MAPPING OF IMPEDANCE TO VOLTAMMETRIC CURVES

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Introduction

Impedance and voltammetry are two quite common techniques used in studies of electrochemical materials or electrochemical systems, including those in power sources. Due to the differing instrumentation, usually only one of the two methods is performed. We are here focusing on finding the commonalities of the two methods. The studies system is the classical electrochemical laboratory couple ferro-ferricyanide. Voltammetric curves for several scan rates are shown in Figure 1.

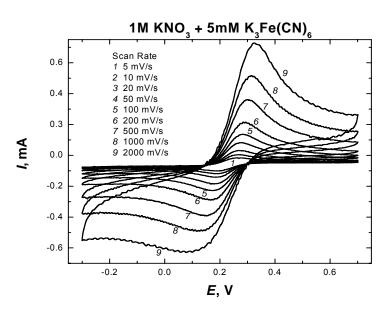


Fig. 1 A sequence of voltammetric curves for the ferro-ferricyanide couple.

In demonstrating electrochemical impedance spectroscopy (EIS) it is also desirable to have a model system to verify performance of the setup. The classical solid state parallel resistor and capacitor are good in showing the requisite semicircle; however, such a model response is rare and it is much more useful to engage in EIS a system that is already well known from voltammetric experiments.

It is not possible with the instrumentation used (Solartron Impedance Analyzer 1255) to measure impedance live, along voltammetric curves. Instead, we measured the

impedance at different points of a voltammetric curve obtained on a steady state system realized rotated disk platinum electrode. A curve similar to that shown in Fig. 2 is obtained. Along the curve are region that are commonly associated with double layer capacitance (Region 1) with no, or very little charge transfer, diffusion limited part (along Region 2) and mass transport limited part (Region 3). In our work we have mapped the curve in small potential increments, obtaining impedance for each point. An illustration of a Nyquist diagram for the three regions in Fig. 2 is shown in Fig. 3.

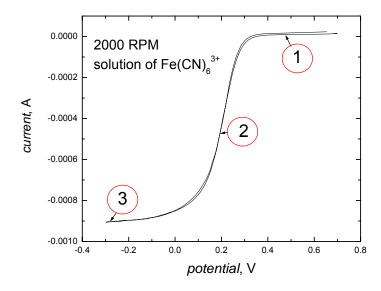


Fig. 2 Steady state voltammetric curve or RDE at 2000 RPM. 3 regions of interest for impedance interpretation are marked

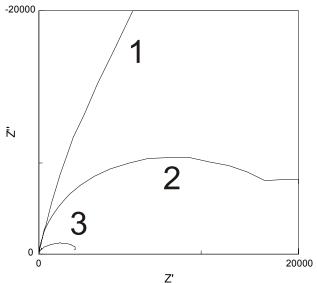


Fig. 3 Impedance response (Nyquist diagram) of the steady state voltammetric curve (Fig. 2) for the 3 regions of interest.

The interpretation of the impedance response of the points in the curve is used to evaluate parameters for diffusion control as well as kinetic parameters. Additional kinetic parameters were obtained by fitting the voltammetric scans using Digisim software. The kinetic rates for the four solutions were as follows:

 $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O < FeCl_3 \cdot 6H_2O < K_3Fe(CN)_6 < Ru(NH_3)_6Cl_3.$