Autolab Application Note EC01

Study of the Mass Transport Characteristics of $K_3[Fe(CN)_6]$/ $K_4[Fe(CN)_6]$ Oxidation and Reduction Reaction Using AUTOLAB RDE

Keywords

Forced convection; Rotating disc electrode; Levich equation; Hydrodynamic conditions; Linear sweep voltammetry; Electrochemical impedance spectroscopy

Summary

The mass transport characteristics of the diffusion controlled oxidation and reduction of ferri/ferro cyanide couple was studied using the AUTOLAB RDE with a low noise liquid Hg contact.

Experimental conditions

Linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) experiments were performed on a 3mm diameter platinum disc immersed in an electrolyte containing 0.05 M potassium ferrocyanide ($K_4[Fe(CN)_6]$) and 0.05 M potassium ferricyanide ($K_3[Fe(CN)_6]$) in 0.2 M NaOH supporting electrolyte. The electrode was polished to 3 µm finish before the start of the experiment. A large area platinum counter electrode and Ag/AgCl (KCl saturated) reference electrode were used for the measurements.

For EIS measurements, a 50nF capacitor was put in parallel with the reference electrode to compensate for the phase shift introduced by the slow response of the reference electrode at high frequencies.

For the LSV experiments, the potential was swept between -0.5 V and 0.5 V (vs. OCP). A scan rate of 0.1 V/s was used for the measurements. The EIS measurements were done at OCP with 10 mV potential perturbation. A frequency range of 100 kHz – 0.1 Hz was used.

Measurements were performed using AUTOLAB PGSTAT302N with FRA2 module. The LSV and EIS measurements were performed using the Autolab NOVA software. The rotation speed of the RDE was controlled directly from the software. The rate was varied from 100 rpm to 3200 rpm.

Test results with AUTOLAB RDE

The LSV results for the various rotation rates are shown in Figure 1. The oxidation and reduction limiting currents increase with the increase in rotation speed. In Figure 2, the oxidation and reduction limiting currents are plotted as a function of the square root of rotation speed.

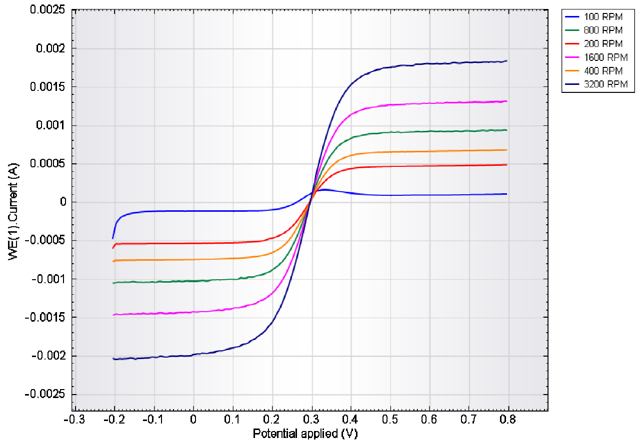

Figure 1 – Overlay of the LSV curves recorded at different rotation rates using the Autolab RDE

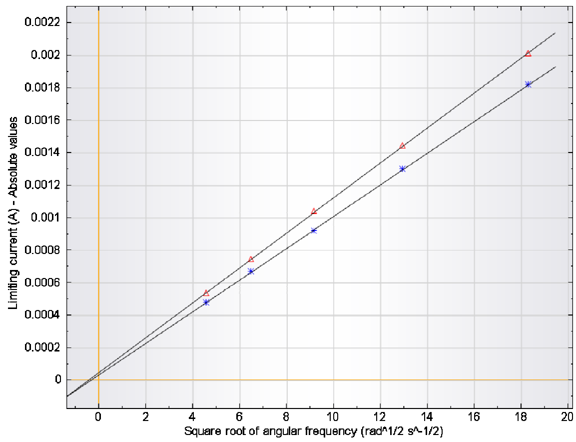

Figure 2 - The Levich plots obtained by plotting the absolute values of the limiting currents (anodic (*) and cathodic (Δ) part of the LSV) versus the square root of the angular frequency

The data points fall exactly on a straight line as predicted by Levich theory.

$$i_{lim} = 0.62 \cdot AnFC^{\infty}D^{2/3}\nu^{-1/6}\omega^{1/2}$$

where:

A is the area of the electrode

n is the number of electrons

F is Faraday's constant

C^{∞} is the bulk concentration of the electroactive species

D is the diffusion coefficient

ν is the kinetic viscosity

ω is the angular frequency

The Bode and Nyquist plots for the EIS measurements are shown in Figures 3 and 4 respectively.

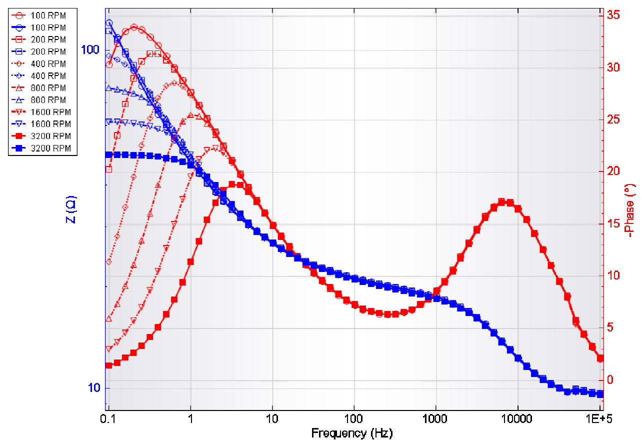

Figure 3 – Bode plot (phase shift – red curve and total impedance – blue curve) for each rotation rate

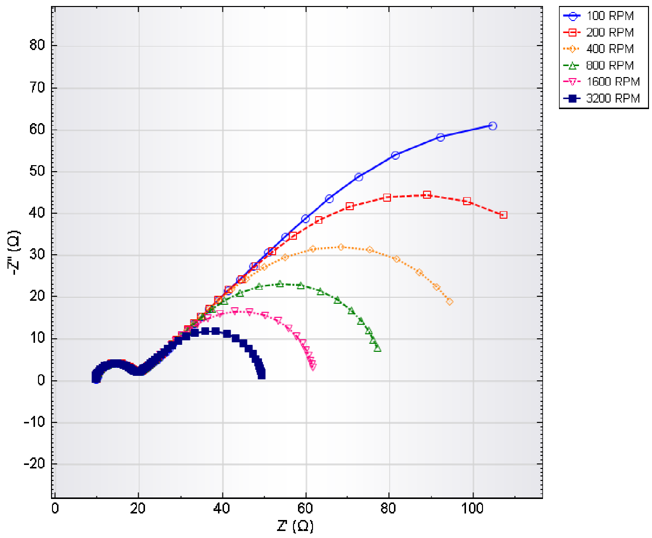

Figure 4 – Nyquist plot for each rotation rate

At high frequency the impedance is independent of the rotation speed of the RDE. The semicircle corresponds to the fast oxidation and reduction kinetics. At low frequency, the impedance decreases with the increase in the rotation speed and corresponds to a finite length diffusion Warburg impedance.

Date

1 July 2011