

Common Equivalent Circuit Models

Part 3



CORROSION



BATTERY TESTING



COATINGS



PHOTOVOLTAICS



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Common Equivalent Circuits Models

In the following section we show some common equivalent circuit models. These models can be used to interpret simple EIS data. Many of these models have been included as standard models in the Gamry EIS300 Electrochemical Impedance Spectroscopy Software.

The elements used in the following equivalent circuits are presented in Table 3. Equations for both the admittance and impedance are given for each element.

Table 3. Circuit Elements Used in the Models

Equivalent Element	Admittance	Impedance
R	$1/R$	R
C	$j\omega C$	$1/j\omega C$
L	$1/j\omega L$	$j\omega L$
W (infinite Warburg)	$Y_0\sqrt{(j\omega)}$	$1/Y_0\sqrt{(j\omega)}$
O (finite Warburg)	$Y_0\sqrt{(j\omega)}\text{Coth}(B\sqrt{(j\omega)})$	$\text{Tanh}(B\sqrt{(j\omega)})/Y_0\sqrt{(j\omega)}$
Q (CPE)	$Y_0(j\omega)^\alpha$	$1/Y_0(j\omega)^\alpha$

The dependent variables used in these equations are R, C, L, Y_0 , B, and α . The EIS300 uses these as fit parameters.

Purely Capacitive Coating

A metal covered with an undamaged coating generally has a very high impedance. The equivalent circuit for such a situation is in Figure 11.

Figure 11. Purely Capacitive Coating

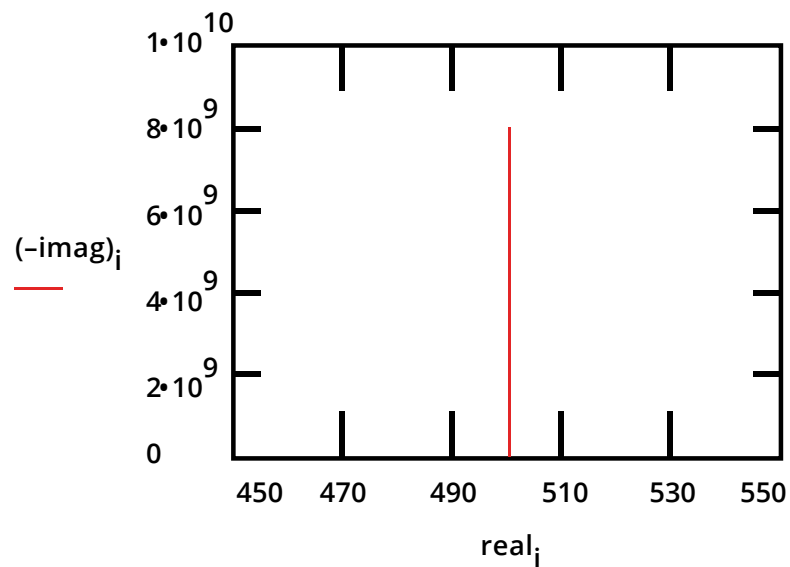


The model includes a resistor (due primarily to the electrolyte) and the coating capacitance in series.

A Nyquist Plot for this model is shown in Figure 12. In making this plot, the following values were assigned:

$R = 500 \Omega$	(a bit high but realistic for a poorly conductive solution)
$C = 200 \text{ pF}$	(realistic for a 1 cm^2 sample, a $25 \mu\text{m}$ coating, and $\epsilon_r = 6$)
$F_i = 0.1 \text{ Hz}$	(lowest frequency is a bit higher than typical)
$F_f = 1 \text{ MHz}$	(highest frequency at the EIS300 limit)

Figure 12. Typical Nyquist Plot for an Excellent Coating

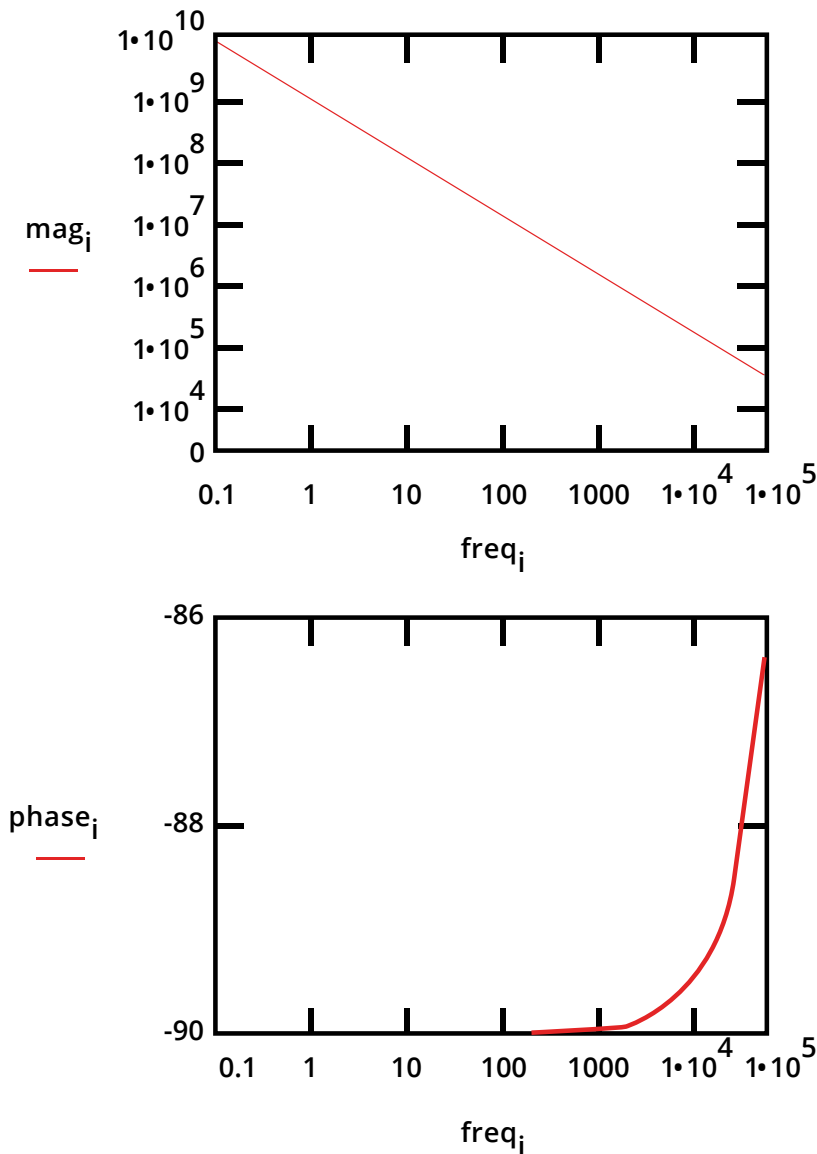


The value of the capacitance cannot be determined from the Nyquist Plot. It can be determined by a curve fit or from an examination of the data points. Notice that the intercept of the curve with the real axis gives an estimate of the solution resistance.

The highest impedance on this graph is close to $10^{10} \Omega$. This is close to or above the limit of measurement capability of most EIS instruments.

The same data are shown in a Bode Plot in Figure 13. Notice that the capacitance can be estimated from the graph but the solution resistance value does not appear on the chart. Even at 100 kHz, the impedance of the coating is higher than the solution resistance.

Figure 13. Typical Bode Plot for an Excellent Coating



Water uptake into the film is usually a fairly slow process. It can be measured by taking EIS spectra at set time intervals. An increase in the film capacitance can be attributed to water uptake.

Simplified Randles Cell

The Simplified Randles cell is one of most common cell models. It includes a solution resistance, a double layer capacitor and a charge transfer (or polarization resistance). The double-layer capacitance is in parallel with the charge-transfer resistance. In addition to being a useful model in its own right, the Simplified Randles Cell is the starting point for other more complex models.

The equivalent circuit for a Simplified Randles Cell is shown in Figure 14.

Figure 14. Simplified Randles Cell Schematic Diagram

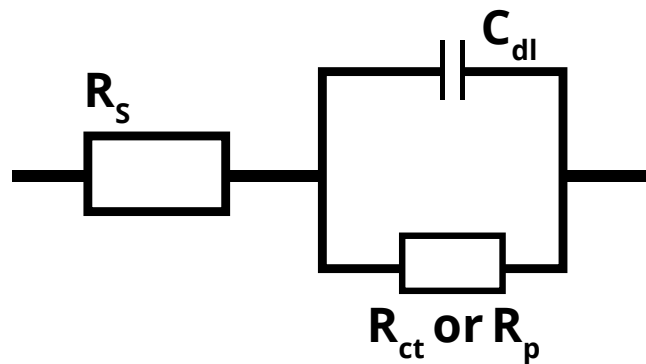
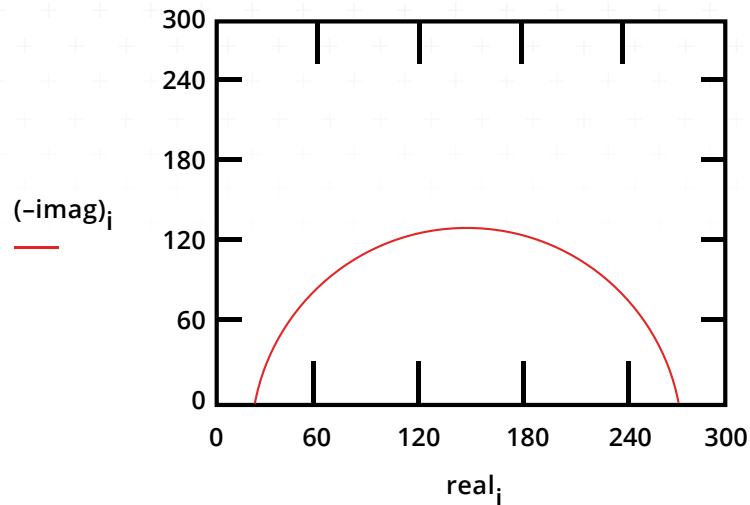


Figure 15 is the Nyquist Plot for a typical Simplified Randles cell. The parameters in this plot were calculated assuming a 1 cm^2 electrode undergoing uniform corrosion at a rate of 1 mm/year . Reasonable assumptions were made for the Tafel coefficients, metal density and equivalent weight. The polarization resistance under these conditions was calculated to be 250Ω . A capacitance of $40 \mu\text{F/cm}^2$ and a solution resistance of 20Ω were also assumed.

Figure 15. Nyquist Plot for 1 mm/year Corrosion Rate

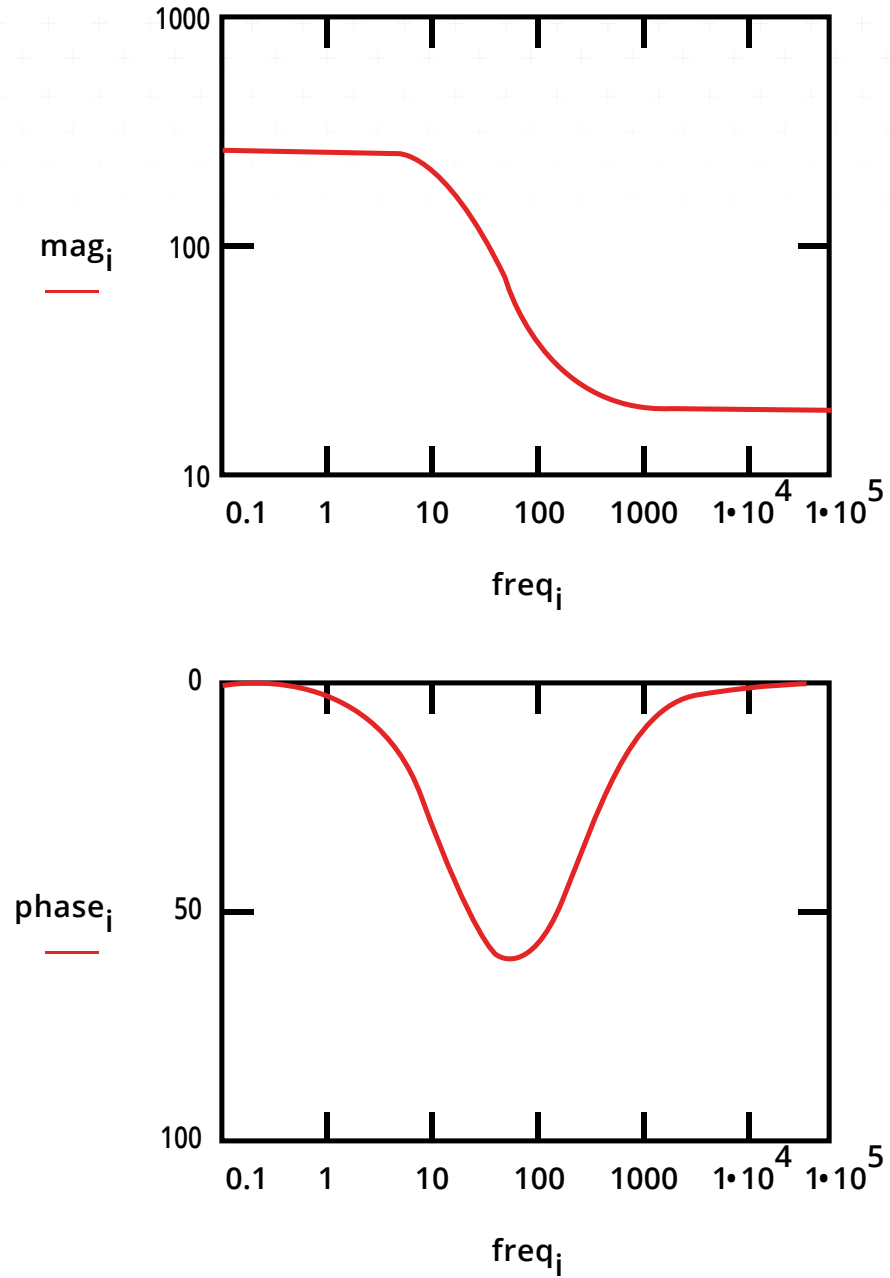


The Nyquist Plot for a Simplified Randles cell is always a semicircle. The solution resistance can be found by reading the real axis value at the high frequency intercept. This is the intercept near the origin of the plot. Remember this plot was generated assuming that $R_s = 20 \Omega$ and $R_p = 250 \Omega$

The real axis value at the other (low frequency) intercept is the sum of the polarization resistance and the solution resistance. The diameter of the semicircle is therefore equal to the polarization resistance (in this case 250Ω).

Figure 16 is the Bode Plot for the same cell.

Figure 16. Bode Plot for 1 mm/year Corrosion Rate

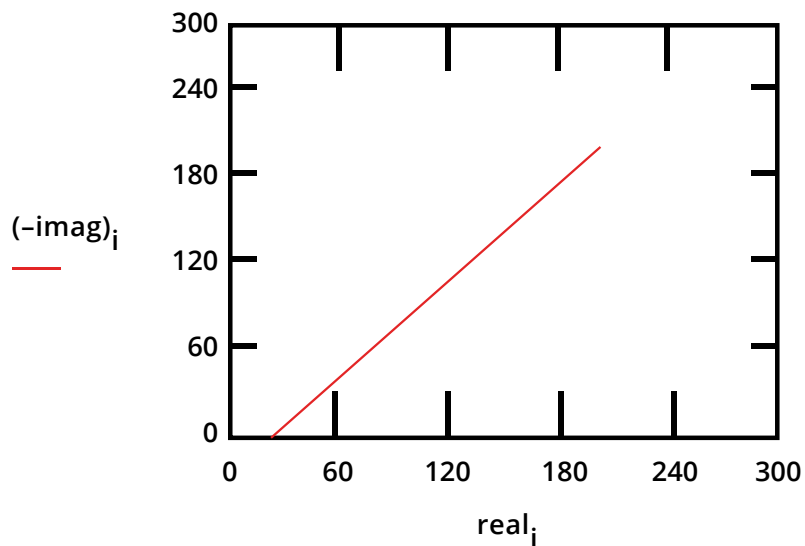


Mixed Kinetic and Diffusion Control

First consider a cell where semi-infinite diffusion is the rate determining step, with a series solution resistance as the only other cell impedance.

A Nyquist Plot for this cell is shown in Figure 17. R_s was assumed to be 20Ω . The Warburg coefficient, σ , is calculated to be about 150 for the diffusion of a species with a bulk concentration of $100 \mu\text{M}$ and a typical diffusion coefficient of $1.6 \times 10^{-5} \text{ cm}^2/\text{s}$. Notice that the Warburg impedance appears as a straight line with a slope of 45° .

Figure 17. Nyquist Plot for a Warburg Impedance



The same data is plotted in the Bode format in Figure 18. The phase angle of a Warburg impedance is 45° .

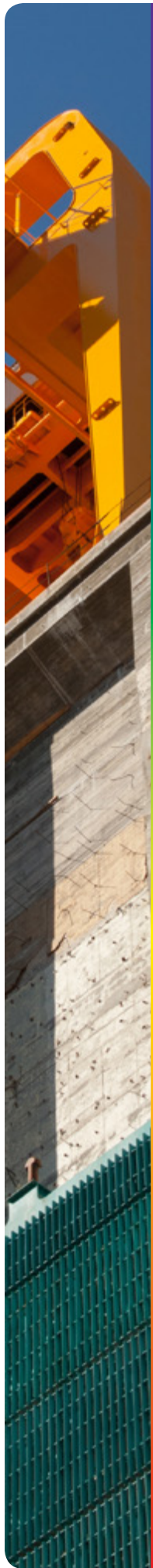
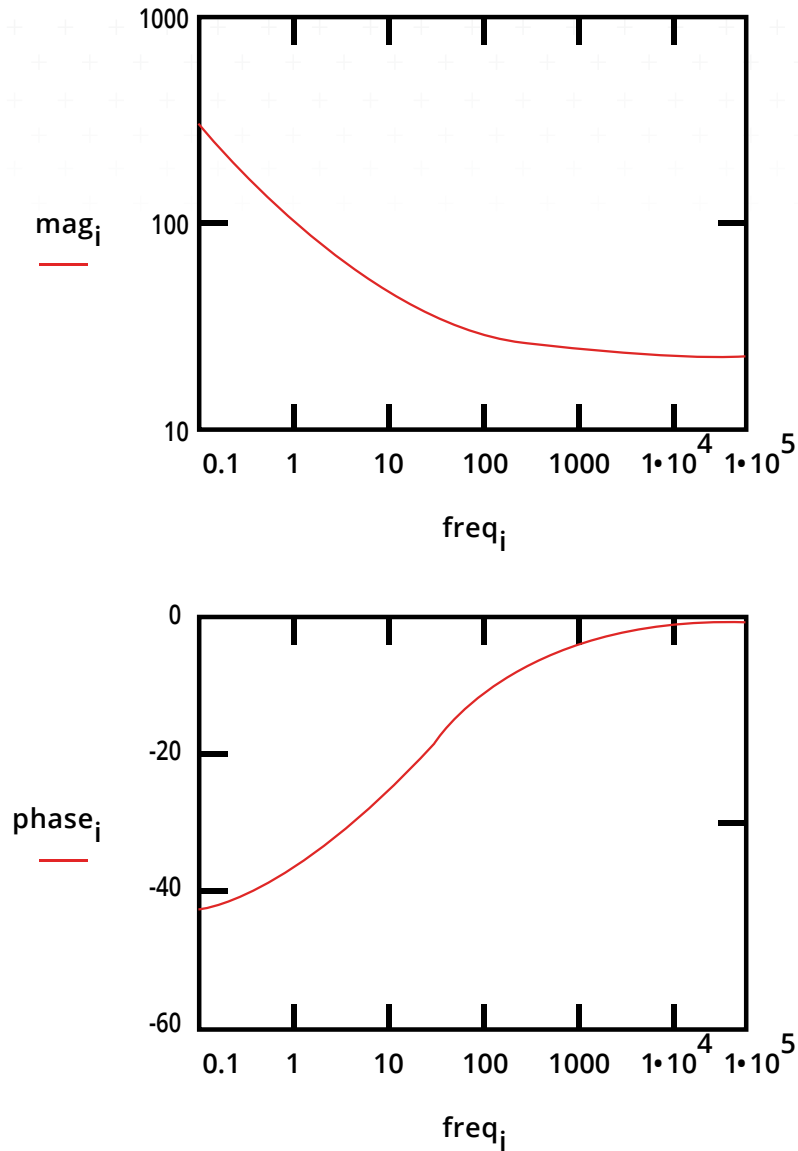
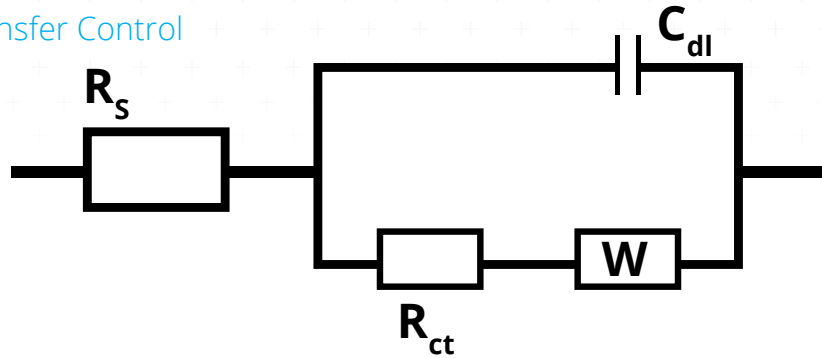


Figure 18. Bode Plot for a Warburg Impedance



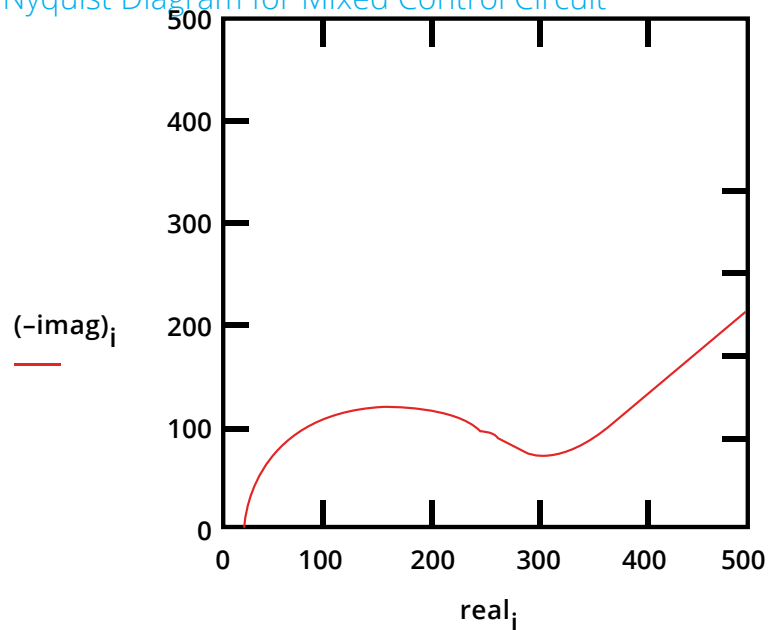
Adding a double layer capacitance and a charge transfer impedance, we get the equivalent circuit in Figure 19. This is the Randles Cell; the name is taken from an article by J.E.B. Randles in the Discussions of the Faraday Society in 1947. Since there is no simple element to model a Warburg impedance, it isn't possible to construct a dummy cell that models the Randles Cell.

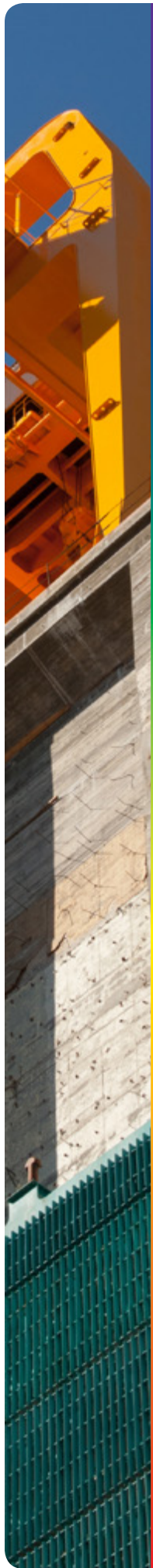
Figure 19. Randles Cell: Equivalent Circuit with Mixed Kinetic and Charge-Transfer Control



This circuit models a cell where polarization is due to a combination of kinetic and diffusion processes. The Nyquist Plot for this circuit is shown in Figure 20. As in the above example, the Warburg coefficient, σ , is assumed to be about 150. Other assumptions: $R_s = 20 \Omega$, $R_{ct} = 250 \Omega$ and $C_{dl} = 40 \mu F$.

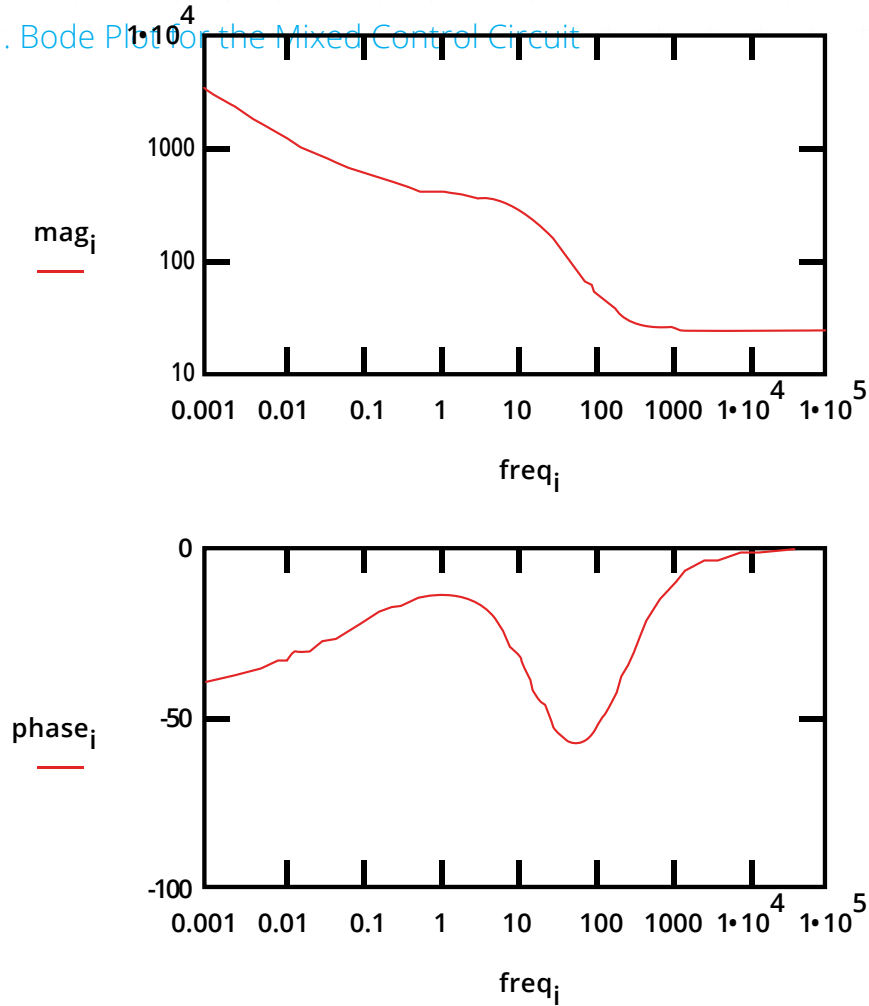
Figure 20. Nyquist Diagram for Mixed Control Circuit





The Bode Plot for the same data is shown in Figure 21. The lower frequency limit was moved down to 1 mHz to better illustrate the differences in the slope of the magnitude and in the phase between the capacitor and the Warburg impedance.

Figure 21. Bode Plot for the Mixed Control Circuit



This ends our section on Common Equivalent Circuit Models. In the next chapter of our Introduction to Electrochemical Spectroscopy series we will discuss the EIS of Coated Metals.

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