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# A New Look at Graphical Representation of Impedance Data with Application to Corrosion in Saline Solutions

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Graphical methods provide the first step toward interpretation and evaluation of impedance data. IR-corrected Bode plots, log-log plots of the imaginary component of the impedance, and effective capacitance plots are shown to be useful complements to the more traditionally used complex-plane and Bode representations for impedance data. Bode plots, in particular, are confounded by the influence of electrolyte resistance. The plots proposed here provide useful guides to model development for both reactive and blocking systems.

The presence of electrolyte resistance confounds the use of phase angle plots to estimate characteristic frequencies. Phase angle plots suggest, incorrectly, that the current and potential should be in-phase at high frequencies; whereas, at high frequencies, for ideally capacitive systems, the current and potential are exactly out of phase. If an accurate estimate for electrolyte resistance $R_{e,\mathrm{est}}$ is available, a modified Bode representation is possible following

$$|Z|^{*} = \sqrt{\left(Z_r - R_{e,\mathrm{est}}\right)^2 + Z_j^2} \quad (1)$$

and

$$f^{*} = \tan^{-1}\left(\frac{Z_j}{Z_r - R_{e,\mathrm{est}}}\right) \quad (2)$$

The resulting figures show the expected asymptotic behavior at high frequencies. The IR-corrected phase angle tends toward a non-zero constant value, and slope of the IR-corrected magnitude yields the coefficient for a high-frequency constant-phase element (CPE). Caution should be used, however, when interpreting IR-corrected Bode plots. Incorrect estimates for $R_{e,\mathrm{est}}$ can give the appearance of an additional high-frequency relaxation process. Perhaps more important, the subtraction $Z_r - R_{e,\mathrm{est}}$ yields a result dominated by stochastic noise at high frequencies.

The difficulties associated with the IR-corrected Bode plots can be obviated by plotting the real and imaginary components of the impedance. Plots of the imaginary part of the impedance as a function of frequency on a log-log scale are particularly helpful. The slopes of the lines at low and high frequency indicate the number of time constants that can be discerned and whether the features have CPE characteristics. Characteristic frequencies are correctly identified as the peaks of the imaginary impedance plot. The slopes of the lines at low and high frequency are directly related to the coefficients of CPE elements.

Such plots can also indicate whether time constants are coupled through a double-layer capacitance. Log-log plots of imaginary impedance can be used to distinguish between a depressed impedance plane semicircle caused by a continuous distribution of time constants associated with a CPE and that caused by contributions of discrete processes with closely overlapping but discrete time constants. Similar information can be obtained from plots of the real part of the impedance as a function of frequency on a log-log scale.

The information obtained from plotting the real and imaginary parts of the impedance as a function of frequency can be complemented by use of an effective capacitance representation, given as

$$C_{\mathrm{eff}} = \cos\left(\frac{ap}{2}\right) - \frac{Z_{\mathrm{j}}(w)}{w} \quad (3)$$

where $a$ is the CPE coefficient defined such that

$$Z_{\mathrm{CPE}} = \frac{1}{Q_{\mathrm{CPE}}\left(jw\right)^{1-a}} \quad (4)$$

The high-frequency limit of the effective capacitance yields, for purely capacitive systems, the high-frequency capacitance of the system. In the case of CPE behavior, the effective capacitance representation yields an effective CPE coefficient $Q_{\mathrm{CPE}}$, which can be related to the double layer capacitance through a model of the distributed time constants following Brug et al.[1]

The graphical methods described above are illustrated both by synthetic data and by experimental data associated with corrosion in saline environments. IR-corrected Bode plots, log-log plots of the imaginary component of the impedance, and effective capacitance plots are shown to be useful complements to the traditional complex-impedance-plane and Bode representations for impedance data. Bode plots are shown, in particular, to be confounded by the influence of electrolyte resistance. The plots proposed here provide useful guides to model development for both reactive and blocking systems.

## References

[1] G. J. Brug, A. L. G. Van den Eeden, M. Sluyters-Rehbach, and J. H. Sluyters, Journal of Electroanalytical Chemistry, 176 (1984), 275-295.