁹

All electrochemical experiments were performed using a low-noise homemade potentiostat connected to a computer running CorView software. All potentials were referenced to a saturated calomel electrode (SCE). Experiments concerning the oxidation of methanol were carried out in a thermostatic bath (25 ± 0.5°C) with an electrolyte solution of 0.01 M H₂SO₄ containing 0.1 M methanol.

The monolayer-adsorbed carbon monoxide was prepared by bubbling carbon monoxide into the electrolyte solution where the electrode potential is fixed on 0.2 V (vs. SCE). Similar action was performed for the experiments related to the O₂ oxidation. The residual carbon monoxide in the electrolyte solution was removed by passing N₂ gas from the solution.

Electrode preparation.—Two different types of electrode were fabricated for the present study, real electrodes based on Pt particles with different sizes and an artificial electrode with a known fractal pattern. The Pt particle-based electrodes were fabricated by vacuum-evaporation of platinum onto glassy carbon (GC) substrate electrodes. The amount of platinum deposited *Ma* onto the substrate surfaces was estimated with a quartz thickness monitor. The numerical mean diameter *d* of the Pt particles was determined using a high-resolution scanning electron microscope. This method is common for the fabrication of Pt particle-based electrodes with different particle sizes and detailed characterizations of Pt particle-based electrodes with such particle sizes have been well described in the literature.²⁷⁻²⁹

The artificial electrode was prepared according to the method proposed by Pajkossy and Nyikos.¹⁵ Briefly, a master mask corresponding to the tenth order Sierpinski gasket¹ was produced by standard microelectronic techniques using a pattern generator and a stepping camera. As the silicon wafer substrate is smooth even on a micrometer scale due to the single crystal substrate used for the electrode fabrication, the dimension of the electrode surface is equal to the theoretical fractal dimension $D_f = \log(3)/\log(2) = 1.585$.¹ The detailed experimental procedure for the fabrication of such artificial electrode is described in Ref. 15. Indeed, both types of electrodes used in the present research are not new and have been well characterized in the literature.

Determination of fractal dimension.—The electrochemical reaction of ferricyanide, a well-characterized anion, at the gold surface is used as a redox-probe to demonstrate capabilities in the determination of the fractal dimension of the electrode surfaces. The electrolyte was an aqueous solution of 3 M NaCl and 15 mM K₄Fe(CN)₆ and 15 mM K₃(CN)₆. The initial potential was 0.6 V where no electrochemical reduction of Fe(CN)₆³⁻ occurs. By stepping the potential to a low value, 0 V, essentially all the ferricyanide was reduced to Fe(CN)₆⁴⁻. This is the most reliable electrochemical method for the determination of the fractal dimension of the electrode surface.

Results and Discussion

Reaction dimension of typical electrochemical processes.—Platinum particles are one of the most interesting catalysts for fuel cell applications.³⁰⁻³² Due to their importance, size effects of Pt particles on the electro-oxidation of different fuels (particularly methanol) have been extensively studied in the literature.²⁴⁻²⁶ Therefore, electro-oxidation of methanol was chosen as a typical electrochemical reaction for the investigation. The CV characteristics of the methanol oxidation at the Pt catalysts with different particle sizes are illustrated in Fig. 1. According to the above-mentioned analysis a moderate value of scan rate was used as a typical one throughout this research to gain diffusion-controlled behavior of the electrochemical systems under investigations. The typical value of 100 mV s⁻¹ is a common value used in the literature for studies of such electrochemical systems. The curves show higher electrochemical activity toward the methanol oxidation for the Pt catalysts with larger particles. To calculate the catalytic activities, the electrochemical activities can be estimated per unit of mass.

Figure 2 shows the dependence of the peak current on the particle size for the electro-oxidation of methanol at Pt particles plotted on a log-log scale. As the electrochemical activities were normalized in accordance with the catalyst mass ($d = 3.6$ nm, $Ma = 2.02 \times 10^{15}$ Pt atoms/cm²; $d = 5.2$, $Ma = 5.95 \times 10^{15}$ Pt atoms/cm²; $d = 9.3$, $Ma = 24.90 \times 10^{15}$ Pt atoms/cm²), it is observable that

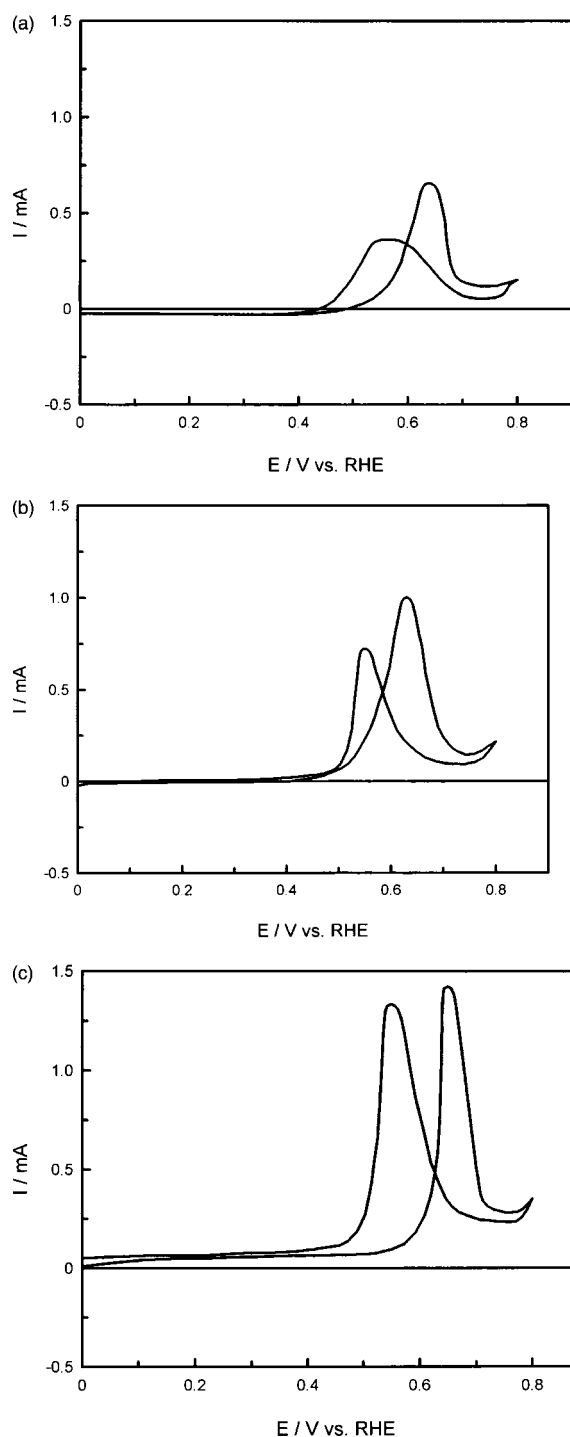


Figure 1. CV characteristics of the electrooxidation of metal at the Pt catalysts with particle sizes (a) 3.6, (b) 5.2, and (c) 9.3 nm. Electrolyte solution 0.01 H₂SO₄ + 0.1 M methanol. Scan rate 100 mV s⁻¹.

the Pt catalysts with smaller particles have higher catalytic activities. According to the relation noted in Eq. 3, the curve slope is equal to the value of D_R for the methanol oxidation reaction. Based on the presented results, a value of 1.817 was determined for the reaction dimension.

Similar CV behaviors can be obtained for the electrooxidation of CO at the Pt catalysts with different particle sizes. By normalizing the peak currents obtained from CV measurements (not shown), Eq. 3 can be employed to estimate the value of the fractal dimension of the CO oxidation (Fig. 3). The results suggest a value of 1.915 for

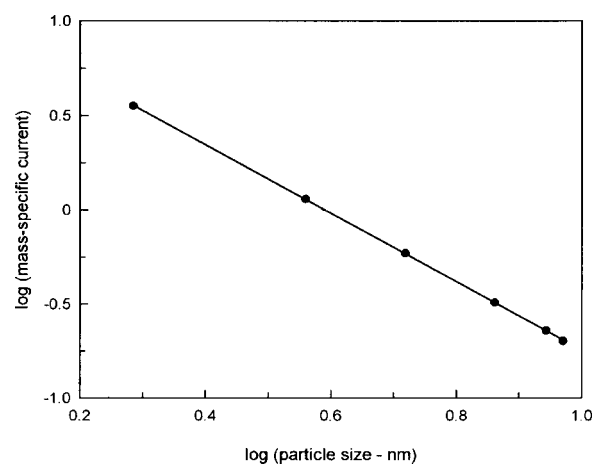


Figure 2. Relationship of the mass-specific current of the electro-oxidation of methanol as a function of particle size of the Pt catalyst.

the reaction dimension. In addition to the electro-oxidation of fuels, the approach was examined for electroreduction of O₂ (Fig. 4), from which the value of D_R was determined to be 1.879.

Although the value of D_R is different for the reactions investigated, however, the reaction dimension for all of them is less than 2. This indicates that the catalyst surfaces do not participate in the catalytic reaction with a complete two-dimensional surface and the surfaces are only partially active,¹⁵ meaning that all parts of the catalyst are not accessible for the reactants.

On the other hand, it is of interest that the fractal dimensions of the mentioned reaction are close to 2. It is well known that particles have noninteger dimensions between one and two, as they do not have a complete structure of two-dimensional surfaces.¹⁴ It has been reported that the fractal dimension of Pt particles is about 1.75.¹⁸ We obtained similar results for the electrodes made for this research. The interesting point is that for all cases studied in the present research, the reaction dimension was higher than the fractal dimension of the catalyst. Farin and Avnir¹⁰ have classified the relation between these two parameters into four different categories (*i*) screening, (*ii*) chemical selectivity, (*iii*) roughening and smoothing, and (*iv*) trapping, obtained from many theoretical simulations proposing such effects.³³⁻³⁵ The first and second categories are related to the case of $D_R < D_f$ and the third and fourth categories suggesting $D_R > D_f$. The third category refers to the dissolution and deposition processes and is not applicable for the cases under investigation. The fourth

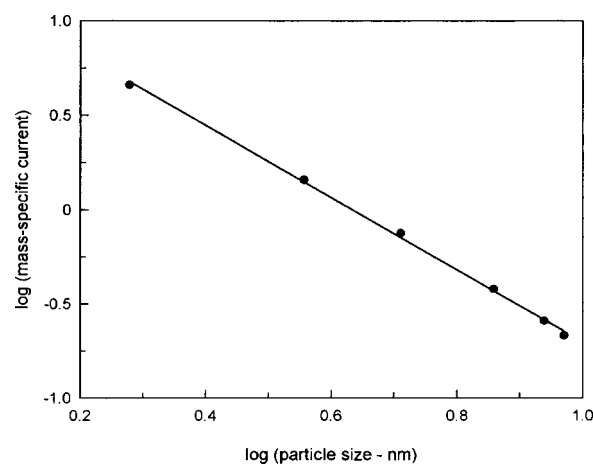


Figure 3. Dependence of the mass-specific current of the electro-oxidation of CO on the catalyst particle size.

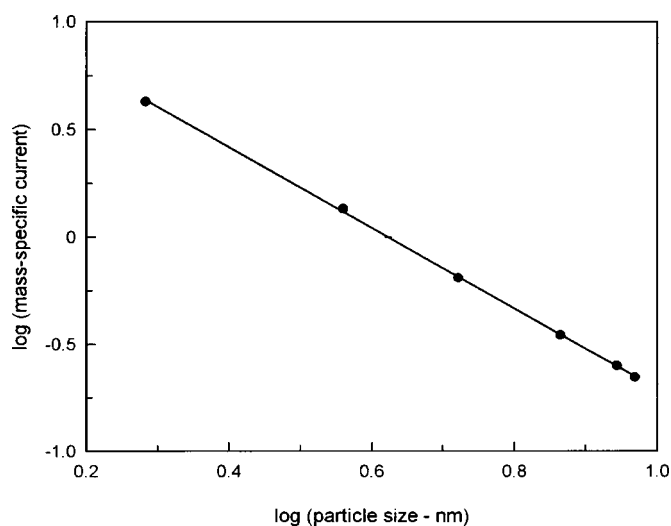


Figure 4. Mass-specific current of the electroreduction of O_2 presented for Pt particle-based electrodes with different particle size.

category can be used to describe the observed effect, as it is related to the roughness and the existence of possible pores on the catalyst which are accessible for the incoming molecules. However, we did not intend a detailed study of the catalysis mechanism for the typical examples. Interestingly, it is noticeable that the reaction dimension is dependent to the molecule size of the reactants, as $D_R(CO) > D_R(O_2) > D_R(MeOH)$.

Fractality factor and generalization of the proposed approach.—One may think that the approach proposed is only applicable for fractal electrodes. Unfortunately only a few electrodes have been shown to have a fractal structure and no information about the fractality of most electrodes is available. In other words, the fractality of most electrodes is questionable. Here, we would suggest briefly that the proposed approach can be used for all electrodes and the existence of known fractal structure of electrode surfaces is not needed for an electrochemical reaction to obey the above-mentioned relationships.

Two different features have been elaborated from the concepts of fractal geometry,¹ (i) the objects are more complicated than defined by Euclidean geometry (with simple dimensions) and they have noninteger dimensions depending on their complexity, and (ii) the complex objects can be defined by terms of self-similarity or self-affinity. We know of various fractal models and real objects, which have simple patterns of self-similarity or self-affinity. For such electrode surfaces similar patterns can be recognized in the surface structures in scanning electron microscopy (SEM) images, which have been widely presented in the literature. However only a few electrode surfaces obey these simple patterns and most real electrodes cannot be defined with the known fractal patterns. Nonetheless, the revolutionary feature of fractal geometry is the first feature, which made it a universal theory.

It is obvious that all surfaces are subject to the first feature of fractal geometry. In fact, it is very hard to find a surface, which does not have a noninteger dimension. An electrode surface with integer (Euclidean) dimension of 2 is accompanied by the same values for its geometrical and real areas, whereas, it is well known that the roughness factor of electrode surfaces is not equal to 1 and even for the smooth Au surface, the real surface area is at least 1.2 times higher than its geometrical area.³⁶ Therefore, every electrode surface can be involved in the above-mentioned approach due to its noninteger dimension.

However, the question remains as to what is the difference between fractal and nonfractal surfaces? The question can be answered by introducing fractality factor ζ , which is a dimensionless factor

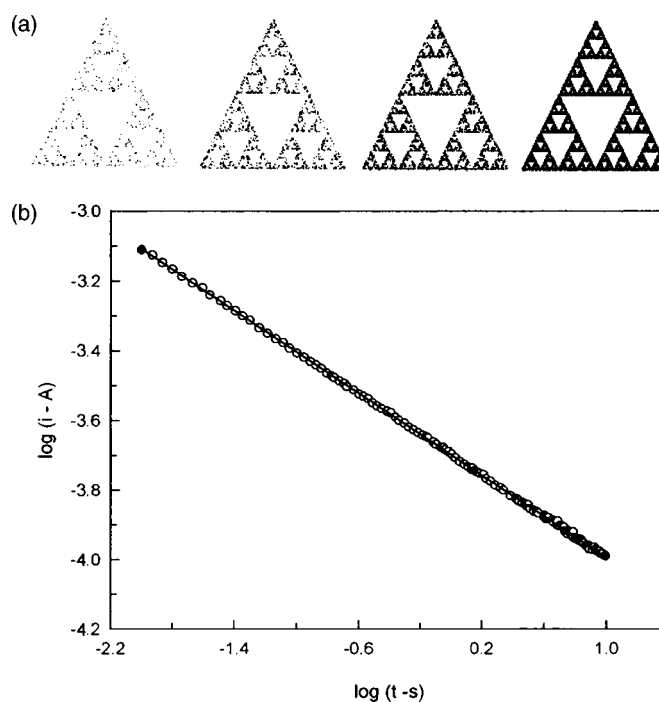


Figure 5. (a) A Sierpinski pattern and (b) electrochemical approach to determine the fractal dimension of the artificial electrode.

between 0 and 1 (presented in percentages) to calculate how much the surface is defined by the fractal patterns. To understand the physical meaning of ζ , an artificial electrode with a known fractal pattern was investigated. The electrode was constructed by gold masking with the known pattern of a Sierpinski gasket (Fig. 5a). The Sierpinski gasket is one of the most famous fractal patterns with a certain fractal dimension ($\log(3)/\log(2) = 1.58496$).¹ According to the Sierpinski Gasket pattern, all four gaskets displayed in Fig. 5a have fractal dimension of 1.58496. But have they the same fractality? If the fabricated electrode has the ideal pattern of the right gasket, the electrode surface can be exhausted and change to the left gasket as the result of time progress or any other damaging factors such as corrosion. Although, the fractal dimension of all gaskets is the same, they lose their fractality from right to left, which can be expressed with decreasing ζ .

To determine the fractal dimension of the electrode surface, a chronoamperometric technique was employed. The concept of such methods is based on diffusion of electroactive species towards electrode surfaces. For this purpose, a fast electrochemical redox couple ($Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$) was used for the process providing diffusion towards the electrode surface.

This is one of the oldest methods for this purpose, which is based on an extended form of the Cottrell equation. In the conventional, planar case, the diffusion controlled current shows well-known inverse square root time dependence, as $I \propto t^{-1/2}$.²³ For rough (fractal) electrodes, it has been claimed that the Cottrell equation transforms to an extended form¹²

$$\langle I(t) = \sigma_F t^{-\alpha} \rangle \quad [4]$$

where σ_F is a proportionality factor. This indicates that in a certain time range, the current is a power-law function of time, and the fractal dimension is included in the exponent as $\alpha = (D_f - 1)/2$. Therefore, the fractal dimension can be determined from the slope of the relationship of current to time, plotted in a log-log scale. The validity of the method has been examined by numerical calculations including Monte Carlo simulations of random walk¹² and by experiments using artificial fractal electrodes and real ones.^{13,17}

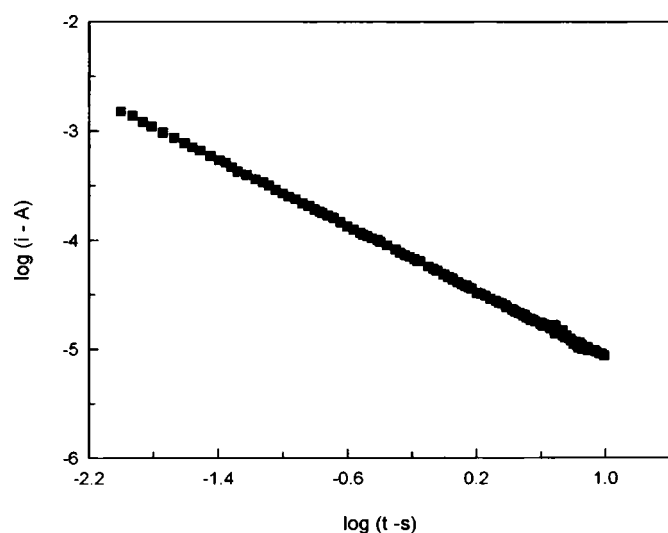


Figure 6. Electrochemical approach for estimating the fractal dimension of a real electrode, Au-electrodeposit.

The log current-log time relationship for the artificial electrode is presented in Fig. 5b. As seen, this shows a well-defined Cottrell behavior for the fractal surface. Such well-defined behavior has also been reported by Pajkossy and Nyikos for different artificial fractal electrodes (the oxidation process occurring at gold surface).¹⁵ However, it has not been reported for any real electrode surfaces, as such data reported for fractal studies of real electrode surfaces are accompanied by significant degrees of dispersion, which are the subject of the best fitting curve to estimate the fractal dimension. As expected from chronoamperometric behavior of electrochemical systems, there is deviation from the ideal behavior at short times due to capacitive currents as the result of double layer charging and at long times where planar diffusion is perturbed. However, for the artificial electrode with a well-defined fractal pattern, the electrochemical reaction of ferricyanide/ferricyanide system at a gold surface shows an ideal behavior over 3 decades of time, which can be used for the determination of the fractal dimension.

The curve presented in Fig. 5b has a slope of 0.295 suggesting the fractal dimension of 1.590 for the electrode surface. As seen, there is a tiny difference between the fractal dimension of Sierpinski gasket (which expected to be for the electrode) and the value determined for the artificial electrode surface. It is obvious that the results are accompanied by a small error function due to the methodology problems. However, because this error function is smaller than for the other methods, it is the best method for the determination of the fractal dimension of electrode surfaces. It cannot be completely eliminated, but it can be reduced by increasing the accuracy of experiments.

Even if we eliminate the mentioned error function, the results will not be the same as for the theoretical Sierpinski gasket. It is the main factor involved in ζ showing distance from fractality as the result of difference between theoretical and experimental (real) aspects. In fact, we cannot fabricate an artificial electrode exact pattern of Sierpinski as we calculated on paper. Although, the pattern structure was completely followed to construct the artificial electrode, it should be understood that the applied gold layer is not ideal and has a roughness factor of about 1.3. It is a reason (in combination with other ones), which make distance from fractality of a known pattern different in a real sample. This phenomenon is much stronger for real electrodes, where lower values of ζ are expected. For Au-electrodeposits, which have excellent fractal patterns as well as a powerful method for their analysis (due to fast redox on Au surface),^{16,37} the dispersion in the curve is higher than for the artificial electrode (Fig. 6), however there is a good fractal power law behavior indicating applicability of fractal analysis. This effect is

significantly higher for complex surfaces such as oxides, etc. and sometimes due to the high dispersion the electrode surfaces are referred to as nonfractal objects (due to low values of ζ).

In fact, we cannot reach a complete fractal structure (with ζ 100%) even for an artificial electrode. Analysis is more difficult for real surfaces. For a real surface, which has been generated as the result of complicated natural processes, it can be claimed that most parts of the surface obey the proposed pattern. Whenever, these parts dominate ζ is higher and the surface is more similar to the proposed pattern. For different surfaces, these parts are vary, which directly defines the fractality factor. However, as it is hard to claim a real surface with 100% fractality, it is also improbable to find a surface with $\zeta = 0$, where there is no part obeying from the fractal pattern in various parts of the surface.

Finally, it should be emphasized that every electrode surface can be referred to as a fractal object due to its noninteger dimension. And every electrode has a percent of fractality, although the surfaces with less fractality and low value of ζ are not usually referred to as fractal objects. However, as the first feature of fractal geometry is a universal law and the generalization of Euclidean geometry, the proposed approach can be used for both fractal and nonfractal electrode surfaces. It should also be noted that due to the lack of comprehensive studies in this context, it is too early to claim the proposed approach as a global feature. It needs extensive studies of different systems, whereas now there are a few reports in the literature even for chemical reaction.

Conclusion

The parameter of the reaction dimension was extended to electrochemical reactions. It was proposed theoretically and examined experimentally. Electro-oxidation of some fuels and electroreduction of oxygen are well known electrochemical processes chosen as typical examples to investigate the approach proposed. It was also noted that the approach proposed is not restricted to electrochemical reactions involving fractal electrodes, and that it can be used as a general relationship for all electrochemical reactions involving particle-based electrocatalysts.

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