

Reversible change in surface roughness and the inductive loop at electrodes under corrosion conditions

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Inductive loops are often observed in the electrochemical impedance diagrams of complex electrochemical systems. This feature is generally attributed to the potential-induced adsorption-desorption of a species affecting the electrochemical transfer rate. Interestingly, this behavior appears systematically present for electrodes under corrosion conditions, and a simple relationship between the characteristic frequency f_c of the inductive loop and the steady-state current density J_0 has been pointed out by Ern e and Vanmaekelbergh [1], namely $J_0/2\pi f_c = eN_s$, where e is elementary charge and N_s is a characteristic surface concentration, systematically found to be on the order of a monolayer (10^{15} cm^{-2}). The models based on an adsorption/desorption mechanism may be consistent with such a proportionality relationship, but the expected value for N_s would then be on the order of $k_B TC_H/e^2$, where C_H is Helmholtz capacitance and k_B and T have their usual meanings, a value one to two orders of magnitude smaller than that found experimentally. We show here that a mechanism in terms of a potential-dependent surface roughness, suggested long ago but never assessed, does plausibly account for these experimental findings.

We made numerical simulations of the dissolution of an electrode. The electrode/electrolyte system was modeled in 2D as a square lattice of points, each point bearing an integer code $i = 0$ to 4 representing its nature and environment: $i = 0$ for a bulk-electrode site, 1 to 3 for a surface site (the integer representing the number of electrolyte neighbors, i.e., 1 for a terrace site, 2 for a step site, and 3 for an adatom), and $i = 4$ for an electrolyte site. Each type of surface site i (with $i = 1$ to 3) was assigned a dissolution probability p_i (with $p_1 < p_2 < p_3$, see Fig. 1) and the evolution of the interface shape was monitored by using a Monte-Carlo simulation.

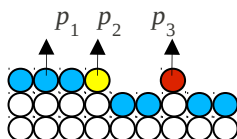


Fig. 1. Scheme for the various dissolution probabilities.

At each step, the average current $I = e\sum p_i n_i$, where n_i is the number of sites of type i , was recorded. It was found that for a given set of dissolution probabilities, and starting from an atomically flat electrode, the current first increases, then becomes more or less constant, that is, it tends to fluctuate around a steady-state value; in other words, the surface roughens up to a steady-state value. Figure 2 shows a typical scheme of the electrode/electrolyte interface in this steady state, for three different sets of probabilities, using a law of the type $p_i \propto \alpha^i$ (with $\alpha > 1$). The roughness is seen to be all the more important as α is smaller (isotropic dissolution).

As a next step, we monitored the behavior of I upon suddenly changing the set of the p_i 's. It first undergoes a step variation, corresponding to the change in the p_i 's at the "frozen" interface, then a relaxation of the roughness takes place, till the new steady state is reached (Fig. 3a). Most importantly, this change is found to be reversible; that is, the same steady-state current, characteristic of the new set, is reached whether the previous surface roughness is higher or lower than the new

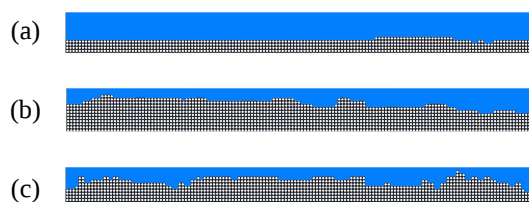


Fig. 2. Scheme of the interface in the steady state for various sets of dissolution probabilities of the type $p_i \propto \alpha^i$. (a) $\alpha = 1000$ (high anisotropy); (b) $\alpha = 100$; (c) $\alpha = 10$ (low anisotropy).

one. Figure 3a shows a typical sequence obtained upon switching the p_i 's between two sets of values. When such a sequence is repeated many times and the resulting response averaged, the statistical noise is reduced (Fig. 3b), and provided that the change in the p_i 's between the two sets is small enough, Fourier-transforming the obtained data leads to a complex response, which can be plotted as a Cole-Cole diagram.

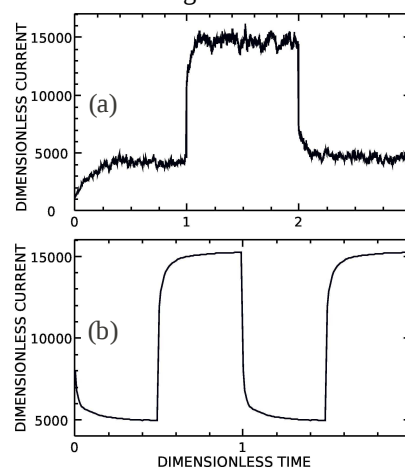


Fig. 3. Change in current induced by a change in the p_i 's. Simulation on a 1000-point wide electrode. (a) $(p_1, p_2, p_3) = (1, 10, 100)$ from $t = 0$ to 1, then $(5, 20, 80)$ from $t = 1$ to 2, and again $(1, 10, 100)$ from $t = 2$ to 3. (b) Periodic square-wave modulation between these two sets, with a period of 1, and averaged over 1000 periods and smoothed.

In practice, the p_i 's plausibly tend to become more isotropic as potential is increased. A convenient law reproducing this behavior is $p_i \propto \exp[(x-yi)e(E-E_0)/k_B T]$, where E_0 is a characteristic potential, and x and y dimensionless parameters. Using such a law and applying a small square-wave modulation (typically ± 10 mV), an electrochemical impedance diagram can be obtained. Figure 4 gives an example of such a diagram. It can generally be fitted as a depressed inductive semi-circle. The ratio $J_0/2\pi e f_c$ comes out on the order of a monolayer, as it may be expected for a relaxation of the surface roughness. This points the mechanism of roughness change as the best candidate for the explanation of the inductive loop at electrodes under corrosion conditions.

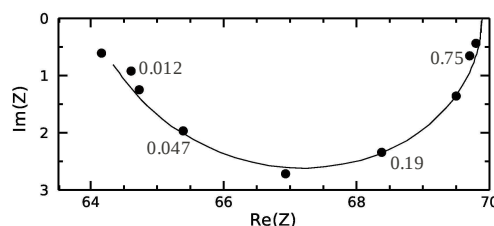


Fig. 4 Typical simulation of an impedance spectrum, fitted as a depressed semicircle $Z = R_p + (R_{ct} - R_p)/(1 - jf_c/f)^\zeta$. The p_i 's are given by $x = 1$, $y = 0.2$, $E - E_0 = -40$ mV. $J_0/2\pi e f_c = 0.61$ monolayer.

[1] B.H. Ern e and D. Vanmaekelbergh, J. Electrochem. Soc. **144**, 3385 (1997).