CAPSULES
notes and applications from Bioanalytical Systems, Inc.
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Electrochemical Impedance Spectroscopy #2
Equivalent Circuits

The interpretation of the data from electrochemical impedance experiments is based on the principle of equivalent circuits, which states that the processes that occur in an electrochemical cell can be modeled using a combination of resistors, capacitors, and other elements; that is, an RC circuit can be built that gives the same response as the electrochemical system. Essentially, the only route for generating an equivalent circuit appropriate for a given electrochemical system is to use simulation software. Such software must not only calculate the impedance response for a given equivalent circuit but should also provide least-squares fitting analysis for comparison of experimental and simulated data.

Once an appropriate equivalent circuit has been generated, the next step is to correlate the various electronic components of this circuit with the physical properties of the electrochemical system. This is typically the most difficult part of the interpretation and requires considerable experience for all but the simplest systems.

It is important to note that the simulation of impedance experiments on its own generally cannot provide a definitive analysis of an electrochemical system, since there is frequently more than one electronic circuit that provides a good fit with the experimental data. Therefore, impedance spectroscopy should be used with other analytical techniques that provide additional insight into the physical characteristics of the system (e.g., scanning electron microscopy is often used to characterize films that grow on electrode surfaces). However, once the appropriate equivalent circuit has been determined, the data provided by the impedance analysis can provide some unique insights into the behavior of the system. Such applications will be discussed in more detail in subsequent notes.

The two most commonly used electronic components in equivalent circuits are the resistor and the capacitor. The frequency dependence of the impedance of these components is illustrated in F1, which shows the Nyquist (A) and Bode (B) plots of a series combination of a resistor R and a capacitor C. Since the impedance of a capacitor is proportional to $1/\omega$, the impedance at high frequencies is due to the resistance; this is shown in the Nyquist plot as the intercept on the real axis and in the Bode plot by a phase angle of zero and a constant value for the impedance. As the frequency is decreased, the impedance due to the capacitor becomes more significant, and this is shown by a change in the phase angle from zero to 90° and an increase in the imaginary impedance (the log impedance *vs.* log frequency plot is a straight line with a slope of -1).

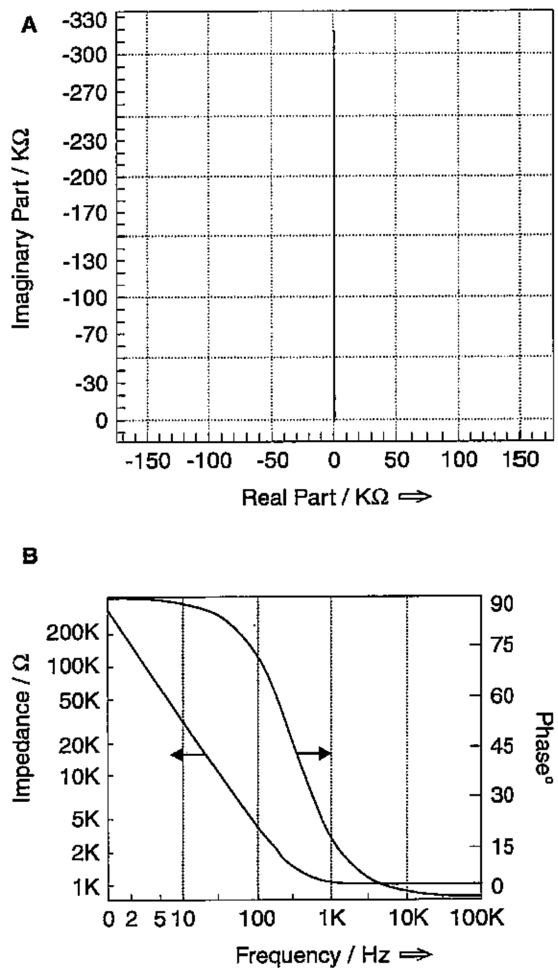

Figure 1. Nyquist (A) and Bode (B) plots for a series combination of R (1000 Ω) and C (0.5 μF).

The fundamental electronic "building block" for many equivalent circuits is a parallel combination of R and C. The Nyquist and Bode plots for this are shown in F2. This circuit shows purely ohmic behavior (i.e., no capacitive effects) at the high and low frequency limits. At high frequencies, the impedance of the capacitor ($\propto 1/\omega$) and the circuit impedance approach zero. At low frequencies, the capacitor impedance tends to infinity and the circuit impedance is

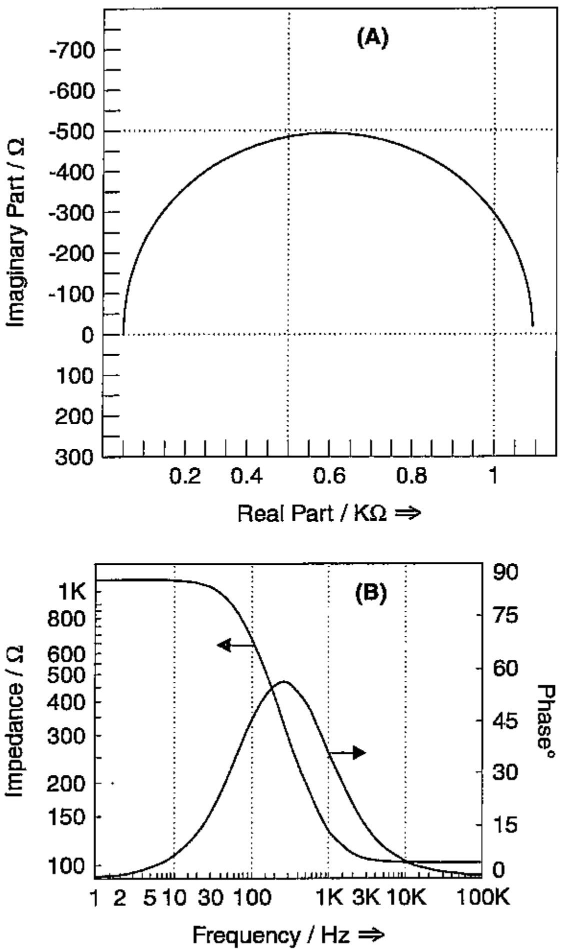

Figure 2. Nyquist (A) and Bode (B) plots for a parallel combination of R (1000 Ω) and C (2 μF) (in series with a resistance of 100

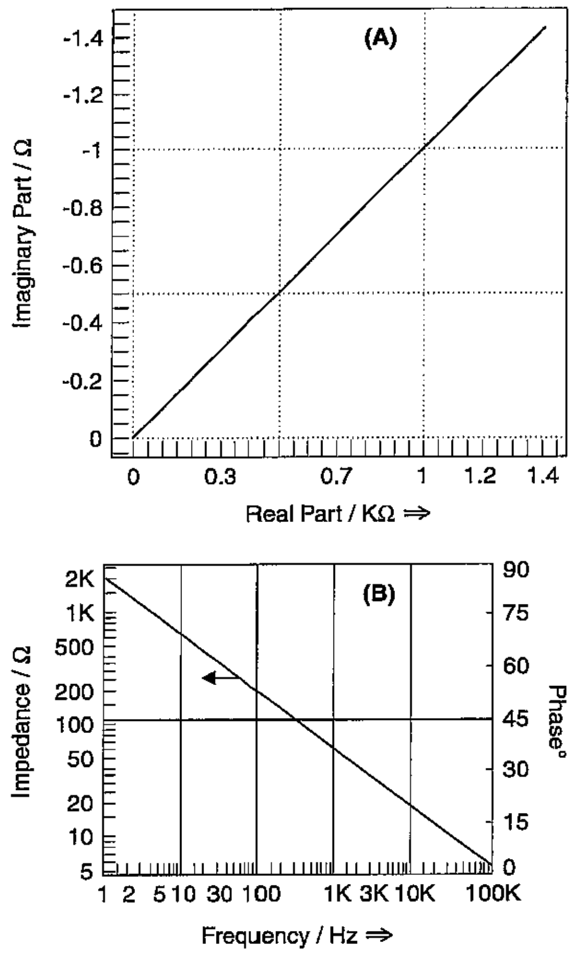

Figure 3. Nyquist (A) and Bode (B) plots for a Warburg impedance element (W = 5000 DW).

solely the resistance R. Ohmic behavior is shown in the Nyquist plot by intersection with the Z' axis. In the Bode plots, ohmic behavior is shown by a horizontal line in the log Z plot and a zero phase angle in the phase angle plot. At intermediate frequencies, there is a contribution to the impedance from the capacitor, which is reflected by non-zero -Z" values in the Nyquist plot, and a sloping line and non-zero phase angles in the log Z and phase angle plots, respectively. It is important to note that the division of the frequency ranges into high, low, and intermediate is relative and depends on the values of R and C.

This simple RC combination can be used to model several components of an electrochemical cell. For example, the bulk electrolyte and a film on the electrode surface each has an associated resistance and capacitance. However, it should be noted that the semi-circle for the bulk electrolyte is often not seen since it typically occurs at frequencies higher than those that can be used in an impedance experiment. Therefore, only the low frequency limit (the intercept at R_u on the Z' axis, where R_u is the uncompensated resistance of the bulk electrolyte) can be measured. This parallel combination can also be used to model the interfacial region; C is the double-layer capacitance (C_{dl}) and R is the charge-transfer resistance (R_{ct}). The rationale for representing the charge-transfer reaction as a resistance is derived from the small overpotential limit of the Butler-Volmer equation:

$$I = I_o(-nFA/RT)\eta$$

where $R_{ct} = RT/I_onFA$. It should be stressed that this linear relationship only applies at low overpotentials between 5 to 10 mV. Hence, the A.C. amplitude used in electrochemical impedance experiments is limited to 5 to 10 mV.

The other fundamental component of an electrochemical cell that must be considered is mass-transport. Semi-infinite diffusion can be modeled using the Warburg impedance Z_w, which is given by the following equation:

$$Z_w = \frac{w}{\sqrt{jw}}$$

This element has a constant phase angle (the impedance *vs.* log frequency plot is a straight line with a slope of -0.5)

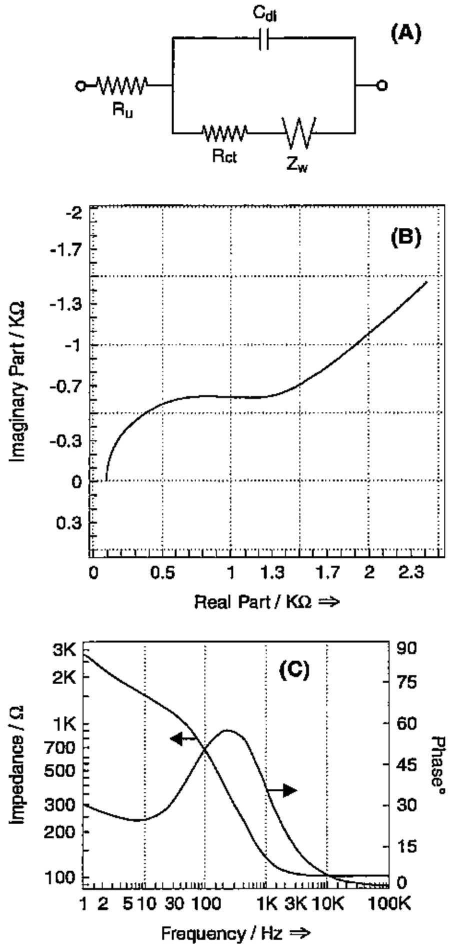

Figure 4. Nyquist (B) and Bode (C) plots for a Randles circuit (A) (R_u = 100 Ω, R_{ct} = 1000 Ω, C_{dl} = 1 μF, and Z_w = 5000 DW).

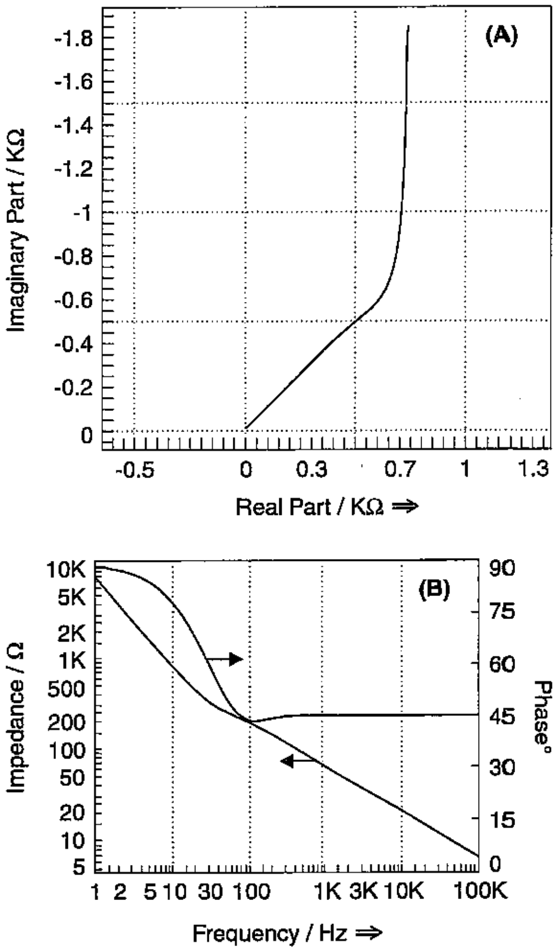

Figure 5. Nyquist (A) and Bode (B) plots for finite diffusion involving a blocked outer boundary (W = 5000 DS, k = 10 (A), 100 (B) 1/s).

and yields a straight line in the Nyquist plot at an angle of 45° (F3).

The equivalent circuit for an electrochemical cell, in which solution species involved in the charge-transfer reaction can be constructed from the components discussed above, is shown in F4. This is frequently referred to as the Randles circuit. The Nyquist plot for the Randles circuit is also shown in F4. The semi-circle at high frequencies indicates charge-transfer control; however, at lower frequencies, the rate of mass-transport (diffusion) becomes the rate limiting factor and is reflected by the transition from a semi-circle to a straight line.

Other related elements are available for modeling finite diffusion. Finite diffusion involving a blocked (impermeable) outer boundary (such as is found for redox-active polymer films on electrode surfaces) is represented by the equation:

$$Z = \frac{w}{\sqrt{jw}} coth \sqrt{\frac{jw}{k_s}}$$

At high frequencies, this equation becomes equivalent to the equation for semi-infinite diffusion, whereas at low frequencies, it becomes equivalent to a series combination of a resistor and a capacitor. Hence, the Nyquist plot for this type of finite diffusion consists of a line at a 45° angle at high frequencies, which changes to 90° at low frequencies (F5) (this variation is also reflected in the plot of the phase angle *vs.* log frequency).

Finite diffusion involving an open outer boundary (such as is found for a metal covered with an oxide film) is represented by the equation:

$$Z = \frac{w}{\sqrt{jw}} tanh \sqrt{\frac{jw}{k_N}}$$

This element tends to purely resistive behavior at low frequencies, and hence the low frequency limit for the phase angle is zero (F6).

(In order to distinguish between these two types of finite diffusion, the editor in the BAS-Zahner simulation program SIM refers to the blocked boundary behavior as finite diffu-

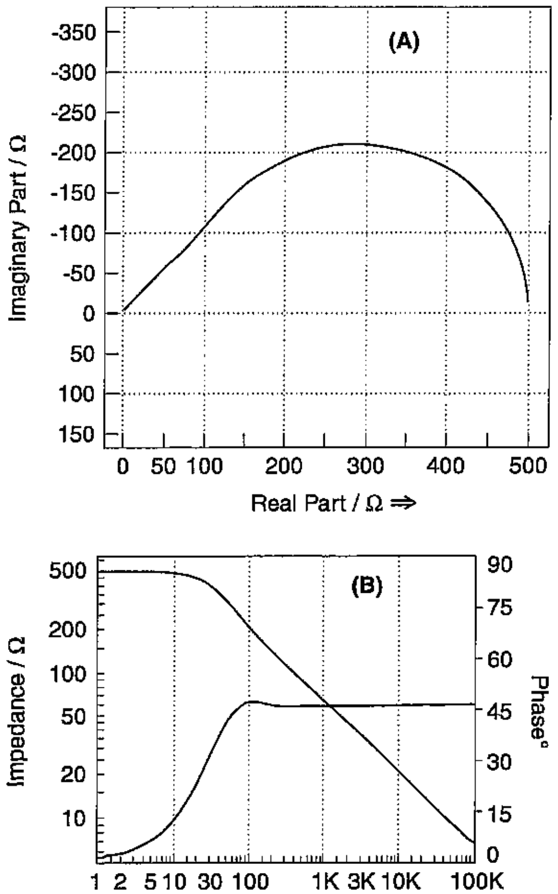

Figure 6. Nyquist (A) and Bode (B) plots for finite diffusion involving an open outer boundary (W = 5000 DW, k = 100 1/s).

sion and the open boundary behavior as Nernst impedance).

Semi-infinite mass transport can also be modeled using an infinite transmission line, which consists of a series of resistors and capacitors. The equation for the electrical properties of this transmission line has the same form as Fick's second law, which is the basis for its use as a model for mass transport. This approach can also be used to model finite diffusion, by making minor modifications to the transmission line. A zero concentration boundary can be modeled by terminating the transmission line in an open circuit (F7), whereas a finite concentration boundary can be modeled by terminating the line using a large resistance.

It is important to realize that the phase angles discussed above only apply to ideal systems. The phase angles for capacitive and semi-infinite behavior observed for real systems are typically lower than the ideal phase angles (e.g., due to porous or rough electrodes). Such deviations from ideality can be accommodated by using a constant phase element (CPE). As can be seen from the Nyquist and Bode plots in F8, the behavior of a constant phase element is similar to that of a capacitor, the major difference being the lower phase angle (the phase angle of a CPE is defined using an exponential factor).

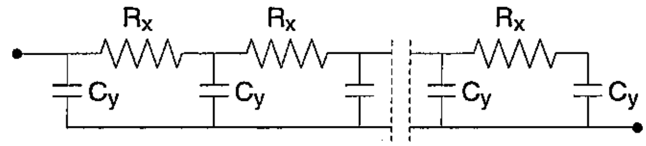

Figure 7. Transmission line model for finite diffusion involving a zero concentration outer boundary.

The equivalent circuits discussed in subsequent notes in this series are typically built from the components discussed in this note (other components, such as inductance, are much less common and will be discussed where appropriate). However, when studying the equivalent circuits discussed in these applications, it is important to remember that the various electrical components are being used to model real physical processes, and there needs to be good correlation between the properties of the electrical circuit and the electrochemical system under study.

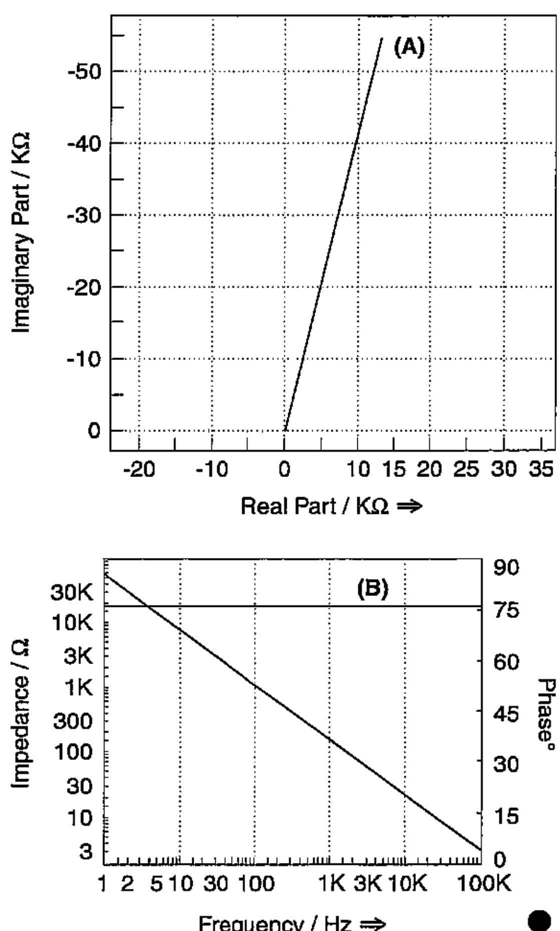

Figure 8. Nyquist (A) and Bode (B) plots for a constant phase element (Z_v = 1 μF, exponent = 0.85).