SHORT COMMUNICATIONS

MEASUREMENT OF POLARIZATION RESISTANCE AND DOUBLE-LAYER CAPACITY OF CORROSION SYSTEM BY EXPONENTIAL LINEAR RELAXATION TECHNIQUE

V. LAKSHMINARAYANAN and
S. R. RAJAGOPALAN*
Raman Research Institute, Bangalore 560080, India.
* *Materials Science Division, National Aeronautical Laboratory, Bangalore 560017, India.*

AN exponential linear relaxation technique for measurement of kinetic parameters of electrochemical systems was proposed by Rangarajan[1]. It was demonstrated that this method could be used to measure the double-layer capacitance as well[2]. In this paper we show that this linear relaxation technique can be used to measure the polarization resistance and double-layer capacitance of corrosion systems.

When an exponentially decaying current input of a small magnitude is applied to a corrosion system which is purely under activation control, the linearized current-potential relationship takes the form,

$$-C_d\frac{d\eta}{dt} - \frac{(\alpha_c+\beta_a)nF\eta\, i_{corr}}{RT} = i = \Delta I \exp(-t/\tau), \quad (1)$$

where $\Delta I \exp(-t/\tau)$ represents the current input, C_d is the double-layer capacitance of the corrosion system, α_c and β_a are respectively the transfer coefficients of the cathodic and anodic conjugate reactions of corrosion and i_{corr} is the corrosion rate.

The solution of (1) is given by,

$$\eta = \frac{\Delta I R_p \tau_d}{(\tau_d - 1)}[\exp(-t/\tau) - \exp(-\tau_d t/\tau)] \quad (2)$$

where $R_p = \frac{RT}{(\alpha_c+\beta_a)nF\, i_{corr}}$ and $\tau_d = \frac{\tau}{R_p C_d}$.

It can be seen from (2) that the potential-time transient exhibits a maximum. This is essentially due to a time lag in overpotential (η) following current (i). For a corrosion system under activation control, the double-layer charging current ($= -C_d(d\eta/dt)$) is zero at the maximum point and the entire current is purely faradaic. Utilising this fact it can be shown,

$$R_p = \frac{-\eta_{max}}{\Delta I \exp(-t_{max}/\tau)} \quad (3)$$

where η_{max} and t_{max} are the co-ordinates of the maximum of $\eta - t$ transient.

For the same case, it can be shown from (2) that

$$(t_{max}/\tau) = \ln \tau_d/(\tau_d - 1). \quad (4)$$

It is clear that using (3) and (4) R_p and C_d can be obtained from a single transient for a corrosion system which is under activation control.

A second method of getting R_p and C_d would be by fitting a curve, represented by (2), to the experimental data. A third method of obtaining R_p, is to plot η_{max} against i (corresponding to t_{max}) and evaluate $d\eta/di$ ($= R_p$). This method is a multitransient approach in contrast to the other two which employ only a single transient. It can be seen that all the three methods yield R_p values uncorrupted by double-layer charging.

The above expectations were verified by using the system, mildsteel (MS) in 1N sulphuric acid (deaerated), employing a galvanostat to impress the exponential current signal and recording the $\eta - t$ transient on a specially designed transient data recorder[3] the details of which will be published elsewhere.

Table 1 *Polarization resistance (R_p) of MS in 1N H_2SO_4 (deaerated) obtained by exponential linear relaxation technique*

	τ (m sec)	R_p from cathodic polarization (ohm.cm^2)	R_p from anodic polarization (ohm.cm^2)
Method 1	1	14.71	14.21
(by using eqn. (3))	1000	13.98	14.56
Method 2 (by curve fitting)	1	15.38	14.25
Method 3	1	14.85	14.52
(multitransient approach	1000	13.72	13.85
Steady-state linear polarization	–	14.02	14.07

Table 2 *Double-layer capacitance (C_d) for the system, MS in 1N H_2SO_4 (deaerated) by the exponential linear relaxation method ($\tau = 1$ m sec)*

	C_d from cathodic polarization ($\mu F/cm^2$)	C_d from anodic polarization ($\mu F/cm^2$)
(i) curve fitting	86.71	93.56
(ii) From η_{max} and t_{max} (using eqs. (3) and (4))	89.78	91.80

R_p values for this system obtained by all the three methods, described above, are shown in table 1. They are in good agreement with R_p values obtained by steady-state linear polarization technique. Thus, the exponential linear relaxation method of Rangarajan[1] could be considered as the transient analogue of linear polarization technique for measurement of corrosion rate but with a difference. The transient technique yields an additional information, namely C_d in the vicinity of corrosion potential.

For the system, mild steel in 1N sulphuric acid C_d value calculated from η_{max} and t_{max} using equations (3) and (4) as well as by curve fitting are shown in table 2. Donahue and Nobe[4] obtained a value of 55 ± 13 $\mu F/cm^2$ (at corrosion potential) for the interfacial capacitance of iron in deaerated 1N H_2SO_4, by galvanostatic charging technique. For the system MS in 0.5 N H_2SO_4 Devarajan and Balakrishnan[5] obtained (by small amplitude cyclic voltammetry) a C_d value of 166 $\mu F/cm^2$. This rather large value has been ascribed by them to be due to pseudocapacitance. Comparing the value given in this work with the reported values, it can be concluded that this method yields C_d data of the correct order of magnitude.

15 April 1986

1. Rangarajan, S. K., *J. Electroanal. Chem.*, 1973, **41**, 491.
2. Tilak, B. V., Rader, C. G. and Rangarajan, S. K., *J. Electro. Chem. Soc.*, 1977, **24**, 1879.
3. Lakshminarayanan, V., Aithu Poojary and Rajagopalan, S. R., (Unpublished work).
4. Donahue, F. M. and Nobe, K., *Proc. Second Int. Conf. Metallic Corrosion*, NACE, Houston, 1966, p. 916.
5. Devarajan, G. and Balakrishnan, K., *Trans., SAEST*, 1984, **19**, 71.