Application NOTE

Electrochemical Impedance at a Rotated Disk Electrode

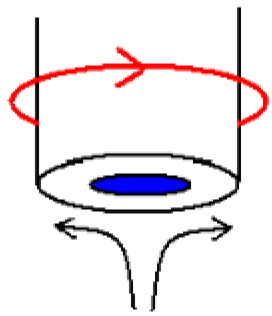
Whenever you read about Electrochemical Impedance, one of the first things they tell you is "The system must be stable and unchanging." Normally that means that should run the EIS experiment at the Open Circuit Potential, where the DC current is zero.

Sometimes, though, you'd like to study the reaction when there IS a net current. A very relevant example is the study of catalysts for fuel cell electrodes. Often you'd like to study the catalyst under conditions very similar to that in an operating fuel cell, where the current density is large.

The Rotated Disk Electrode can come to the rescue! One of the nice things about the RDE is that the DC, mass transport controlled current is at Steady State, so it meets the stability criterion of EIS! It also has a sound theoretical basis.

Rotated Disk Theory

First, a word or two about the Rotated Disk Electrode.



A sketch of the working end of an RDE is shown at the right. The disk electrode (blue) is embedded in a larger, non-conducting rod or shroud. The entire assembly is rotated. Solution is drawn up along the axis of rotation and past the electrode, so there is laminar (i.e., smooth) flow past the electrode surface. However, the solution at the surface is dragged along by the rotating disk, and there is a thin layer (the **N**ernst **D**iffusion **L**ayer) that is unstirred. Within this layer, mass transport is by diffusion alone. The effective thickness of this layer depends on the RPM of the rotator, the viscosity of the solution, and the diffusion coefficient of the electroactive species. As the rotation speed of the RDE is increased the Nernst Diffusion Layer becomes thinner.

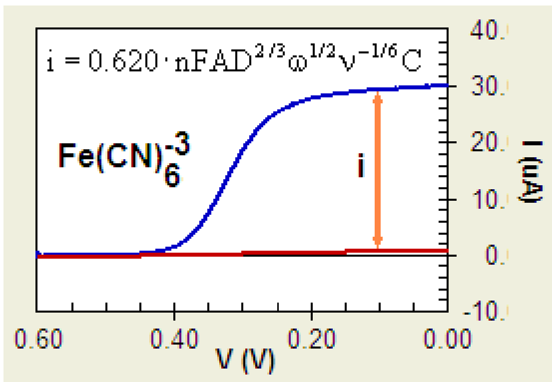
$$\delta = 1.61 \cdot D^{1/3} r^{-1/2} \nu^{1/6}$$

δ = Diffusion Layer Thickness

D = Diffusion coefficient

r = rotation rate (rad/s)

ν = viscosity

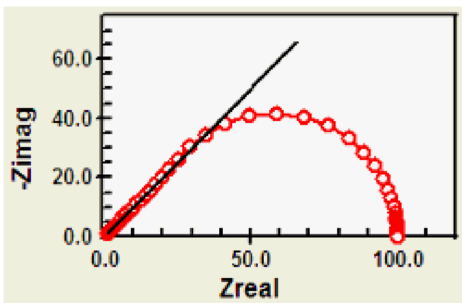


Another consequence of the NDL theory is that the current-voltage curve is S-shaped at scan rates below about 100 mV/s. The limiting current is given by the Levich equation.

With all of THAT out of the way, we can begin to talk about ...

EIS at an RDE - the Porous Bounded Warbug

The hydrodynamics described above fits the requisites for a 'Porous Bounded Warbug': There is a thin layer of unstirred solution next to the electrode, and large, stirred, homogeneous source of material outside that layer. In between these regions there is a (virtual) membrane that is porous to the diffusing molecule. Some people refer to this equivalent circuit element as a **Nernst** circuit element because it fits the model of the Nernst Diffusion Layer. The porous bounded Warburg impedance is most easily recognized from its Nyquist plot. At high frequency, this circuit element looks like a traditional Warburg impedance and shows a 45° line on the Nyquist plot. At low frequency, it looks like the semicircle of a Randles Cell.



There is a short discussion of the Porous Bounded Warburg in Gamry's EIS Primer.

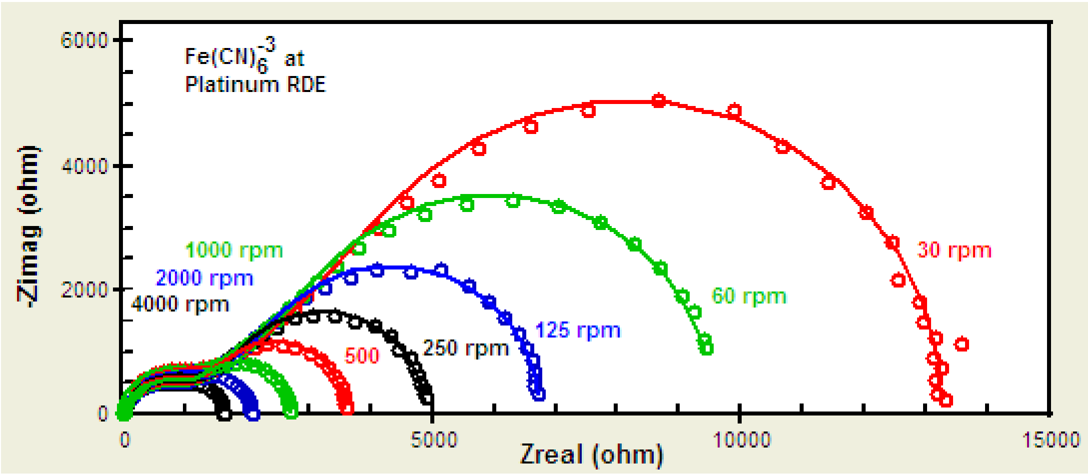
$$Z = \left[(1/Y_0)/\sqrt{(j\cdot\omega)}\right]\tanh\left\{B\sqrt{(j\cdot\omega)}\right\}$$

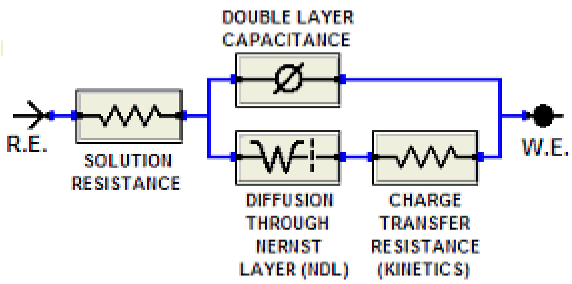
$$B = \delta/\sqrt{D} = 1.61\cdot r^{1/2}\cdot(\nu/D)^{1/6}$$

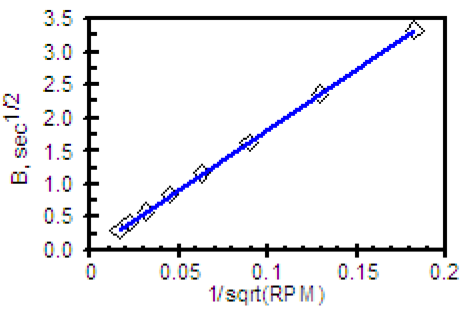
$$Y_0 = \frac{n^2F^2A}{RT\left(\frac{1}{C_O D_O^{1/2}} + \frac{1}{C_R D_R^{1/2}}\right)}$$

The Porous Bounded Warburg is characterized by two parameters, Y_O and B. The equation for Z is shown here, along with the gruesome definitions of Y_O and B. The parameter B (in $sec^{1/2}$) is a measure of the time it takes for the reactant to diffuse across the Nernst Diffusion Layer. What is interesting is that B depends upon the NDL thickness, which in turn, depends upon the rotation speed (r) of the electrode!

The results of a sequence of experiments at different rotation rates is shown below. The small semicircle at the higher frequencies (near Z=0) represents the double layer capacitance and the charge transfer resistance for the ferri-/ferro-cyanide reaction. The rotation rate-dependent arc at low frequencies (towards the right on the Nyquist plot, below), arises from the NDL. The equivalent circuit is shown below.







All of the data were fit to the same equivalent circuit model. The plot on the right shows the B parameter of the Porous Bounded Warburg plotted vs. the inverse of the square root of rotation rate. As predicted, there is a nice, linear relationship over two orders of magnitude in rotation rate!

Summary

The rotated disk electrode is one more tool in your electrochemical toolbox. It is well founded in theory, and can be used for simple voltammetric or potentiodynamic scans, as well as for impedance studies. When diffusion is modeled in an EIS experiment, the Porous Bounded Warburg or Nernst circuit element is the proper one to use. For simple systems, excellent fits can be obtained over a wide range of rotation rates. Varying the rotation rate can be one way to test the validity of your model!

References

- Bard and Faulkner, "Electrochemical Methods", Wiley, 2000.
- Macdonald, "Impedance Spectroscopy", Wiley, 1987.

C3 PROZESS- UND ANALYSENTECHNIK GmbH
Peter-Henlein-Str. 20
D-85540 Haar b. München
Telefon 089/45 60 06 70
Telefax 089/45 60 06 80
info@c3-analysentechnik.de
www.c3-analysentechnik.de