

The Influence of Coupled Faradaic and Charging Currents on Impedance Spectroscopy

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Impedance results showing Constant-Phase-Element (CPE) behavior are ubiquitous in electrochemistry. Jorcin et al.¹ have suggested that such CPE behavior can be attributed to surface and/or normal distributions of time constants. This powerful insight has facilitated categorization of different models for extracting meaningful physical properties from CPE parameters. The current best-of-class models are those presented by Brug et al.² for surface distributions and the power-law model of Hirschorn et al.^{3,4} for normal distributions.

This paper will suggest that another potential origin for CPE behavior may be found in the coupling of faradaic and charging currents. While faradaic and charging currents are usually considered separately for simulations of impedance response,⁵ Delahay⁶ suggested in 1966 that the flux of reacting species should contribute to the charging of the interface as well as to the faradaic reaction. Recent simulations suggest that treatment of coupled faradaic and charging processes will give rise to CPE behavior.⁷ This work made use of a mathematical structure for modeling coupled faradaic and charging processes that was described recently by Nisancioglu and Newman.⁸

The coupling of charging and faradaic currents is shown to yield a high-frequency CPE behavior. This effect is demonstrated for deposition of silver in a moderately-well-supported electrolyte, but the effect diminishes as the concentration of supporting electrolyte increases. The magnitude of these effects is dependent on the specific system studied.

Coupled charging and faradaic currents is thereby shown to provide an additional source of CPE behavior to those associated with normal or surface distributions of time constants. This behavior may be explained in terms of an effective capacitance that accounts for the influence of concentration and that is shown to be a function of frequency. A second feature evident in this work is that the effects of electrode geometry and mass transfer results in the appearance of complex features in the local ohmic impedance response. This may explain the difficulty in obtaining correct values of Schmidt numbers by regressing one-dimensional models to impedance data obtained on a rotating disk electrode.

References

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