University of Groningen

Self-affine roughness influence on redox reaction charge admittance

Palasantzas, G

Published in:
Surface Science

DOI:
[10.1016/j.susc.2005.03.012](https://doi.org/10.1016/j.susc.2005.03.012)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2005

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Palasantzas, G. (2005). Self-affine roughness influence on redox reaction charge admittance. *Surface Science*, 582(1-3), 151-158. <https://doi.org/10.1016/j.susc.2005.03.012>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Self-affine roughness influence on redox reaction charge admittance

George Palasantzas

Department of Applied Physics, Materials Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Received 1 November 2004; accepted for publication 10 March 2005

Available online 28 March 2005

Abstract

In this work we investigate the influence of self-affine electrode roughness on the admittance of redox reactions during facile charge transfer kinetics. The self-affine roughness is characterized by the rms roughness amplitude w , the correlation length ξ , and the roughness exponent H ($0 < H < 1$). Our calculations allow analytic expressions to be derived for the admittance as a function of the characteristic self-affine roughness parameters. Furthermore, it is shown that the magnitude of the reaction admittance is strongly influenced by the local roughness exponent H or the fine roughness details at short roughness wavelengths, while the influence of the lateral correlation length ξ or the long wavelength roughness ratio w/ξ is of secondary importance. In addition, the dynamic roughness evolution can strongly influence the reaction admittance and it should be taken carefully into consideration.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Metal–electrolyte interfaces; Surface roughness; Surface electrical transport; Oxidation

1. Introduction

Studies related to transport to and across a rough interface are of general interest in a wide variety of research fields as for example spin relaxation [1], fluorescence quenching [1,2], heterogeneous catalysis [3], enzyme kinetics [4], heat

diffusion [5], membrane transport [6,7], and electrochemistry [8–26]. In the latter case, the exploration of the mechanism of interfacial processes and the evaluation of parameters such as double-layer capacitance and charge rate constants can be performed by impedance spectroscopy [8,9]. Notably the calculation of impedance strongly depends on cell configurations and electrode geometries (e.g., planar, cylindrical, spherical etc.) [8,9]. The frequency response of rough interface depends on the regime under consideration such as for example (i) the capacitive behavior of rough electrodes

E-mail address: g.palasantzas@phys.rug.nl

[24–36], and (ii) diffusion controlled charge transfer on rough interfaces [12–26].

Scaling arguments in combination with numerical and experimental studies [2,12–17,24–26] have shown that the reaction admittance follows approximately a power-law of the frequency of the form $Y(\omega) \sim \omega^\gamma$. Indeed, $\gamma = (D_H - 1)/2$ for the problem of diffusion-controlled nuclear magnetic relaxation in porous media with fractal dimension D_H [1]. Similar results were derived for other diffusion-controlled cases, such as adsorption on a porous fractal catalyst [3], heat diffusion from a self-affine fractal boundary [4], and the impedance of rough electrodes [15]. In the more general case, the power-law flux transient on a fractal interface with Euclidean dimension D_E of the embedding space has the form $\gamma = (D_H + 2 - D_E)/2$ [8,12,13]. Other general results were obtained in understanding the effect of roughness on the interfacial reaction current in terms of an arbitrary weak roughness profile and an arbitrary roughness power spectrum [18–21,23] without however addressing the questions related to finite scale-invariant interfaces.

Recently a theory was developed for the electrical admittance of a rough interface under partial diffusion-limited charge transfer conditions [37]. In this development, the large and small-frequency expansion gave the relationships between the average admittance and various morphological features of the rough electrode i.e. area, curvature, and interface width [37]. So far the diffusion-limited reaction admittance was determined on an approximately self-affine surface without, however, analytic results for all lateral roughness wavelengths [37] spanning the range from $q\xi \ll 1$ to $q\xi \gg 1$ where ξ is the characteristic lateral roughness correlation length and q the lateral roughness wave vector.

In this work we will calculate the admittance of diffusion-limited reaction rates on random self-affine rough surfaces including contributions from all relevant lateral roughness wavelengths including also the necessary power law regimes. In all cases the admittance is described as a functional of a roughness power spectrum where analytic calculations are feasible as will be illustrated in the following sections.

2. Admittance theory for rough electrodes

The total admittance $Y(\omega)$ of an interfacial redox reaction, $O + ne^- \leftrightarrow R$ (O: oxidized, R: reduced species, and 'n' the number of electrons transferred in the redox reaction; see Fig. 1), driven by a sinusoidal interfacial potential $\delta V = V_o \exp(-j\omega t)$ ($V_o = E - E_{eq}$; E the working electrode potential and E_{eq} the equilibrium potential) is obtained by solving the diffusion equations for the local concentration profile [37]

$$j\omega \delta c_a = D_a \nabla^2 \delta c_a \quad (1)$$

with $\delta c_a(r, t) = \delta c_a(r, \omega) \exp(-j\omega t)$. δc_a is difference in the concentration at an arbitrary point and the bulk concentration of a -th species. In the following we denote by R the gas constant, F the faraday constant, J_o the exchange current density, D_a the bulk molecular diffusion constant, c_a^o bulk or volume concentration of a -th species, and $\delta c_a(z)$ the difference between surface and bulk concentration. By making the simplification $D = D_{O,R}$ and considering the balance condition $\delta c_O + \delta c_R = 0$, at the interface the kinetics limitation has the form

$$(\hat{n} \cdot \nabla \delta c_O) = k_e \delta c_O + (J_o / RTD) V_o \quad (2)$$

with $k_e = (J_o / nFDc_O^o)(1 + c_O^o / c_R^o)$. Indeed, k_e^{-1} is the interfacial reaction length and provides a relative measure of facility of bulk diffusion versus the surface reaction. k_e^{-1} is small for fast interfacial reaction or slow bulk diffusion (e.g., $k_e^{-1} \rightarrow 0$ for the diffusion-limited reaction) and large for the slow interfacial reactions.

The total admittance is given by the Laplace transform of the interfacial surface current $I(t)$ or [37]

$$Y(\omega) = (j\omega / n_o) \int_0^{+\infty} e^{-j\omega t} I(t) dt, \quad (3)$$

$$I(t) = nFD \int_{z=h(r)} (\hat{n} \cdot \nabla \delta c) ds$$

which yields after ensemble average over possible roughness configurations (and facile charge transfer kinetic or $k_e^{-1} \sqrt{\omega/D} \ll 1$ which corresponds to the low frequency regime) [37]

Fig. 1. Schematic of the rough electrode and the redox reaction process.

$$\langle Y(\omega) \rangle = \hat{Y}_p \left\{ 1 + \frac{\omega_o}{(2\pi)^2} \int [\omega_{\parallel} - \omega_o] \langle |h(q)|^2 \rangle d^2q \right\} \quad (4)$$

with $\hat{Y}_p = A_o \Gamma \sqrt{j\omega D}$, $\Gamma = n^2 F^2 / [RT(C_o^{-1} + C_R^{-1})]$, $\omega_o = \sqrt{j\omega/D}$, and $\omega_{\parallel} = \sqrt{q^2 + j\omega/D}$. In Eq. (4) $\langle |h(q)|^2 \rangle$ is the interface roughness spectrum.

3. Roughness model

In the following we will consider a model for the roughness spectrum $\langle |h(q)|^2 \rangle$, which is necessary for the calculation of the admittance $\langle Y \rangle$. Indeed, a wide variety of surfaces and interfaces appearing in various physical systems (i.e., films grown under non equilibrium conditions) possess roughness, which is termed as self-affine [38]. Any physical self-affine morphology is characterized by a finite correlation length ξ , an rms roughness amplitude w , and a roughness exponent H ($0 < H < 1$) which is a measure of the degree of

surface irregularity. [38,39] Small values of H (~ 0) characterize extremely jagged or irregular surfaces, while large values H (~ 1) surfaces with smooth hills and valleys [38,39]. For self-affine fractals the roughness spectrum $\langle |h(q)|^2 \rangle$ is characterized by the power law scaling behavior, namely, $\langle |h(q)|^2 \rangle \propto q^{-2-2H}$ if $q\xi \gg 1$ and $\langle |h(q)|^2 \rangle \propto \text{const}$ if $q\xi \ll 1$ [38]. This scaling behavior is satisfied by the simple model for $\langle |h(q)|^2 \rangle$ [39]

$$\langle |h(q)|^2 \rangle = \frac{2\pi w^2 \xi^2}{(1 + a q^2 \xi^2)^{1+H}} \quad (5)$$

with $a = 1/2H[1 - (1 + aQ_c^2 \xi^2)^{-H}]$ ($0 < H < 1$), and $a = 1/2 \ln(1 + aQ_c^2 \xi^2)$ ($H = 0$). For other correlation models see also Ref. [40].

4. Results-discussion

Studies on fractal interfaces have led to two important conclusions namely that (i) the scale-invariant frequency or time response is obtained under diffusion-limited transport conditions on a scale-invariant interface, (ii) the scaling exponents of the frequency or time response and phase are related to the scaling exponent of the interfacial and spatial geometry [37]. However, there are several drawbacks in these studies since they are based on unrealistic interface roughness models where the direct influence of all the characteristic roughness parameters (w , ξ , and H) was not taken into account.

Initially we should state that the present theory applied in the limit of weak roughness. The latter can be reformulated more precisely by the requirement that the average local interface slope to be small or $\rho_{\text{rms}} = \sqrt{\langle |\nabla h|^2 \rangle} \ll 1$. ρ_{rms} is given in terms of the roughness spectrum $\langle |h(q)|^2 \rangle$ as we will see later. In general, the admittance will have a simpler dependence on the roughness amplitude w since $\langle |h(q)|^2 \rangle \propto w^2$ (assuming weak roughness), while any more complex dependence will arise from the roughness parameters H and ξ . In addition, our calculations were performed for lower roughness cut-off $c = 0.3$ nm. The latter corresponds to a typical lattice constant for metals. However, a lower value might be necessary for a

physical system (depending on the material) since the actual smallest step height might be smaller than the lattice constant.

Before we proceed for the calculations of the admittance we will present some analytic results. Indeed, if we substitute in Eq. (4) the expansion

$$\omega_{\parallel} \simeq \omega_0 \left[1 + \frac{1}{2} \frac{q^2}{\omega_0^2} - \frac{1}{8} \frac{q^4}{\omega_0^4} + \frac{1}{16} \frac{q^6}{\omega_0^6} + \dots \sum_{k=4}^{+\infty} \frac{(-1)^k 1 \cdot 3 \cdot 5 \dots (2k-3)}{2^k k!} \frac{q^{2k}}{\omega_0^{2k}} \right] \quad (6)$$

and take into account the expression $\hat{Y}_p = (A_0 \Gamma \sqrt{\omega D}) / (1/\sqrt{2})(1+j)$, we obtain

$$\begin{aligned} \langle Y(\omega) \rangle &= Y_p \left\{ \left(1 + \frac{m_2}{2} - \frac{D^2 m_6}{16 \omega^2} - \frac{D m_4}{8 \omega} \right) \right. \\ &\quad \left. + j \left(1 + \frac{m_2}{2} - \frac{D^2 m_6}{16 \omega^2} + \frac{D m_4}{8 \omega} \right) \right\} + \dots \\ &\quad + Y_p (1+j) \sum_{k=4}^{+\infty} \frac{(-1)^k 1 \cdot 3 \cdot 5 \dots (2k-3)}{2^k k!} \\ &\quad \times \frac{1}{\omega^{2k-1}} m_{2k} \end{aligned} \quad (7)$$

with $Y_p = A_0 \Gamma \sqrt{\omega D / 2}$ and $\Gamma = n^2 F^2 / [RT(C_o^{-1} + C_R^{-1})]$. The necessary roughness factors m_{2k} ($k = 1, 2, 3, \dots$) are given by

$$m_{2k} = \int_{0 < q < Q_c} q^{2k} \langle |h(q)|^2 \rangle \frac{d^2 q}{(2\pi)^2} \quad (k = 1, 2, 3, \dots). \quad (8)$$

Note that the square root of m_2 yields the local surface slope ρ_{rms} as we mentioned earlier. Upon substitution of Eq. (5) into Eq. (8), all the roughness factors (or moments) m_{2k} ($k = 1, 2, 3, \dots$) can be computed in analytic form. Below we give such an example for the factors m_2 and m_4 . Indeed, we obtain

$$m_2 = \frac{w^2}{2a^3 \xi^2} \left\{ \frac{1}{1-H} [X_C^{1-H} - 1] - 2a \right\} \quad (9)$$

$$\begin{aligned} m_4 &= \frac{w^2}{2a^3 \xi^4} \left\{ \frac{1}{2-H} [X_C^{2-H} - 1] + \frac{2}{1-H} [1 - X_C^{1-H}] \right. \\ &\quad \left. - \frac{1}{H} [X_C^{-H} - 1] \right\} \end{aligned} \quad (10)$$

with $X_C = 1 + a Q_c^2 \xi^2$. The limiting cases of $H = 0$ and $H = 1$ can be obtained by Eqs. (9) and (10) if we consider the identity $\lim_{B \rightarrow 0} (1/B)(x^B - 1) = \ln(x)$ to obtain the logarithmic factors. The roughness model given by Eq. (5) which is used for the computation of the factors m_{2k} is a single valued function of the wave vector q and any contribution from the short and long length scales appears only in the integrals for m_{2k} . Despite the integration the analytic calculations in Eqs. (9) and (10) show clearly that the signature of short wavelength roughness as expressed through the roughness exponent H is still evident and has a strong effect as will be shown below.

Moreover, up to second order terms Eq. (7) can be further written in the simpler form

$$|\langle Y \rangle| = Y_p \sqrt{2} \left\{ \left(1 + \frac{m_2}{2} \right)^2 + \left(\frac{D}{8\omega} \right)^2 m_4^2 \right\}^{1/2} \quad (11)$$

where together with Eqs. (9) and (10) provide a complete analytic form for the magnitude of the reaction admittance as well as its phase

$$\phi = \tan^{-1} \left\{ \left(1 + \frac{m_2}{2} + \frac{D m_4}{8\omega} \right) / \left(1 + \frac{m_2}{2} - \frac{D m_4}{8\omega} \right) \right\} \quad (12)$$

Fig. 2 shows direct calculation of the magnitude of the interface admittance $|\langle Y \rangle|$ for various roughness exponents H . Clearly the influence of the roughness exponent is very significant on $|\langle Y \rangle|$

Fig. 2. Absolute magnitude of total admittance $|\langle Y \rangle|$ vs the ratio D/ω for various roughness exponents H , $w = 1$ nm, and $\xi = 100$ nm.

for relatively high ratios D/ω ($\gg 1$), while it is minimized in the regime $D/\omega \ll 1$. However, the magnitude of the admittance $|\langle Y \rangle|$ increases very rapidly for small roughness exponents H within the regime $D/\omega \leq 1$. In any case, it is evident that the change of the roughness exponent by an order of magnitude within the range $0 < H < 1$ can lead to strong variations of the reaction admittance even by more than an order of magnitude.

If we compare with the dependence of $|\langle Y \rangle|$ on the lateral roughness correlation length ξ , as it is depicted in Fig. 3, we observe a smoother increment of $|\langle Y \rangle|$ as a function of the ratio D/ω without the presence of regimes of fast or slow increment as it is shown in Fig. 2. Moreover, a change of ξ by an order of magnitude does lead in the regime $D/\omega \gg 1$ to a weaker increment of the magnitude of the admittance in comparison with the corresponding regime in Fig. 2. Therefore, we can infer that fine roughness details at short wavelengths ($< \xi$) can readily influence reaction kinetics stronger than long roughness wavelengths as they are described in the more general case by the ratio w/ξ .

Besides the magnitude of $\langle Y \rangle$ also its phase deserves some further attention as a function of the roughness parameters H and ξ . Any dependence on the roughness amplitude is weak since both $m_{2,4} \propto w^2$. Indeed, as Fig. 4 shows the phase of the admittance as a function of the roughness exponent H is positive and increasing with increas-

Fig. 3. Absolute magnitude of total admittance $|\langle Y \rangle|$ vs the ratio D/ω for various roughness correlation lengths ξ , roughness exponents $H = 0.6$, and $w = 1$ nm.

Fig. 4. (a) Phase angle ϕ vs the ratio D/ω for various roughness exponents H , correlation length $\xi = 100$ nm, and $w = 1$ nm. (b) and (c) Similar plots as in (a) but for the $\text{Re}(\langle Y \rangle)$ and $\text{Im}(\langle Y \rangle)$ vs. D/ω and roughness exponents H as indicated.

ing D/ω showing a change to negative values with decreasing roughness exponent H (or equivalently for surface roughening at short wavelengths). This is due to the fact that the real part of $\langle Y \rangle$ has a dependence on the moments $m_{2,4}$ as

$\text{Re}(\langle Y \rangle) \sim 1 + (m_2/2) - (Dm_4/8\omega)$, which leads to negative values for the phase if the fourth order moment m_4 becomes significant, and for sufficiently large values of the D/ω (see Fig. 4(b) and (c)). The phase variation shows a similar behavior as a function of the correlation length ξ (Fig. 5). Indeed, the transition region to negative values as a function of the ratio D/ω is shifted drastically to larger values with increasing correlation length ξ and roughness exponent H (Fig. 5).

Finally we will consider how the dynamic evolution of the interface roughness can influence the roughness contribution to the reaction admittance. This is a secondary consequence (not by considering any simultaneous temporal system evolution that would require simultaneous solution of time dependent equations of motion for the surface and the diffusion to the surface) we will consider how separately the evolution of electrode rough-

Fig. 5. Phase angle ϕ vs the ratio D/ω for various correlation lengths ξ , $w = 1$ nm, (a) $H = 0.6$ and (b) $H = 0.9$.

ness can influence the roughness contribution to the reaction admittance. The electrode surface morphology can be for example modified by metal deposition prior to any reaction experiment and this is the case under consideration in the present paper. Indeed, if both roughness parameters w and ξ evolve with time τ as $w \propto \tau^\beta$ (β known as the growth exponent) [38] and $\xi \propto \tau^{1/z}$ (z known as the dynamic exponent) [38] with ' z ' for example given by $z = 2H/\beta$, then the evolution of the admittance magnitude for various times τ in Fig. 6(a) indicates that interface roughening becomes more dominant at higher ratios D/ω . Roughening occurs since the choice of the dynamic exponent z so that $z \neq H/\beta$ leads to an evolution of the local interface slope [41]. Indeed, since $\rho_{\text{rms}} \propto w/\xi^H$ [41] we obtain

Fig. 6. (a) Absolute magnitude of total admittance $|\langle Y \rangle|$ vs the ratio D/ω for various growth times τ with $\beta = 0.25$, $H = 0.5$, and $z = 2\beta/H$. (b) Absolute magnitude of total admittance $|\langle Y \rangle|$ vs the ratio D/ω with $\beta = 0.25$, various dynamic exponents z as indicated, $\tau = 50$, and $H = 0.5$. In both cases we considered the power law relations $w = 1(\tau/10)^\beta$ (nm) and $\xi = 100(\tau/10)^{1/z}$ (nm).

for $z = 2H/\beta$ the temporal evolution $\rho_{\text{rms}} \propto \tau^\beta$, which leads to interface roughening. Note that for $z = H/\beta$ the local slope is time invariant ($\partial\rho_{\text{rms}}/\partial\tau = 0$). If on the other hand $z = H/2\beta$ then the local slope decreases at later evolution times as $\rho_{\text{rms}} \propto \tau^{-\beta}$ leading to smoothening and thus the decrement of the magnitude of the reaction admittance (Fig. 6(b)) at higher ratios D/ω . In any case, the previous examples indicate that dynamic evolution of interface roughness can strongly influence the reaction admittance and should be taken carefully into consideration.

5. Conclusions

In summary, we have shown that the magnitude of redox reaction admittance (for facile charge transfer kinetic or interfacial reaction lengths $k_e^{-1} \ll 1$) on self-affine rough surfaces is strongly influenced by the local roughness exponent H or equivalently by the fine roughness details at short roughness wavelengths ($< \xi$). The influence of the lateral correlation length ξ is of secondary importance. On the other hand the phase of the admittance shows peculiar behavior for small roughness exponents H and smaller correlation lengths ξ related to increasing magnitude of the fourth order roughness moments. In addition, the dynamic evolution of interface roughness can strongly influence the reaction admittance and should taken carefully into consideration. Notably our calculations allow analytic expressions to be derived for the reaction admittance as a function of the rms roughness amplitude w , the lateral roughness correlation length, and the roughness exponent H . Further studies are in progress to extended our calculations for less facile charge transfer kinetic or finite interfacial reaction lengths so that higher frequency regimes ($k_e^{-1}\sqrt{\omega/D} \geq 1$) can be probed [37].

Acknowledgement

I would like to acknowledge useful discussion with Dr. G. Backx.

References

- [1] P.G. de Gennes, C.R. Acad. Sci. (Paris) Ser. II 295 (1982) 1061.
- [2] R. Kopelman, J. Stat. Phys. 42 (1986) 185; R. Kopelman, Science 241 (1988) 1620.
- [3] P. Pfeifer, D. Avnir, D. Farin, Stat. Phys. 36 (1984) 699.
- [4] P. Pfeifer, U. Welz, H. Wippermann, Chem. Phys. Lett. 113 (1985) 535.
- [5] D. Vandembroucq, A.C. Boccardo, S. Roux, Europhys. Lett. 30 (1995) 209.
- [6] R. Gutfraind, B. Sapoval, J. Phys. I Fr. 3 (1993) 1801.
- [7] B. Sapoval, in: A. Bunde, S. Havlin (Eds.), Fractal Electrodes, Fractal Membranes and Fractal Catalyst in Fractals and Disordered Systems, Springer, Heidelberg, 1996.
- [8] A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, Wiley, New York, 1980.
- [9] A. Lasia, in: B.E. Conway et al. (Eds.), Modern Aspects of Electrochemistry, vol. 32, Kluwer Academic/Plenum, NY, 1999.
- [10] S.K. Rangarajan, J. Electroanal. Chem. 22 (1969) 89.
- [11] X.B. Zuo, C.S. Xu, H.W. Xin, Electrochim. Acta 42 (1997) 2555.
- [12] B. Sapoval, J.N. Chazalviel, J. Peyriere, Phys. Rev. A 38 (1988) 5867.
- [13] L. Nyikos, T. Pajkossy, Electrochim. Acta 31 (1986) 1347.
- [14] L. Nyikos, T. Pajkossy, Electrochim. Acta 34 (1989) 171.
- [15] T. Pajkossy, A.P. Borosy, A. Imre, S.A. Martemyanov, R. Schiller, L. Nyikos, J. Electroanal. Chem. 366 (1994) 69.
- [16] A. Imre, T. Pajkossy, L. Nyikos, Acta Metall. 40 (1992) 1819.
- [17] A.P. Borosy, L. Nyikos, T. Pajkossy, Electrochim. Acta 36 (1991) 163.
- [18] R. Kant, Electrochemistry at Complex Interfacial Geometries, Ph.D. Thesis, Indian Institute of Science, Bangalore, 1993.
- [19] R. Kant, Phys. Rev. Lett. 70 (1993) 4094.
- [20] R. Kant, J. Phys. Chem. 98 (1994) 1663.
- [21] R. Kant, S.K. Rangarajan, J. Electroanal. Chem. 368 (1994) 1.
- [22] R. Kant, J. Phys. Chem. 101 (1997) 3781.
- [23] R. Kant, S.K. Rangarajan, J. Electroanal. Chem. 396 (1995) 285.
- [24] L. Nyikos, T. Pajkossy, Electrochim. Acta 35 (1990) 1567.
- [25] T. Pajkossy, J. Electroanal. Chem. 300 (1991) 1.
- [26] R. de Levie, J. Electroanal. Chem. 281 (1990) 1.
- [27] T.C. Halsey, M. Leibig, Ann. Phys. (NY) 219 (1992) 109; T.C. Halsey, M. Leibig, Europhys. Lett. 14 (1991) 815.
- [28] W.H. Mulder, J.H. Sluyters, Electrochim. Acta 33 (1988) 303.
- [29] R. Ball, M. Blunt, J. Phys. A: Math. Gen. 21 (1988) 197.
- [30] L.I. Daikhin, A.A. Kornyshev, M. Urbakh, Electrochim. Acta 42 (1997) 2853.
- [31] L.I. Daikhin, A.A. Kornyshev, M. Urbakh, Phys. Rev. E 53 (1996) 6192.
- [32] Y.P. Zhao, G.C. Wang, T.M. Lu, G. Palasantzas, J.T.M. Dehossion, Phys. Rev. B 60 (1999) 9157.
- [33] A. Garciavalenzuela, N.C. Bruce, D. Kouznetsov, J. Phys. D Appl. Phys. 31 (1998) 240.

- [34] N.C. Bruce, A. Garciavalenzuela, D. Kouznetsov, J. Phys. D Appl. Phys. 32 (1999) 2692.
- [35] Z. Kerner, T. Pajkossy, J. Electroanal. Chem. 448 (1998) 139.
- [36] J. Fleig, J. Maier, Solid State Ionics 94 (1997) 199.
- [37] R. Kant, S.K. Rangarajan, J. Electroanal. Chem. 552 (2003) 141.
- [38] P. Meakin, Phys. Rep. 235 (1994) 1991;
J. Krim, G. Palasantzas, Int. J. Mod. Phys. B 9 (1995) 599;
F. Family, T. Viscek, Dynamics of Fractal Surfaces, World Scientific, Singapore, 1991;
Y.P. Zhao, G.C. Wang, T.M. Lu, Characterization of Amorphous and Crystalline Rough Surfaces-principles and Applications Experimental Methods in the Physical Science, vol. 37, Academic Press, 2000;
P. Meakin, Fractals, Scaling, and Growth far from Equilibrium, Cambridge University Press, Cambridge, 1998.
- [39] G. Palasantzas, Phys. Rev. B 48 (1993) 14472;
G. Palasantzas, Phys. Rev. B 49 (1994) 5785.
- [40] S.K. Sinha, E.B. Sirota, S. Garoff, H.B. Stanley, Phys. Rev. B 38 (1988) 2297;
H.N. Yang, T.M. Lu, Phys. Rev. E 51 (1995) 2479;
Y.P. Zhao, G.C. Wang, T.M. Lu, Phys. Rev. B 55 (1997) 13938.
- [41] G. Palasantzas, Phys. Rev. E 56 (1997) 1254.