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The Influence of Coupled Faradaic and Charging Currents on Impedance Spectroscopy

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ABSTRACT

The coupling of faradaic and charging currents is shown, by numerical simulation, to result in impedance responses showing high-frequency frequency dispersion that resembles pseudo-Constant-Phase-Element (CPE) behavior. The results show that coupling of faradaic and charging currents should be considered when modeling the impedance response for systems influenced by mass transfer, even for large concentrations of supporting electrolyte.

1. Introduction

A controversy from the late 1960s over the correct method for developing deterministic models for impedance response has been largely neglected by the electrochemical community until it was raised in 2012 by Nisancioglu and Newman. [1] In electrochemical systems, the passage of current through an electrode can be attributed to faradaic reactions and to double-layer charging. As proposed by Sluyters, [2] the two processes are usually considered separately for simulating impedance response. The total current is subsequently obtained by adding the double-layer charging current to the faradaic current. This approach was criticized by Delahay and co-workers [3–5] because part of the flux of reacting species should, in principle, contribute to the charging of the interface as well as to the faradaic reaction. Nevertheless, the accepted procedure for model development has been to assume that the faradaic and charging currents are independent.[6] Indeed, the formalism in which faradaic and charging processes are considered to be uncoupled is documented in standard textbooks on impedance spectroscopy. [7,8]

The opposing viewpoints are presented schematically in Fig. 1. With *a-priori* separation (APS) of charging and faradaic currents, the flux of reacting species contributes only to the faradaic reaction, as shown in Fig. 1(a), and the charging current has contribution only from inert species. This corresponds to the currently accepted procedure for model development. The schematic representation of the case with no *a-priori* separation (NAPS) of charging and faradaic currents is presented in Fig. 1(b). The reacting species are seen to contribute to both the faradaic reaction and, along with the inert species, to the charging current. The representation shown in Fig. 1(b) is consistent with the arguments presented by Delahay. [3–5]

Relaxation of the assumption that faradaic and charging currents are independent requires coupling an explicit model of the double layer to the convective diffusion equations for each ionic species. Nisancioglu and Newman [1] provided an appropriate mathematical formalism that provides the foundation for the present work. Nisancioglu and Newman suggest that the coupling of faradaic and charging currents must be considered in general, but that the effect is not significant for well-supported electrolytes for which the reacting species contributes little to the interfacial charge. The object of this work is to use numerical simulations to explore the influence that the coupling of faradaic and charging currents has on the impedance response.

2. Model Development

A two-dimensional impedance model was developed to study the effect of nonuniform mass transfer, rotating disk electrode geometry, and the coupling of charging and faradaic currents on the impedance response. [9]

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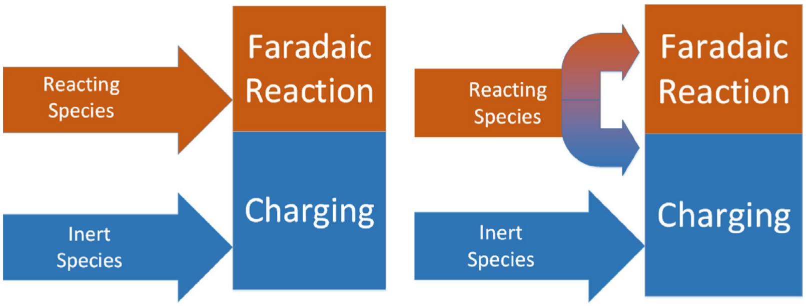

(a) (b)

Fig. 1. Schematic representation illustrating the contribution of the reacting species to the charging of the electrode-electrolyte interface corresponding to: a) the case with *a-priori* separation (APS); and b) the case with no *a-priori* separation (NAPS).

2.1. Mass Transport in Dilute Solutions

Conservation of species is expressed as

$$\frac{\partial c_\mathrm{i}}{\partial t} = -\nabla \cdot \mathbf{N}_\mathrm{i} + R_\mathrm{i} \tag{1}$$

where the flux is given by

$$\mathbf{N}_\mathrm{i} = -D_\mathrm{i}\left(z_\mathrm{i} c_\mathrm{i} \frac{\mathrm{F}}{RT}\nabla\Phi + \nabla c_\mathrm{i}\right) + c_\mathrm{i}\mathbf{v} \tag{2}$$

c_i is the concentration of species i, z_i is the charge number, D_i is the diffusivity, $\mathbf{v}$ is the mass-averaged velocity associated with the rotating disk, and R_i represents the production of species i by homogeneous reactions. In the absence of homogeneous reactions and under assumption that the diffusion coefficients are uniform,

$$\frac{\partial c_\mathrm{i}}{\partial t} + \mathbf{v}\cdot\nabla c_\mathrm{i} = z_\mathrm{i} D_\mathrm{i} \frac{\mathrm{F}}{RT}\nabla\cdot(c_\mathrm{i}\nabla\Phi) + D_\mathrm{i}\nabla^2 c_\mathrm{i} \tag{3}$$

For a system with n species, n expressions in the form of equation (3) are required; whereas the conservation of charge implies that

$$\nabla\cdot\mathbf{i} = -\nabla\cdot\left(\mathrm{F}\sum_\mathrm{i} D_\mathrm{i} z_\mathrm{i}\left(z_\mathrm{i} c_\mathrm{i}\frac{\mathrm{F}}{RT}\nabla\Phi + \nabla c_\mathrm{i}\right)\right) = 0 \tag{4}$$

Equations (3) and (4) constitute a set of nonlinear equations.

In the frequency domain, the concentrations of each species are described by

$$c_\mathrm{i} = \bar{c}_\mathrm{i} + \mathrm{Re}\left\{\widetilde{c}_\mathrm{i}\exp(\mathrm{j}\omega t)\right\} \tag{5}$$

where the bar notation represents the steady-state component, and the tilde notation represents the oscillating component which depends only on position. Similar definitions are applied for all variables. The mass and charge conservation equations become

$$\mathrm{j}\omega\widetilde{c}_\mathrm{i} + \mathbf{v}\cdot\nabla\widetilde{c}_\mathrm{i} = D_\mathrm{i}\nabla\cdot\left(\nabla\widetilde{c}_\mathrm{i} + \frac{z_\mathrm{i}\mathrm{F}}{RT}\left(\bar{c}_\mathrm{i}\nabla\widetilde{\Phi} + \widetilde{c}_\mathrm{i}\nabla\bar{\Phi}\right)\right) \tag{6}$$

and

$$\nabla\cdot\left(\sum_\mathrm{i} z_\mathrm{i} D_\mathrm{i}\left(\nabla\widetilde{c}_\mathrm{i} + \frac{z_\mathrm{i}\mathrm{F}}{RT}\left(\bar{c}_\mathrm{i}\nabla\widetilde{\Phi} + \widetilde{c}_\mathrm{i}\nabla\bar{\Phi}\right)\right)\right) = 0 \tag{7}$$

respectively, where the higher order terms such as $\widetilde{c}_\mathrm{i}\nabla\widetilde{\Phi}$ were neglected. At the electrode surface, the flux of each species may be expressed as

$$\widetilde{N}_{\mathrm{i,y}}(0) = -D_\mathrm{i}\left(\left.\frac{\mathrm{d}\widetilde{c}_\mathrm{i}}{\mathrm{d}y}\right|_{y=0} + \frac{z_\mathrm{i}\mathrm{F}}{RT}\left(\bar{c}_\mathrm{i}\left.\frac{\mathrm{d}\widetilde{\Phi}}{\mathrm{d}y}\right|_{y=0} + \widetilde{c}_\mathrm{i}\left.\frac{\mathrm{d}\bar{\Phi}}{\mathrm{d}y}\right|_{y=0}\right)\right) \tag{8}$$

The correlation between the flux and the current oscillations at electrode boundary is discussed in two cases where the faradaic current and the double-layer charging current are considered with and without a priori separation of faradaic and charging currents.

2.2. No a Priori Separation of Faradaic and Charging Currents (NAPS)

Under the assumption that the charge density on the metal surface q_m is dependent on the interfacial potential V and on the concentration $c_\mathrm{i}(0)$ of each species i, located outside the diffuse region of charge, the variation of the surface charge density is given by

$$\mathrm{d}q_\mathrm{m} = \left(\frac{\partial q_\mathrm{m}}{\partial V}\right)_{c_\mathrm{i}(0)}\mathrm{d}V + \sum_\mathrm{i}\left(\frac{\partial q_\mathrm{m}}{\partial c_\mathrm{i}(0)}\right)_{V,c_{\mathrm{j}\neq(\mathrm{i})(0)}}\mathrm{d}c_\mathrm{i}(0) \tag{9}$$

Equation (9) is written in terms of $n+1$ parameters which are treated as properties of the interface. These can be expressed as

$$C_0 = \left(\frac{\partial q_\mathrm{m}}{\partial V}\right)_{c_\mathrm{i}(0)} \tag{10}$$

where C_0 is the usual differential capacitance, and

$$C_\mathrm{i} = \left(\frac{\partial q_\mathrm{m}}{\partial c_\mathrm{i}(0)}\right)_{V,c_{\mathrm{j}\neq(\mathrm{i})(0)}} \tag{11}$$

which can be expressed for species i = 1, . . ., n. Both terms may be obtained from detailed models of the diffuse double layer.

The current at the electrode surface may be expressed as

$$\widetilde{i} = \mathrm{j}\omega\widetilde{q}_\mathrm{m} + \widetilde{i}_\mathrm{F} \tag{12}$$

where the oscillations of the surface charge density and the faradaic current density are approximated by Taylor series expansions about their steady values as

$$\widetilde{q}_\mathrm{m} = \left(\frac{\partial\bar{q}_\mathrm{m}}{\partial V}\right)_{c_\mathrm{i}(0)}\widetilde{V} + \sum_\mathrm{i}\left(\frac{\partial\bar{q}_\mathrm{m}}{\partial c_\mathrm{i}(0)}\right)_{V,c_{\mathrm{j}\neq(\mathrm{i})(0)}}\widetilde{c}_\mathrm{i}(0) \tag{13}$$

and

$$\widetilde{i}_\mathrm{F} = \left(\frac{\partial\bar{i}_\mathrm{F}}{\partial V}\right)_{c_\mathrm{i}(0)}\widetilde{V} + \sum_\mathrm{i}\left(\frac{\partial\bar{i}_\mathrm{F}}{\partial c_\mathrm{i}(0)}\right)_{V,c_{\mathrm{j}\neq(\mathrm{i})(0)}}\widetilde{c}_\mathrm{i}(0) \tag{14}$$

respectively. The surface flux can be expressed as

$$\widetilde{N}_{\mathrm{i,y}}(0) = -\frac{\partial\Gamma_\mathrm{i}}{\partial c_\mathrm{i}(0)}\frac{\partial c_\mathrm{i}(0)}{\partial q_\mathrm{m}}\mathrm{j}\omega\widetilde{q}_\mathrm{m} - \frac{s_\mathrm{i}}{n\mathrm{F}}\widetilde{i}_\mathrm{F} \tag{15}$$

where s_i is the stoichiometric coefficient for the reaction and Γ_i is the surface concentration of species i. Equations (12) and (15) were applied as the boundary conditions to evaluate the impedance response without a priori assumption of the separation of faradaic and charging currents.