

EIS Response of a Contaminated Disk Electrode

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There is an ever increasing use of equivalent circuits to aid in the interpretation of experimental electrochemical impedance spectroscopic data. Readily available software allows the regression of circuits consisting of passive electrical elements of resistors, capacitors and even inductors to EIS data. Improvement in the fitting of the circuit to the data is achieved by using non-passive elements of which the most popular is the constant phase element (CPE). The impedance of a CPE is given by

$$Z_{CPE} = \frac{1}{(j\omega)^\alpha Q} \quad (1)$$

where j is $\sqrt{-1}$, ω is the angular frequency and Q and α are the CPE parameters. The CPE element is associated with EIS data where a particular phenomenon is associated with a distribution of time-constants. In the presence of a single time-constant for a given phenomenon, then the CPE element reduces to a capacitor with $\alpha=1$.

Time-constant distributions for a non-ideal electrode may occur along the electrode surface and/or normal to the surface.¹ The distribution of time-constants along the surface may be attributed to surface heterogeneity or current and/or potential distributions along the surface. The distribution of time-constants normal to the electrode surface may be due to surface roughness. Experimental reports indicated that the CPE behavior along an electrode surface is attributed to surface contamination with roughness not a significant contributor.²

The influence of surface contamination on the EIS behavior of a disk electrode is presented in this report. The EIS behavior is simulated for an embedded disk electrode system similar to that used by Newman.³

Simulation Method

The solution potential Φ between two electrodes separated by an electrolyte where an alternating current is applied can be written as the sum of the steady-state potential and the complex oscillating potential³

$$\Phi = \bar{\Phi} + \text{Re}\{\tilde{\Phi}e^{j\omega t}\} \quad (2)$$

Simulation of the EIS between the two electrodes can be achieved by assigning one electrode, the working electrode, a boundary condition of current density

$$i = C_0 \frac{\partial(V - \Phi_0)}{\partial t} + \frac{(\alpha_a + \alpha_c)i_0 F}{RT} (V - \Phi_0) \quad (3)$$

where V is the applied potential, Φ_0 the solution potential adjacent to the electrode, and C_0 the interfacial capacitance. The boundary condition in the electrolyte far from the disk electrode is set to a zero value while the non-electrode surface surrounding the disk is assigned an insulating boundary condition. The solution of the

governing Laplace equation for Φ with the boundary conditions can be used to obtain the complex current on the working electrode by integrating across the surface. The impedance of the working electrode can be obtained by the ratio of the complex potential and the complex current. The procedure was performed using COMSOL[®] version 4.1. The simulated EIS spectrum was constructed by solving for a range of ω .

A schematic of a disk electrode is shown in Fig.1, where there are three contaminated areas. Contaminants differed from the base metal by exchange current density and interfacial capacitance properties. Simulated impedance data is shown in Fig. 2 for a 0.25 cm disk with no contaminants and with 11.5% of the surface area contaminated. The exchange current density and interfacial capacitance were scaled ten times for more active contaminants and 0.1 times for less active contaminants. The polarization resistance of the contaminated disks relative to the contaminant-free disk was expected. The contamination did influence α values in the high frequency range with values of 0.834 and 0.864 for the more and less active contaminants, respectively, different than the 0.862 value for the contaminant-free disk. An additional high frequency loop was introduced by the contaminants with the loop visible for the disk with the more active contaminants. Results will be presented to demonstrate the influence of the contamination's area and properties on the global and local impedance of the disk electrode.

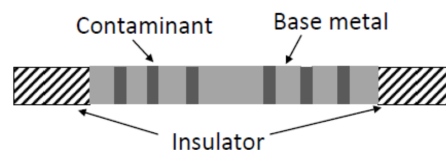


Fig.1. A schematic diagram of the cross-section of a contaminated disk electrode.

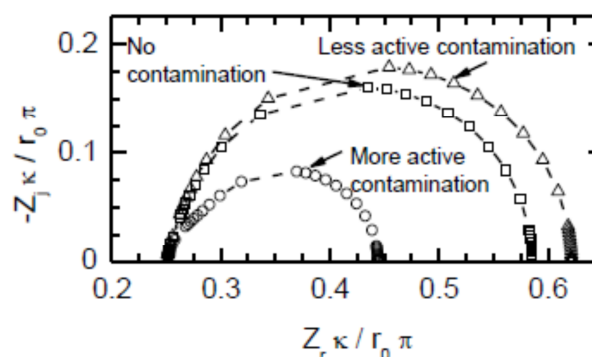


Figure 2. Nyquist plots of the impedance data for a 0.25 cm disk electrode in a 5 Sm⁻¹ electrolyte with the disk contaminated and contaminant-free.

Acknowledgements

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References

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3. J. Newman, *J. Electrochem. Soc.* 117 (1970) p 198.