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Corrosion.m, a *Mathematica™* PACKAGE for doing ELECTROCHEMISTRY and CORROSION by COMPUTER

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Mathematica™ is a general system for doing numerical and symbolics calculations or two and three-dimensionals graphics, as well as a programming language and a computing environment [1]. Corrosion.m is a package designed for electrochemistry and corrosion studies in the field of research and education. Corrosion.m is available upon request by e.mail at erase@grenet.fr. Two examples of use are presented below.

Validity of the Tafel slope extrapolation method

Built-in Mathematica graphics functions such as Plot are useful for drawing and studying the influence of parameters upon the shapes of the polarization curves and limitations of the so-called Tafel slope extrapolation method (fig. 1)[2,3,4]. Corrosion.m includes, for this purpose, Butler-Volmer equations. Figure 1 shows the Tafel slope extrapolation method for a corroding metal when the corrosion potential lies close to the reversible potential of the metal. The corrosion density current error can be estimated for equal Tafel slopes ($b_{a1} = b_{a2} = b_a$, $b_{c1} = b_{c2} = b_c$) in the absence of transport limitations. In this restricted case the corrosion current $i_{corTafel}$ measured by Tafel slope extrapolation method is given by

$$\begin{aligned} i_{corTafel} &= i_{01} \exp [2.3 (E_c - E_{th1})/b_a] + i_{02} \exp [2.3 (E_c - E_{th2})/b_a] \\ &= i_{01} \exp [-2.3 (E_c - E_{th1})/b_c] + i_{02} \exp [-2.3 (E_c - E_{th2})/b_c] \end{aligned} \qquad (1)$$

[1] S. Wolfram, Mathematica™, Addison Wesley, Redwood City (1988).

[2] F. Mansfeld, The polarization resistance technique for measuring corrosion currents, Advances in Corrosion and Technology, Vol. 6, Ed. M. G. Fontana and R. W. Staehle, Plenum Press, New York, 1976.

[3] D. Landolt, Corrosion et chimie des surfaces des métaux, Presses Polytechniques et Universitaires Romandes, Lausanne, 1993.

[4] J.-P. Diard, B. Le Gorrec, C. Montella, Cinétique Électrochimique, to be published.

where i_{01} and i_{02} are the exchange density currents, E_{th1} and E_{th2} the reversible potentials, and E_c is the corrosion potential. The true corrosion current i_{cor} is given by

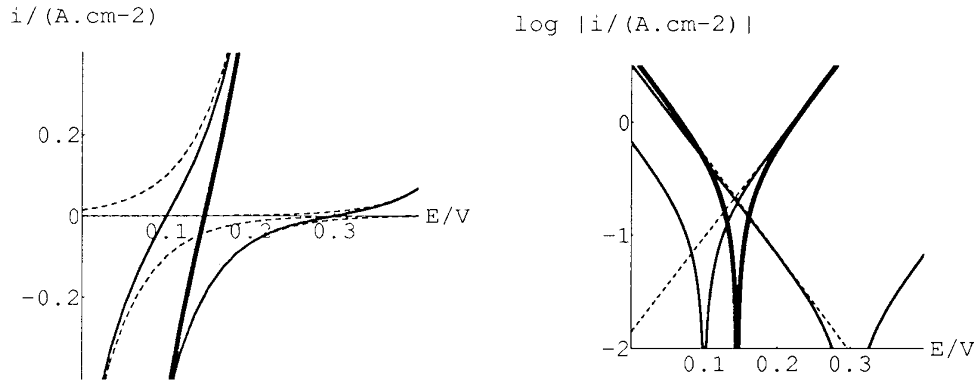

Figure 1 : Theoretical polarization curves for a corroding metal when the corrosion potential lies close to the reversible potential of the metal. Thick and thin lines : overall current, dashed lines : partial currents (i vs E curve) or Tafel lines. E_{th1} = 0.1 V, E_{th2} = 0.3 V, i_{01} = 10^{-1} A.cm^{-2}, i_{02} = 10^{-2} A.cm^{-2}, $b_{a1} = b_{c1} = b_{a2} = b_{c2} = 0.12$ V.

$$i_{cor} = i_{01} (\exp [2.3 (E_c - E_{th1})/b_{a1}] - \exp [2.3 (E_c - E_{th1})/b_{c1}]) \quad (2)$$

The relative error can be expressed as[5]

$$\text{er } i_{cor} = 100 (i_{corTafel} - i_{cor})/i_{cor} \quad (3)$$

For the example in Fig. 2 the above error is equal to ≈ 20 %. The corrosion potential is numerically calculable with the FindRoot function allowing to plot the isoerror diagram using the ContourPlot function (Fig. 2).

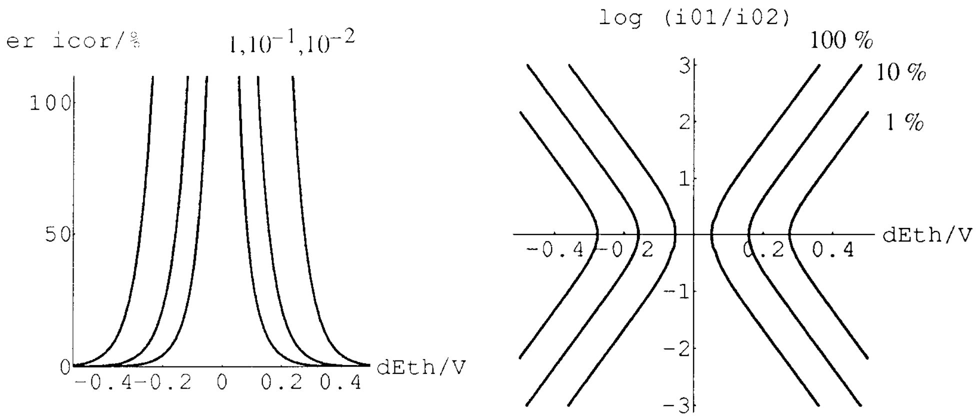

Figure 2 : Plot of er i_{cor} against $dE_{th} = E_{th1} - E_{th2}$ calculated for i_{01}/i_{02} = 1, 10^{-1}, 10^{-2} and isoerror diagram. $b_a = b_c$ = 0.12 V. The contours correspond to errors of 1 %, 10 % and 100 %.

[5] Z. Nagy, DC Electrochemical techniques for the measurement of corrosion rates, Modern Aspect of Electrochemistry, N° 25, edited by J. O'M Bockris et al. Plenum Press, New York, 1993.

Corrosion current measurements by curve fitting

Mathematica's numerical functions as NonlinearFit can be used to design new measuring method in the field of corrosion studies.

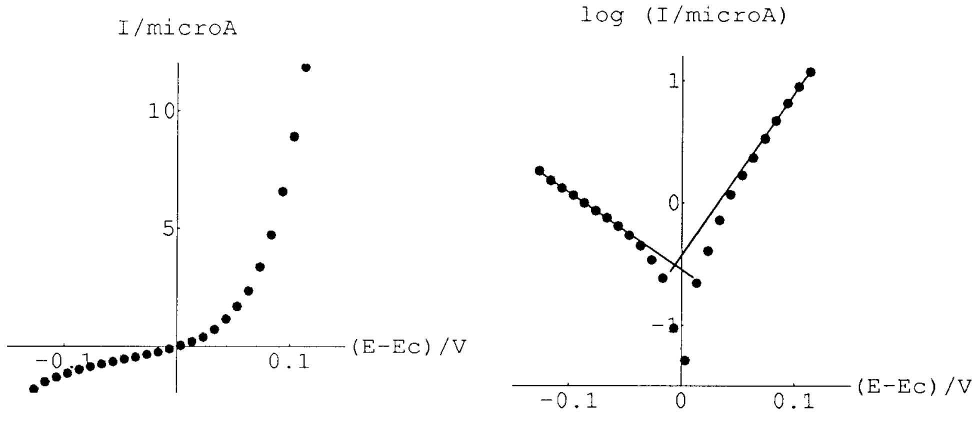

Figure 3 : Experimental data and Tafel slope extrapolation method (4 anodic experimental points and 7 cathodic one). Rotating disk electrode : Fe (Johnson Mattey 99.9985 %) in deaerated acidic medium (HCl 0.1 M, KCl 0.9 M), S = 7.85 10^{-3} cm^2, Ω = 10^3 rpm. I_{cor} = 0.31 µA, b_a = 0.075 V, b_c = 0.16 V.

As an example the current vs potential curve for a Fe rotating disk electrode in an acidic medium is shown in the figure 3. The measurements were carried out within a narrow range of potential (≈ 0.25 V). It is nevertheless possible to determine the corrosion current by Tafel slope extrapolation (Fig. 3) or by curve fitting of the experimental polarization curve to the theoretical curve[6,7].

(i) 3-parameter curve fitting (I_{cor}, b_a and b_c)
The corrosion current may be obtained from experimental data $I_{exp}(E_i)$ by minimising the least square criterium D_{expth}

$$D_{expth} = \Sigma_i \, [I_{exp}(E_i) - I_{th}(E_i)]^2 \tag{4}$$

where $i_{th}(E)$ is supposed to be given by

$$i_{th}(E) = I_{cor} \{\exp [2.3 (E - E_c)/b_a] - \exp [- 2.3 (E - E_c)/b_c]\} \tag{5}$$

The model I_{th} is a 3-parameter model : I_{cor} , b_a and b_c. It is always possible to take 0.12 V for initial starting value of the Tafel slopes, it is then necessary to choose an initial starting value for the corrosion current.

[6] F. Mansfeld, Werkstoffe Korros. 28 (1977) 6.

[7] P. Hougaard and D. H. Britz, Corrosion Science, 23 (1983) 271.

(ii) 2-parameter curve fitting (b_a and b_c)
The corrosion current density I_{cor} is a linear parameter and b_a and b_c are non-linear parameters, so it is possible to eliminate I_{cor} in a nonlinear regression [8,9,10]. As a matter of fact differentiating D_{expth} (eq. 4) with respect to I_{cor} gives :

$$\partial D_{expth}/\partial I_{cor} = -2\,\Sigma_i\,[I_{exp}(E_i) - I_{th}(E_i)]\,\partial I_{th}(E_i)/\partial I_{cor} = 0 \qquad (6)$$

provided that D_{expth} is minimal. From eq. 6, linear in the parameter I_{cor}, one obtains

$$I_{cor} = \frac{\Sigma_i\; I_{exp}(E_i)\,\{\exp[2.3\,(E_i - E_{cor})/b_a] - \exp[-2.3\,(E_i - E_{cor})/b_c]\}}{\Sigma_i\,\{\exp[2.3\,(E_i - E_{cor})/b_a] - \exp[-2.3\,(E_i - E_{cor})/b_c]\}^2} \qquad (7)$$

Substituting I_{cor} in eq. 5 using eq. 7 gives a reduced model. The reduced model is a non-linear model with only two unknown parameters b_a and b_c. The advantage of this new method is to reduce the dimension of the space of parametric search and to avoid the need of a starting value for I_{cor}. The method is not quicker with 2 parameters than with 3 as the calculation of the current (eq. 7) is now longer. Example of use of the method is given in the figure 4.

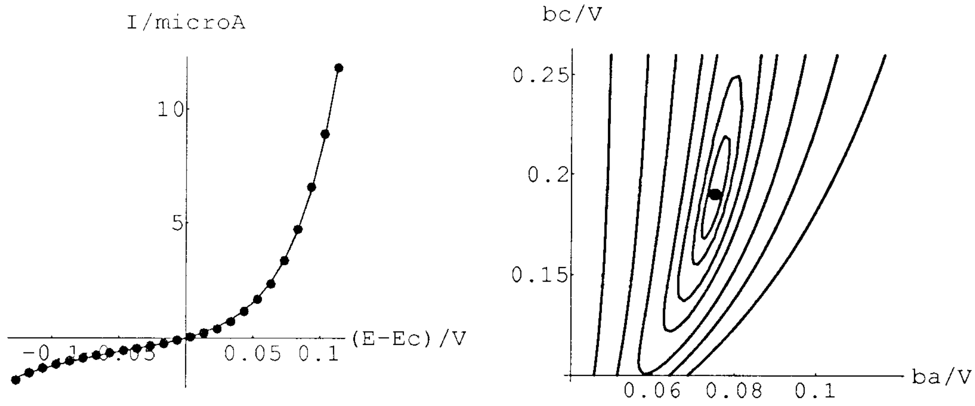

Figure 4 : Experimental data (points) and fitted curve (solid line) and isocriterium curve. I_{cor} = 0.37 µA, b_a = 0.075 V, b_c = 0.19 V.

Since the model now only depends on 2 parameters, it is possible to plot 2D isocriterium curves. Figure 4 shows that the parameter b_a is determined more precisely than b_c.

[8] Identification de modèles paramétriques à partir de données expérimentales, E. Walter et L. Pronzato, Masson, Paris, 1994.
[9] W. H. Lawton and E. A. Sylvestre, Technometrics, 13 (1971) 461.
[10] R. H. Barham and W. Drane, Technometrics, 14 (1972) 757.