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## Technical Note: On Ambiguities in Modeling Electrochemical Impedance Spectra Using Circuit Analogues ☆

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### DISCUSSION

Electrochemical impedance spectroscopy (EIS) is often used to obtain corrosion-related information when knowledge of the corrosion mechanism and the environment is incomplete. This dilemma often forces the corrosion practitioner to resort to phenomenological circuit models to make the required prediction from the experimental information. The recent proliferation of "all-purpose" computer programs that can be used to estimate values for linear circuit analogues from the spectra is making such modeling a routine exercise.<sup>1-4</sup> The tendency might be to assume that good agreement between the measured impedance spectrum and that calculated from the modeling circuit means that the model used is the best representation of the corrosion mechanism and provides an explanation for it. However, one cannot assume the uniqueness of a circuit model merely on the basis of a good fit to the observed spectrum.

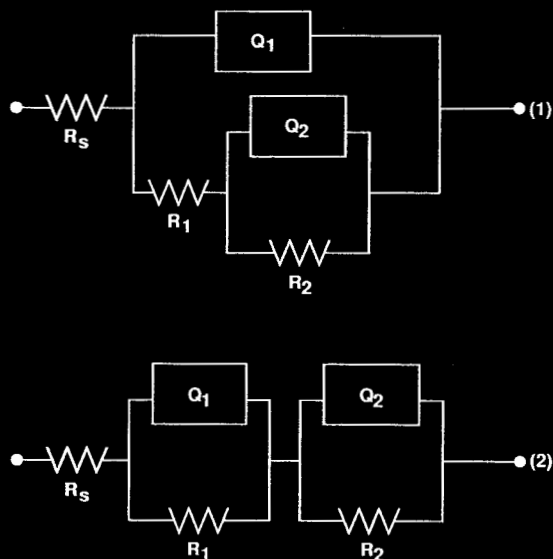
Impedance spectra having two relaxation time constants are commonly encountered when examining corrosion under organic coatings,<sup>5,6</sup> certain instances of localized corrosion,<sup>7</sup> inhibited systems,<sup>8,9</sup> and systems in which a surface layer or crust can form.<sup>10</sup> The two-time-constant model often used to explain these results is that shown as Circuit (1) in Figure 1. The meanings of

the circuit elements depends on the physical situation. In some cases  $R_1$  is related to the charge transfer resistance.<sup>9</sup> In other cases  $R_2$  is related to the polarization resistance.<sup>5,6,8,10</sup> These studies demonstrated through either additional measurements or additional calculations that at least some of the elements could be related to actual subprocesses. As shown below, two different models with identical circuit elements can fit the same impedance spectrum. This ambiguity depends on the values of certain circuit elements in systems exhibiting two time constants.

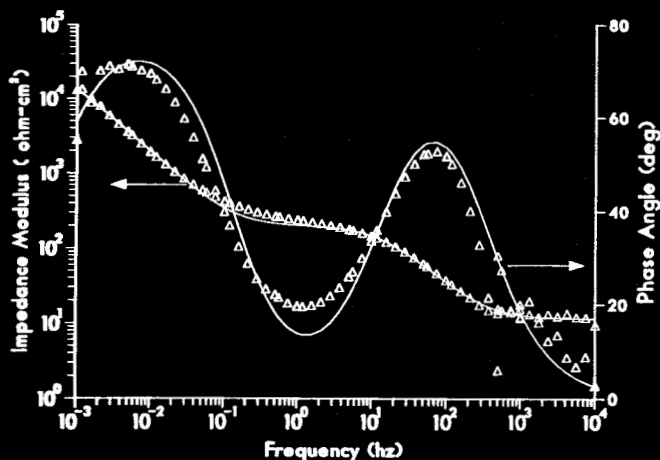
Recently, impedance spectra were used to predict corrosion rates rapidly in poorly characterized fluids.<sup>10,11</sup> In those studies, the models were never stated to be the best representations of the corrosion mechanism. They were only stated to be adequate for providing estimates of the polarization resistance. Figure 2 shows the impedance spectrum from the waste stream study<sup>10</sup> for exposure of steel at pH 9 after 139 hours of exposure. The calculated curve corresponds to Circuit (1) with elements estimated from the nonlinear regression routine reported elsewhere.<sup>1</sup> Table 1 shows the circuit elements. However, Circuit (2) in Figure 1 can also create two relaxation time constants. Figure 3 shows the results using Circuit (2) for the calculated curve. The circuit elements used to generate the calculated curve in Figure 3 are the same as those used in Figure 2. The program EQUIVORT of Boukamp<sup>12</sup> was used for the simulation to generate both figures. The regression had difficulty performing a curve-fit using the entire data set.

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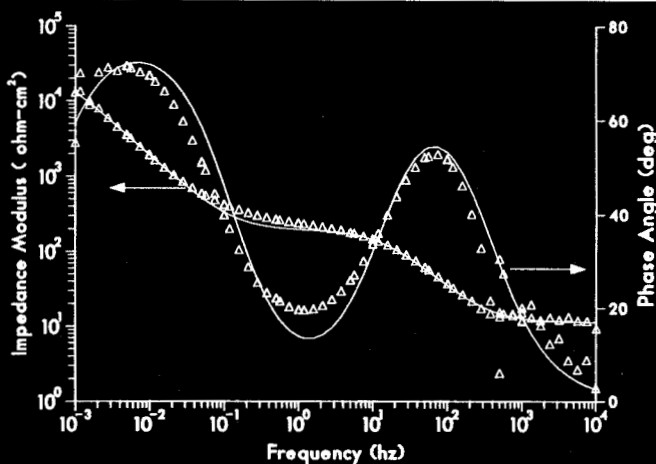
**FIGURE 1.** Circuit models that yield impedance spectra with two relaxation time constants: (1) nested parallel circuit, (2) series circuit.



**FIGURE 2.** Measured impedance spectrum (Bode format) versus that calculated using Circuit (1) in Figure 1 and parameters in Table 1. Solid line is calculated curve. Data are from Reference 10.

**TABLE 1**  
Values of Circuit Elements  
for the Two Circuits in Figure 1

Circuit Element	Value
$R_s$ (ohm-cm <sup>2</sup> )	$1.14 \times 10$
$R_2$ (ohm-cm <sup>2</sup> )	$1.87 \times 10^2$
$A_1$ (farad/cm <sup>2</sup> )	$1.04 \times 10^{-4}$
$\beta_1$	$8.88 \times 10^{-1}$
$R_1$ (ohm-cm <sup>2</sup> )	$3.72 \times 10^4$
$A_2$ (farad/cm <sup>2</sup> )	$6.12 \times 10^{-3}$
$\beta_2$	$8.91 \times 10^{-1}$



**FIGURE 3.** Measured impedance spectrum (Bode format) versus that calculated using Circuit (2) in Figure 1 and parameters in Table 1. Solid line is calculated curve. Data are from Reference 10.

Therefore, the high- and low-frequency portions of the spectra were each fit to a circuit containing a parallel combination of a resistor and constant phase element. Then the entire spectrum was regenerated from the calculated elements using the circuits shown in Figure 1. Corrosion rates estimated from the values of  $R_2$  agreed with those estimated from the short-term mass loss of the electrode.<sup>10</sup>

The agreement between calculated and measured impedance spectra for the two models is caused by the relative values of the constant phase elements. Following Boukamp, the term Q is used for the impedance contribution of the capacitance including a constant phase element. It is equivalent to the term  $(A(j\omega)^\beta)^{-1}$  where A is the magnitude of the constant phase element,  $\omega$  is the frequency in rad-s<sup>-1</sup>,  $\beta$  is a constant usually lying between 0.5 and 1, and R is the resistance. The equation that describes the overall impedance of the nested parallel Circuit (1) after appropriate simplification is

$$Z = R_s + \frac{R_1 R_2 Q_1 + R_1 Q_1 Q_2 + R_2 Q_1 Q_2}{R_1 R_2 + R_1 Q_2 + R_2 Q_1 \left(1 + \frac{Q_2}{Q_1}\right) + Q_1 Q_2} \quad (1)$$

The comparable equation for the series Circuit (2) is

$$Z = R_s + \frac{R_1 R_2 Q_1 \left(1 + \frac{Q_2}{Q_1}\right) + R_1 Q_1 Q_2 + R_2 Q_1 Q_2}{R_1 R_2 + R_1 Q_2 + R_2 Q_1 + Q_1 Q_2} \quad (2)$$

The only difference between these equations is the location of the term containing  $(Q_2/Q_1)$ . If this term is much less than 1, then  $1 + (Q_2/Q_1)$  becomes approximately equal to 1. The magnitude of Q is the inverse of the value of A reported in Table 1.

Thus, the magnitude of  $Q_2/Q_1$  is equal to  $A_1/A_2$ . The quotient  $A_1/A_2$  equals 0.017. This number is very small relative to 1. Since the experimental data have scatter, the effect of the small value of this ratio is probably buried within the numerical "noise". Nonlinear regression analysis would not easily distinguish between the two models. Large differences in the values of the constant phase elements  $A_1$  and  $A_2$  can lead to an inability to distinguish between the two models.

From the standpoint of screening for corrosion rates, which was the main thrust of the original study, use of either model to obtain  $R_p$ , the polarization resistance, leads to about the same value of corrosion rate. The lack of sensitivity of the regression analysis to distinguish between the models does not detract from the ability of the impedance technique to be used for practical and rapid corrosion rate screening<sup>10</sup> as long as some corroboration of the corrosion rate is available. However, this type of ambiguity does mean that making conclusions about the corrosion mechanism from the circuit used to model the impedance spectrum must be done with care. Agreement between corrosion rates calculated from the polarization resistance and those from the weight change of the electrode does not confirm the validity of the circuit model. Additional characterization measurements are required to verify that the model is consistent with the physics and chemistry of the mechanism. This conclusion means that while the new personal computer-based software greatly increases the ability to model impedance spectra, the resulting circuit models must be used with care when applied to explanations of corrosion mechanisms.

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