Anomalous kinetic roughening during anodic dissolution of polycrystalline Fe

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Dynamics of surface roughness during polycrystalline pure iron electrodissolution is investigated at constant current density by means of *ex situ* atomic force microscopy. The scaling of the local surface width reveals that surface kinetic roughening is anomalous with both the exponents of local roughness, α_{loc}, and growth, β, close to 1 pointing out that interface evolution is unstable. We show that this anomalous unstable behavior results from the development of a faceted surface structure exposing different crystal orientations. The presence of smooth faceted walls is consistent with the value $\alpha_{local} \sim 1$, whereas the difference in the dissolution rates on the different crystallographic planes account for the nonlocal effects causing the unstable growth. Results are discussed in the context of a recently reported anomalous scaling which accounts for dynamics of self-organized depinning models displaying faceted interfaces. The influence of the electrode potential on the dissolution rates of the different crystallographic planes, along with its effect on the mobility of metal adatoms, are discussed to be behind the complex behavior of local roughness when the current density is varied.

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I. INTRODUCTION

Kinetic roughening during interface evolution in far from equilibrium conditions is a widely studied phenomenon [1,2]. The principal idea beneath those works is very simple: roughness dynamics provides information about the processes that are taking part in the surface growth. A quantitative description of that dynamics is based on scaling laws for the correlation lengths of the system, which reflect the scale invariance of the problem. Those scaling properties introduce a series of scaling exponents that do not depend on the particular details of the model thus allowing a classification of the different types of surface growth into universality classes. In very few words, that is the well known dynamic scaling theory [3].

Identification of universalities and its surface origin has been a subject of major interest in the past two decades. Most of the works have been devoted to the study of solid phase growth because of its considerable practical importance in thin film growth processes [1]. However, by far, less work has been devoted to the study of roughness dynamics when material is removed from the surface. Here we are interested in those processes, in particular, in the dynamics of anodic dissolving electrodes [4–11].

Despite the wide range of systems and the complexity of the processes involved in each case, surface roughening very often obeys simple scaling properties. In general, when the interface evolution is controlled by local surface processes a self-affine surface is expected [1–3]. Under the assumption of self-affinity, scale invariance predicts the same dynamics for the local and global scales. In particular, the local width $w(l,t)$ measuring surface fluctuations over a window of size l, with $l \ll L$ and L being the total lateral size system, should scale according to the Family-Vicsek (FV) scaling [12], hence

$$w(l,t) \sim \begin{cases} l^\alpha & \text{if } l \ll t^{1/z}, \\ t^\beta & \text{if } l \gg t^{1/z}. \end{cases} \quad (1)$$

However, FV dynamic scaling for the local width is not guaranteed if the interface is not self-affine, which may occur when nonlocal effects take part in the roughening process [13]. Such nonlocal effects have been usually related to the presence of electric or concentration Laplacian fields that limit the interface evolution kinetics [2]. Then, local and global surface fluctuations may have different scaling exponents. This different type of scaling is termed in the literature as anomalous scaling and it has been extensively investigated theoretically [13–19] and reported experimentally (see, e.g., [20,21] for molecular-beam epitaxy growth, [22] for vapor deposition, [23,24] for sputter-deposition growth, [25–29] for electrodeposition, [30] for electrodissolution, [31] for etching by ion sputtering, or [32] for fluid invasion).

The following scaling relation has successfully accounted for those results:

$$w(l,t) \sim l^\alpha f_A\left(\frac{l}{t^{1/z}}\right), \quad (2)$$

with the anomalous function

$$f_A(u) \sim \begin{cases} u^{-(\alpha-\alpha_{loc})} & \text{if } u \ll 1, \\ u^{-\alpha} & \text{if } u \gg 1, \end{cases} \quad (3)$$

where we have assumed that horizontal correlation length $\xi \sim t^{1/z}$ has not reached the system size L ($t^{1/z} \ll L$). This ansatz yields to a different behavior than that of the Family-Vicsek given in Eq. (1):

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$$w \sim \begin{cases} l^{\alpha_{\text{loc}}} t^{\beta*} & \text{if } l \ll t^{1/z}, \\ t^{\beta} & \text{if } l \gg t^{1/z}, \end{cases} \qquad (4)$$

with the global (α and β), local (α_{loc}), and anomalous (β^*) exponents related in this form,

$$\alpha_{\text{loc}} = \alpha \left(1 - \frac{\beta^*}{\beta} \right). \qquad (5)$$

In this case, three exponents, α_{loc}, α, and β, must be considered to give a complete description of the scaling behavior of the surface.

Generally, anomalous scaling has been either associated with a super-roughening $\alpha > 1$, for which $\alpha_{\text{loc}} = 1$, or with what has been termed intrinsic anomalous roughening, characterized by an independent local roughness exponent $\alpha_{\text{loc}} < 1$ and a global exponent α that may be larger or smaller than 1, but always larger than α_{loc} [16,17]. However, it has been recently predicted [16] the existence of a new class of anomalous dynamic scaling that accounts for the coarsening kinetics of faceted surfaces [33]. Examples of that new dynamics are models for self-organized depinning and interface growth in disordered media [34]. Roughness dynamic scaling in those cases is related to the faceted form of the interface at saturation and is characterized by a local roughness exponent $\alpha_{\text{loc}} = 1$ [16].

In this paper we report experimental evidences of unstable anomalous roughening during pure iron electrodissolution. As we shall see, atomic force microscopy (AFM) images reveal that this behavior is due to the establishment of a faceted surface exposing different crystallographic planes. Results are discussed in terms of the new class of anomalous dynamic scaling. We conclude by analyzing preliminary results on the influence of the electrode potential on the local surface topography.

II. EXPERIMENTAL SETUP

Pure polycrystalline iron (99.99%) 5.0 mm diameter rods were used as the working electrode. The lateral surface was insulated with a Teflon™ sheath so that the only active surface exposed to the electrolyte was the cross section polished with emery paper down to 1200 grid and after with diamond paste down to 0.3 μm. They were then degreased with alcohol, sonicated in deionized water, and finally dried with hot air. A classical three-electrode electrochemical cell was used with a large surface Pt grid as the counter-electrode and a saturated sulfate electrode (sse) reference one. The samples were immersed in a 0.5 M H_2SO_4 solution prepared from analytical-grade chemicals and pure water (Millipore-Q). They were then submitted to galvanostatic control anodic dissolution at different currents densities and dissolution charges. Polarization curves were performed under potentiostatic control at 1 mV s^{-1} scan rate.

The surface morphology investigation was carried out on a Veeco D3100 AFM in tapping mode. Acquisition fields were saved only when drift effect was minimized between successive scans of the same area. The scaling analysis was carried out with images of 512×512 pixels resolution at different windows up to 30 μm.
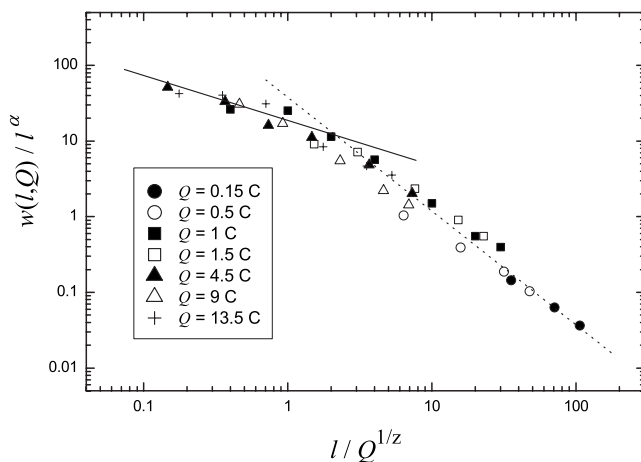

FIG. 1. Collapse of local width data obtained from AFM images. Exponents used for the collapse are $\alpha = z = 1.5$. The straight lines are plotted as a guide to the eye having slopes -1.5 (dashed) and -0.6 (solid).

III. RESULTS AND DISCUSSION

In order to study the dynamic scaling of the dissolving Fe surface we have fixed the anodic current within the active dissolution region to a value of 2.5 mA cm^{-2} and measured the local width $w(l,t)$ for surface windows of different lateral size l at different dissolution times.

The proper way to recognize the scaling properties of a growing surface from the behavior of the local width is by determining the form of the scaling function $f(u)$ involved in Eq. (2) [17]. We have done it through the data collapse shown in Fig. 1, in which the dissolution time has been replaced by the total dissolution charge Q since the current density has been kept constant. Scaling exponents used for the collapse are $\alpha = z = 1.5$. It can be seen that the form of the scaling function is consistent with that of the anomalous roughening described by Eq. (3) with $\alpha_{\text{loc}} \approx 0.9$.

According to those results, a large growth exponent $\beta = 1$, and an anomalous growth exponent $\beta^* \approx 0.4$ for small windows at large times ($l \ll t^{1/z}$), are expected. In fact, those values are in good agreement with the time evolution of the local width displayed in Fig. 2. Large windows ($l \gg t^{1/z}$) seems to grow linearly with time, whereas local surface width ($l \ll t^{1/z}$) increases anomalously, with an effective growth exponent close to β^*.

The origin of anomalous scaling has been extensively discussed in the literature. It has been theoretically argued that intrinsic anomalous roughening cannot occur in local growth models [13]. This conclusion agrees with the results of discrete models [18] and experimental evidences reported in the literature [25,26], focused mainly on electrodeposited films, which show that (nonlocal) bulk diffusion effects are responsible for such behavior. On the other hand, the new anomalous dynamics discussed in the Introduction section can be related to growth models in which the stationary state consists of faceted interfaces.

In the present work, the influence of a diffusion field in the electrolyte can be disregarded as a possible cause since it
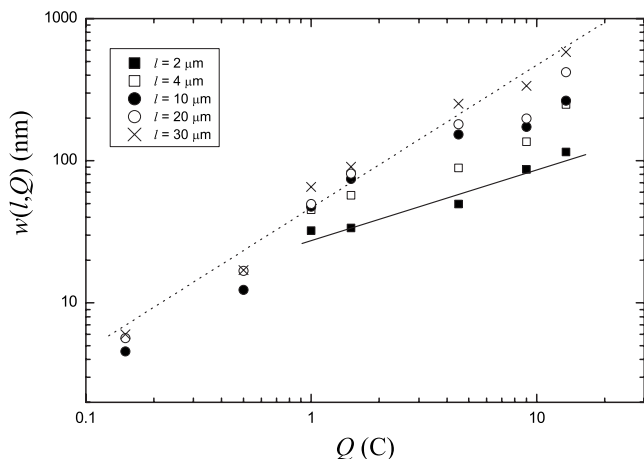
FIG. 2. Time increase of local surface width for windows of different size. Straight lines correspond to the expected behavior from Fig. 1: $\beta^*=0.4$ for $l<\xi$ (solid line) and $\beta=1$ for $l>\xi$ (dotted line). Data fit of the largest window (crosses) gives an effective growth exponent $\beta_{eff}=1.0\pm0.11$, in agreement with the expected value. All experiments under constant $j=2.5$ mA cm^{-2}.

was not observed in the electrochemical data Indeed, at the 2.5 mA cm^{-2} value held for the dynamic surface analysis, the electrode was polarized by *ca* 120 mV above the corrosion potential and was in the active dissolution domain, which confirms previous results from other authors [35,36]. The dissolution was hence kinetically controlled by the charge-transfer surface reactions.

To deep into the origin of the anomalous behavior found in the roughening of the polycrystalline Fe electrode we have shown in Fig. 3 an electric charge sequence of AFM images
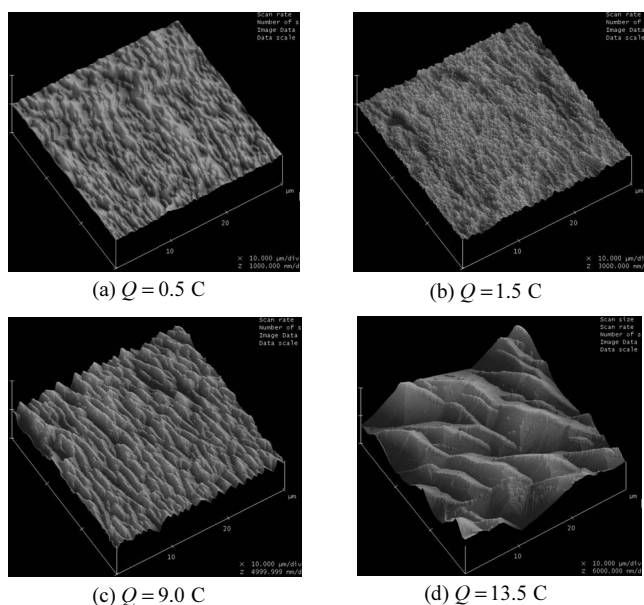

(a) $Q=0.5$ C

(b) $Q=1.5$ C

(c) $Q=9.0$ C

(d) $Q=13.5$ C

FIG. 3. Sequence of 30 μm $\times$ 30 μm AFM images of the Fe electrode after different increasing dissolution charges at constant $j=2.5$ mA cm^{-2}. Height scale in the images increases with dissolution charge.
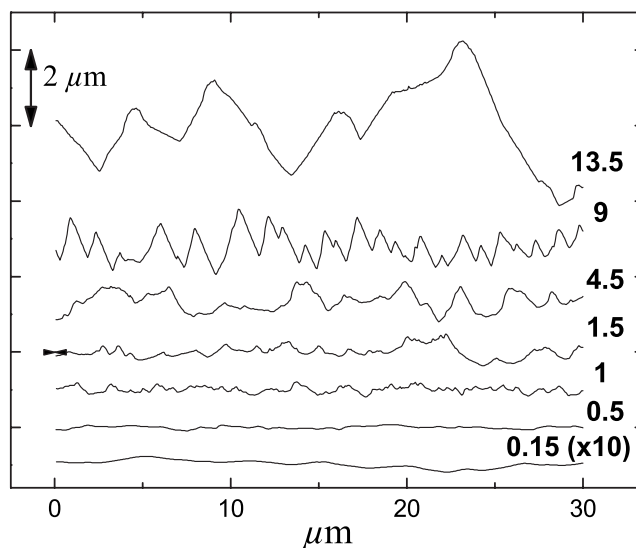

FIG. 4. Cross sections profiles of AFM images, including those displayed in Fig. 3, for increasing dissolution charges.

corresponding to the largest window investigated. Representative surface cross sections of these images are also shown in Fig. 4. The memory of the initial surface topography seems to be reflected in the linear patterned distribution of surface irregularities revealed through Figs. 3(a)–3(c). It has been argued [30] that regular distributed linear scratches usually found after a mechanical polishing may act as preferential sites for the attack thus yielding to this characteristic pattern.

Initial granulated topography evolves toward a smooth mounded surface with mound height increasing faster than width [see Fig. 3(c) and corresponding profile $Q=9$ C, Fig. 4]. In fact, this is an expected behavior for a surface made up of smooth mounds and displaying anomalous scaling [37]. In that case, the average mound lateral size l_c is expected to be the crossover length in Eqs. (2)–(4), scaling according to $l_c \sim t^{1/z}$, and $w_{sat}=w(l,t)$ for $l\gg l_c$ is the corresponding mound height. Since $\alpha_{loc}\sim1$, a simple calculation from Eqs. (4) and (5) leads to the mound aspect ratio w_{sat}/l_c to grow as t^{β^*}. Therefore, for nonzero β^* the aspect ratio increases with the evolution time and surface features become sharper as in the profile corresponding to $Q=9$ C in Fig. 4.

Finally, anisotropic dissolution due to the different crystal orientations exposed in the mounds and cavities drives mound coarsening towards a structured surface formed by facets associated to the different crystallographic textures of the polycrystal. This effect can be clearly seen in Fig. 3(d) and its corresponding profile $Q=13.5$ C of Fig. 4. Differences in the dissolution rates of the different crystallographic orientations yield to preferential dissolution planes and this nonlocal effect is the principal reason of the unstable anomalous dissolution. A similar effect has been found to explain the complex surface dynamic observed during anodic dissolution of Ni [30], although the anomalous scaling exponents differ sensibly, or been argued to explain the driven morphological instabilities observed during the electrodissolution of Cu [5].

The inspection of AFM images seems to suggest that the dynamics of the electrodissolving Fe surface could be described by the new anomalous scaling predicted in [16]. As said, this anomalous kinetics appears in models for interface propagation in random media, as in invasion percolation, in which the stationary state of the equivalent surface growth problem consists of faceted surfaces [33]. A special feature of these systems, as well as in other related models displaying anisotropic growth [38], is that roughening occurs very rapidly, $\beta > 0.5$, and in many cases $\beta \to 1$. This is a consequence of the fact that part of the interface gets stuck in regions with a large local pinning force while other parts advance without resistance. The results reported in this paper agree with this behavior. As we have seen, the local roughness exponent is, within the errors of experimental data, very close to one, the predicted value for this type of scaling. Furthermore, time exponents related to the faceted interface growth reveal an unstable growth $\beta \approx 1$ similar to that already reported for these faceted surfaces. The pinning forces controlling local growth in the invasion phenomenon can be identified with the different dissolution rates of the crystallographic orientations exposed to the electrolyte. That anisotropy in the dissolution leads to those parts of the interface displaying crystal facets with low dissolution rates to become pinned whereas those containing an extremely high density of active sites grow especially rapidly. However, for the present, we cannot affirm if such scaling is taking place in our system since it can be identified only from the scaling of the power spectrum density, and not from the dynamics of either the local width or the height-height correlation function. Therefore, this point remains uncertain and needs additional work.

To finalize, we show preliminary results on the influence of the dissolution potential on the surface structure. Recent results on electrodeposition of Cu under galvanostatic conditions [26] have shown that in the early stages of growth, the electrode potential—or the current density—is the relevant experimental magnitude determining film surface topography. In Fig. 5 we show how the local width varies when anodic current is displaced within the active dissolution region. For consistency, all data correspond to the same dissolution charge.

It can be seen that local width varies in a nonmonotonous way with the current density for the three regions investigated, indicating that competing effects in terms of roughness development—positive and negative—are taking place simultaneously. On the one hand, activation energies for surface transport have been found to be electrode potential dependent [39]. Therefore, as overpotential increases, mobility of metal adatoms is expected to be higher. This effect could be responsible for the decrease of the local roughness with increasing dissolution current density for values lower than 2.5 mA cm^{-2}. On the other hand, at more positive potentials, a rapid dissolution might reveal a roughening controlled by the crystallographic nature of the dissolution, this accounting for the increase of local width with the current after the minimum in Fig. 5. In the case of polycrystalline surfaces, different crystallographic patterns are supposed to establish different profiles in terms of density and localization of kinks and terraces that respond differently to changes of potential val-
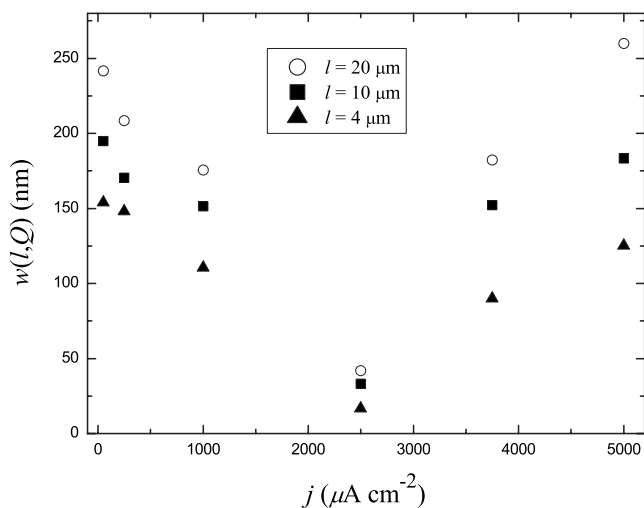

FIG. 5. Variation of the local width with the current density for three electrode windows. Dissolution charge is $Q = 3.6$ C in all cases.

ues. In that case, a variation of the electrode potential affects in a different way distinct crystal orientations, thus varying the relative dissolution crystallographic rates as the potential changes.

Dynamics described above to explain the behavior in Fig. 5 becomes much more complicated if step-edge diffusion energy barriers are considered. It has been shown [40] that the Ehrlich-Schwoebel (ES) barrier also depends on the potential. In that case, another potential-dependent nonlocal effect must be taking into account during driven roughening. Furthermore, the response of the ES barrier to the electrode potential has been found dependent on the crystallographic features of the surface [40], thus yielding to very complex effects on a faceted polycrystalline surface.

The influence of the potential on roughness has already been addressed from a theoretical point of view [9,10]. In all cases that influence is due to the nonlocal effects related to spatial differences in the local dissolution rate. This is observed, for instance, when considering active sites with different reactivity depending on local structure. Then a kinetic-induced roughening transition leading to a monotonous increase of surface roughness with the overpotential is obtained [10]. On the other hand, a heterogeneous surface activity may spontaneously arise from the dynamics of interface evolution. This phenomenon has been observed in models that consider adsorption reactions within the dissolution reactive mechanism [9]. In this case, the interplay between kinetics and roughness leads to a spatial self-organization of adsorbates and this may yield a similar nontrivial behavior such as that displayed in Fig. 5[41].

IV. CONCLUSIONS

Once the scaling properties of the different types of anomalous roughening were properly characterized, further theoretical and experimental effort has then been focused to understand its origin. Since most of the works have been

devoted to the study of growth processes and interface motion in disordered media, most commonly reported nonlocal effects behind anomalous behavior have been related, respectively, to the Laplacian aspect of the growth [18,25,26] and to the nonthermal properties of the quenched noise generated by the medium [32,33]. In this paper we have shown that the study of the less addressed solid phase destruction problem may reveal features on this research.

Dynamic scaling analysis of roughness evolution during anodic dissolution of polycrystalline iron has shown that kinetic roughening is anomalous and unstable. Estimated values of the anomalous scaling exponents, supported by the AFM images displaying the crystallographic nature of the dissolution control, are consistent with a recently reported anomalous scaling that accounts for dynamics of faceted interfaces.

As in the electrodeposition case, the driving force for surface evolution can be adjusted by varying the electrode potential. Very recent results have shown that anomalous exponents in electrodeposited films can be tuned as well [26]. Preliminary evidences reported here indicate that the same might hold in the opposite situation of electrodissolution process. Surface roughness changes nonmonotonously with the applied potential. A rough scaling analysis of these preliminary data points out that scaling exponents are potential dependent, although estimated values are far from being precise. Presently this point is under investigation.

An important question to be addressed also in a future work concerns the long time behavior of the anomalous scaling. Recent reported works on electrodeposition processes [26,29] have shown that thick film behavior is determined by the importance of the nonlocal effect induced by bulk mass transport. When it becomes negligible under the effect of forced convection, anomalous scaling is transient and β^* vanishes for large thick electrodeposited films. On the contrary, when the process becomes controlled by the bulk diffusion, local roughness ($l \ll t^{1/z}$) does not saturate for the thickest films studied and anomalous scaling continues until the film forms overhangs [26], this case corresponding to high current density values. As we have discussed, electrochemical results point out that the possible influence of a diffusion field can be disregarded, which would have a surface smoothening effect on the other side, so within the context of the present results we can expect that anomalous roughening will extend until a crystallographic texture becomes dominant; however, this question needs additional work.

[1] A. L. Barabási and H. E. Stanley, *Fractal Concepts in Surface Growth* (Cambridge University Press, New York, 1995).

[2] P. Meaking, *Fractals, Scaling and Growth Far From Equilibrium* (Cambridge University Press, Cambridge, 1998).

[3] J. Krug, Adv. Phys. **46**, 139 (1997).

[4] A. Iwamoto, T. Yoshinobu, and H. Iwasaki, Phys. Rev. E **59**, 5133 (1999).

[5] S. G. Aziz, M. E. Vela, G. Andreasen, R. C. Salvarezza, A. Hernández-Creus, and A. J. Arvia, Phys. Rev. B **56**, 4166 (1997).

[6] M. E. Vela, G. Andreasen, R. C. Salvarezza, A. Hernández-Creus, and A. J. Arvia, Phys. Rev. B **53**, 10217 (1996).

[7] M. Saitou, A. Makabe, and T. J. Tomoyose, J. Chem. Phys. **113**, 2397 (2000).

[8] H. Martín, P. Carro, A. Hernández Creus, J. Morales, G. Fernández, P. Esparza, S. González, R. C. Salvarezza, and A. J. Arvia, J. Phys. Chem. B **104**, 8229 (2000).

[9] P. Córdoba-Torres, Phys. Rev. B **75**, 115405 (2007).

[10] M. G. Fernandes, R. M. Latanision, and P. C. Searson, Phys. Rev. B **47**, 11749 (1993).

[11] A. Hernández Creus, P. Carro, R. C. Salvarezza, and A. J. Arvia, Langmuir **13**, 833 (1997).

[12] F. Family and T. Vicsek, J. Phys. A **18**, L75 (1985).

[13] J. M. López, M. Castro, and R. Gallego, Phys. Rev. Lett. **94**, 166103 (2005).

[14] R. Cuerno and M. Castro, Phys. Rev. Lett. **87**, 236103 (2001).

[15] J. M. López, Phys. Rev. Lett. **83**, 4594 (1999).

[16] J. J. Ramasco, J. M. López, and M. A. Rodríguez, Phys. Rev. Lett. **84**, 2199 (2000).

[17] J. M. López, M. A. Rodríguez, and R. Cuerno, Phys. Rev. E **56**, 3993 (1997).

[18] M. Castro, R. Cuerno, A. Sánchez, and F. Domínguez-Adame, Phys. Rev. E **57**, R2491 (1998).

[19] J. M. López and M. A. Rodríguez, Phys. Rev. E **54**, R2189 (1996).

[20] S. Yim and T. S. Jones, Phys. Rev. B **73**, 161305(R) (2006).

[21] H.-N. Yang, G.-C. Wang, and T.-M. Lu, Phys. Rev. Lett. **73**, 2348 (1994).

[22] B. A. Sperling and J. R. Abelson, J. Appl. Phys. **101**, 024915 (2007).

[23] J. H. Jeffries, J.-K. Zuo, and M. M. Craig, Phys. Rev. Lett. **76**, 4931 (1996).

[24] M. A. Auger, L. Vázquez, R. Cuerno, M. Castro, M. Jergel, and O. Sánchez, Phys. Rev. B **73**, 045436 (2006).

[25] S. Huo and W. Schwarzacher, Phys. Rev. Lett. **86**, 256 (2001).

[26] M. C. Lafouresse, P. J. Heard, and W. Schwarzacher, Phys. Rev. Lett. **98**, 236101 (2007).

[27] H. Matsushima, Y. Fukunaka, Y. Ito, A. Bund, and W. Plieth, J. Electroanal. Chem. **587**, 93 (2006).

[28] M. Saitou, Phys. Rev. B **66**, 073416 (2002).

[29] A. Osafo-Acquaah, Y. Shapir, and J. Jorne, J. Electrochem. Soc. **153**, C535 (2006).

[30] A. G. Muñoz, M. E. Vela, and R. C. Salvarezza, Langmuir **21**, 9238 (2005).

[31] H.-N. Yang, G.-C. Wang, and T.-M. Lu, Phys. Rev. B **50**, 7635 (1994).

[32] J. Soriano, J. J. Ramasco, M. A. Rodríguez, A. Hernández-Machado, and J. Ortín, Phys. Rev. Lett. **89**, 026102 (2002).

[33] I. G. Szendro, J. M. López, and M. A. Rodríguez, Phys. Rev. E **76**, 011603 (2007).

[34] K. Sneppen, Phys. Rev. Lett. **69**, 3539 (1992).

[35] Z. Lu, D. Huang, W. Yang, J. Congleton, Corros. Sci. **45**, 2233

(2003).

[36] C. Jeyaprabha, S. Sathiyanarayanan, and G. Venkatachari, Appl. Surf. Sci. **246**, 108 (2005).

[37] J. Krug, Physica A **263**, 170 (1999).

[38] R. Cafiero, Phys. Rev. E **63**, 046108 (2001).

[39] M. Giesen, G. Beltramo, S. Dieluweit, J. Müller, H. Ibach, and W. Schmickler, Surf. Sci. **595**, 127 (2005).

[40] M. I. Haftel and M. Rosen, Phys. Rev. B **68**, 165402 (2003).

[41] P. Córdoba-Torres, R. P. Nogueira, and V. Fairén, J. Electroanal. Chem. **529**, 109 (2002).