Influence of Current and Potential Distributions on the Impedance Response of a Rotating Disk Electrode

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The object of this work is to review our recent numerical and experimental study of the influence of geometry on the global and local impedance response of a disk electrode.[1-9] The work may be regarded as an extension to the seminal contribution of Newman.[10] The computational results indicated that the geometry-induced distortions appear at high frequencies and the high-frequency response has an approximate constant-phase-element (CPE) behavior. The calculated results for both global and local impedance were in quantitative agreement with experimental observations. The calculated local impedance revealed high-frequency inductive loops that were also observed in experiments.

The modeling of blocking electrodes or electrodes with a single Faradaic reaction showed that geometry-induced distributions play a role only at frequencies

$$f > \frac{\kappa}{2\pi C_0 r_0} \qquad (1)$$

where C_0 is the interfacial capacitance. Thus, time-constant dispersion for such systems can be avoided by confining the experimental measurement to frequencies below a critical value. The desired frequency range could be extended, for example, by reducing the electrode radius. Examples will be used to demonstrate how this knowledge may be used to facilitate interpretation of impedance data.

One important conceptual result of this work was that both the local and the global Ohmic resistance can be represented as a complex number, having finite imaginary components at the higher frequencies represented by equation (1).

The geometry-induced time-constant dispersion may also play a role at lower frequencies for reactions coupled by adsorbed intermediates. The surface coverage by intermediates is dependent on the surface overpotential which, in turn, is related to the radial position of the electrode. While high-frequency loops appear in the local impedance corresponding to the distribution of current associated with electrode geometry, low-frequency loops associated with intermediates also show geometry-induced dispersion of the impedance response. The geometry effects are reflected in the local Ohmic impedance which has complex behavior at both high and low frequencies. This effect is diminished by use of a recessed electrode.

This presentation will provide a historical perspective on efforts to understand the role of the disk electrode geometry on the measured impedance response, a physical description of the related phenomena, and a guide to experimentalists on the conditions under which geometry-induced time-constant dispersion may be expected to influence the impedance response.

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