CAPSULES
notes and applications from Bioanalytical Systems, Inc.
January 1997

Electrochemical Impedance Spectroscopy #1
Introduction

The impedance of an electrochemical cell (i.e., the opposition that it provides to a current) is determined by the impedances of the various cell "components"; for example, the double layer capacitance of the interfacial region at the electrode surface, the charge transfer reaction, and the mass transport. Hence, measurement of the cell impedance can be used to determine the impedance of a given component and its contribution to the electrochemical reaction.

In a (potentiostatic) A.C. impedance experiment, the D.C. potential is held at a fixed value and a small amplitude A.C. potential is applied. The small amplitude ensures that there is a linear relationship between the current and the potential (which facilitates analysis of the experimental data), and that the response is steady-state; that is, it does not change with time and many measurements can be averaged (this increases the precision of the experiment). A wide range of frequencies is applied (typically over several orders of magnitude), so processes having different time constants can be detected within one experiment; for example, for a system involving simple charge transfer between the electrode surface and a solution species, the impedance may be determined by the charge transfer reaction at high frequencies and by diffusion at low frequencies.

The simplest way to introduce the impedances of various cell components is to consider the A.C current responses when an A.C. potential is applied across a resistor or a capacitor.

If the A.C. potential is $\Delta E\sin(\omega t)$, then the A.C. current through a resistor of impedance R is given by:

$$I = E/R = \Delta E\sin(\omega t)/R$$

and the A.C. current through a capacitor is given by:

$$I = CdE/dt = C(\Delta E\omega\cos(\omega t)) = C\Delta E\omega\sin(\omega t + \pi/2) = \Delta E\sin(\omega t + \pi/2)/X_C$$

The term X_C (= $1/\omega C$) is called the capacitive reactance and represents the impedance of a capacitor. It is used to give the potential-current equations the same form. The above equations show that there is a phase difference between the applied A.C. potential and the A.C. current response for any circuit containing a capacitor. Therefore, it is convenient to consider the A.C. current as a vector, and as such, it can be resolved into two components: one in-phase with the

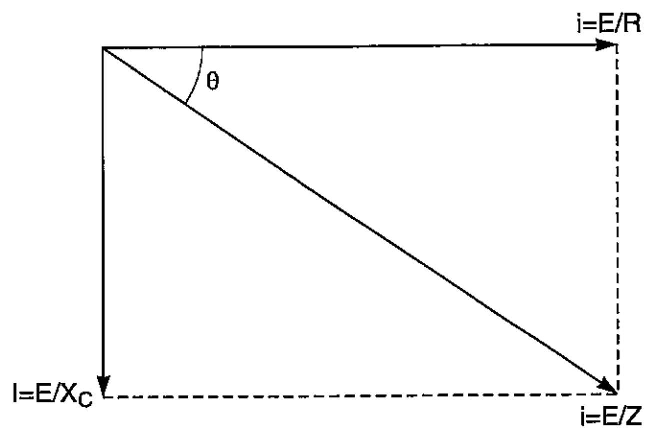

Figure 1. Vector diagram for A.C. current.

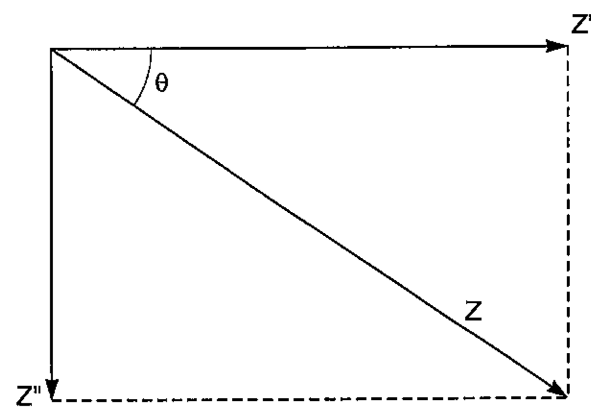

Figure 2. Vector diagram for A.C. Impedance.

applied potential and one out-of-phase (F1). The angle between the current vector and the applied potential is the phase angle θ.

The impedance Z (= E/I) can also be considered in terms of the in-phase components (Z'), the out-of-phase components (Z"), and the phase angle θ (F2). Impedances are often represented using complex notation, Z' and Z" being the real and imaginary axes, respectively (it should be stressed that the terms real and imaginary do not have any physical meaning and are merely convenient terminology). Using this convention, the total impedance (Z) equals Z' - jZ" (where j is the unit vector along the imaginary axis and $j^2 = -1$).

The data from an impedance experiment can be represented in a number of ways, the two most commonly used being the Nyquist and Bode plots. The Nyquist plot (also called a complex plane plot) is a plot of -Z" *vs.* Z' (F3), whereas the Bode plot consists of log Z and θ vs. log ω (F4). Although the Nyquist plot tends to be more commonly used (for historical reasons), the Bode plot is more useful since it explicitly shows the dependence of the total impedance and phase angle on the frequency (the frequency dependence is only implicit in the Nyquist plot). In addition, the Bode plots are logarithmic plots, which are more suitable for displaying data with a wide dynamic range.

Although A.C. impedance can be used for characterization of homogeneous electrochemical reactions, it is most commonly used for the investigation of interfacial reactions. Areas of application include the effectiveness of passivating films and polymer coatings on surfaces undergoing corrosion reactions, the stability of the anode/electrolyte interface in lithium-based primary and secondary batteries, the transport of ions across membranes, the transfer of charge through polymer films immobilized on electrode surfaces, the mechanisms of electroplating, electropolishing and electrowinning processes, and the properties of semi-conducting materials. Many of these applications will be discussed in more detail in subsequent notes in this series.

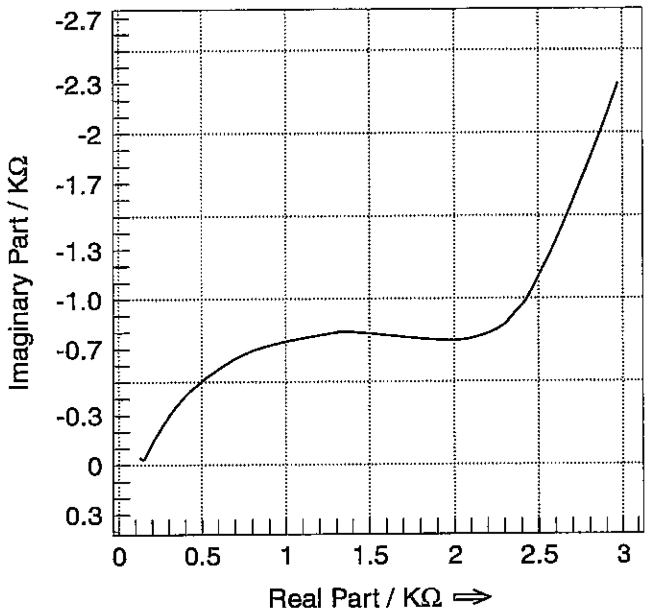

Figure 3. Nyquist plot for an Os(II)/Os(III) complex immobilized in a polymer.

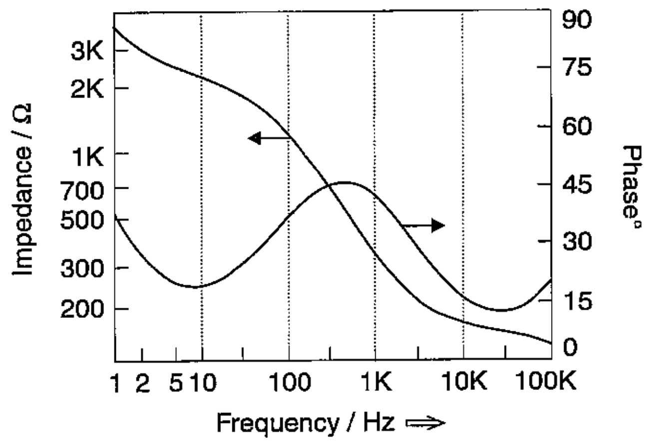

Figure 4. Bode plot for an Os(II)/Os(III) complex immobilized in a polymer.