Application Note AN-EC-001

Study of the mass transport characteristics of $K_3[Fe(CN)_6]$/ $K_4[Fe(CN)_6]$ oxidation and reduction reaction using AUTOLAB RDE

The mass transport characteristics of the diffusion controlled oxidation and reduction of the 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 3 mm diameter platinum disk 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 an Ag/AgCl (KCl saturated) reference electrode were used for the measurements.

For the EIS measurements, a 50 nF 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. open circuit potential (OCP). A scan rate of 0.1 V/s was used for the measurements. The EIS measurements were conducted at OCP with 10 mV potential perturbation. A frequency range from 100 kHz to 0.1 Hz was used.

Measurements were performed using a Metrohm Autolab PGSTAT302N equipped with a FRA32M 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 increased with the increase in rotation speed.

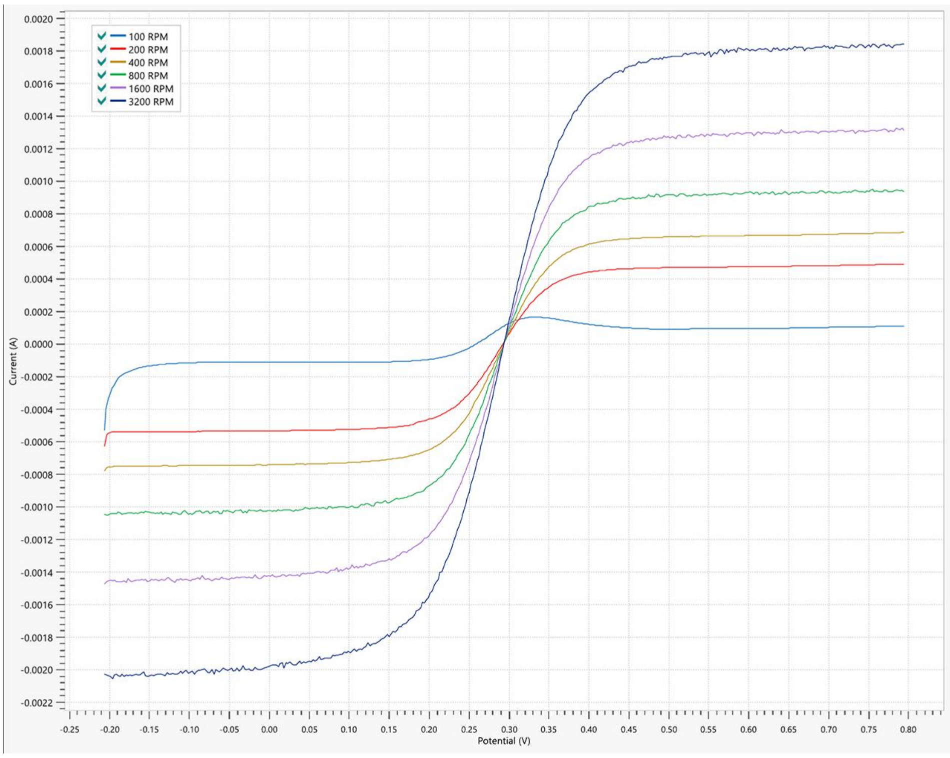


Figure 1. Overlay of the LSV curves recorded at different rotation rates using the Autolab RDE. Light blue: 100 RPM; red: 200 RPM; yellow: 400 RPM; green: 800 RPM; purple: 1600 RPM; dark blue: 3200 RPM.

In Figure 2, the anodic (A) and cathodic (B) limiting currents (absolute values) are plotted as a function of the square root of rotation speed.

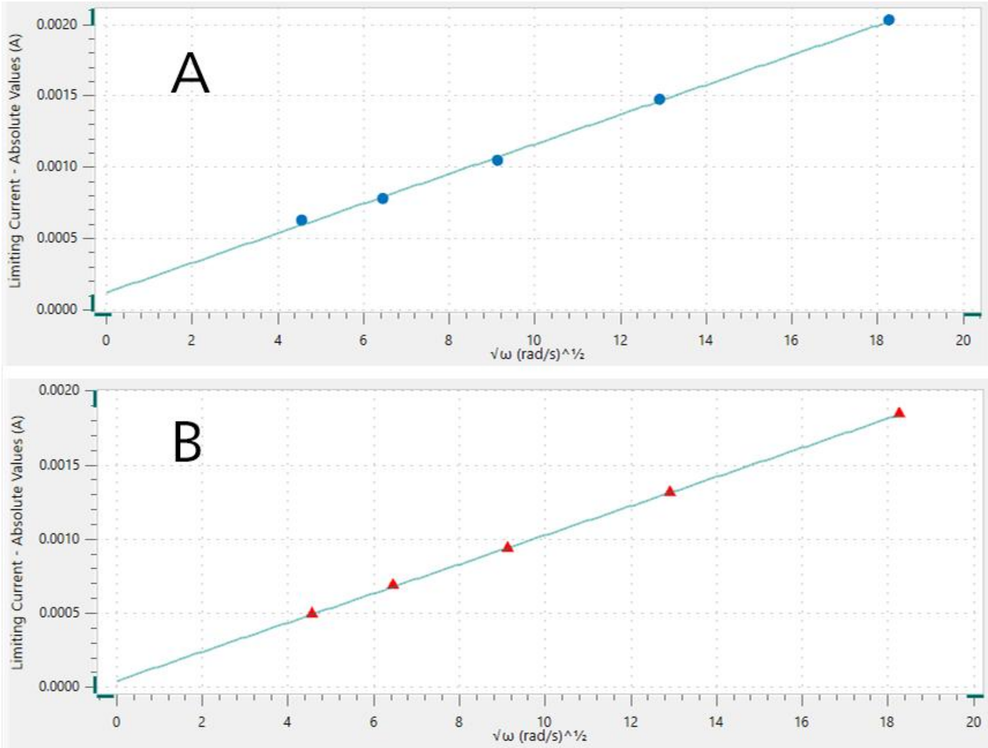


Figure 2. The Levich plots obtained by plotting the absolute values of the limiting currents versus the square root of the angular frequency. A - blue dots: anodic limiting currents. B - red triangles: cathodic limiting currents.

The data points fall exactly on a straight line as predicted by Levich theory, Equation 1.

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

Where: A (cm^2) is the area of the electrode n is the number of electrons involved in the redox reaction F (96485 $C\,mol^{-1}$) is Faraday's constant C^{∞} ($mol\,cm^{-3}$) is the bulk concentration of the electroactive species D ($cm^2\,s^{-1}$) is the diffusion coefficient ν ($cm^2\,s^{-1}$) is the kinematic viscosity of the solution ω ($rad\,s^{-1}$)is the angular rotation rate

The Bode plots for the EIS measurements are shown in Figure 3.

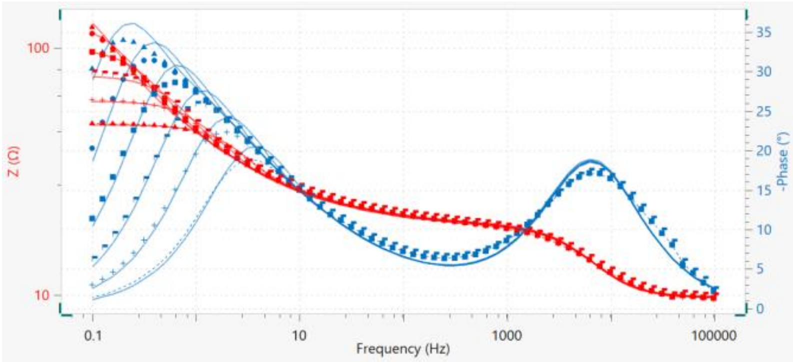


Figure 3. Bode plot (phase shift in blue data and module of the impedance in red data) for each rotation rate. Triangles: 100 RPM; circles: 200 RPM; squares: 400 RPM; flags: 800 RPM; crosses: 1600 RPM; dotted lines: 3200 RPM. The solid lines are the fit results.

The Nyquist plots of the EIS measurements are shown in Figure 4.

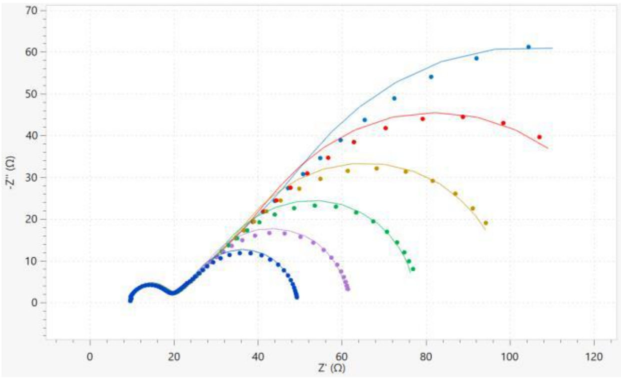


Figure 4. Nyquist plot for each rotation rate. Data are in points and the fit results are in solid lines. Light blue: 100 RPM; red: 200 RPM; yellow: 400 RPM; green: 800 RPM; purple: 1600 RPM; dark blue: 3200 RPM.

In Figure 5, the equivalent circuit used to fit the EIS data is shown.

At high frequencies, the impedance is independent of the rotation rate of the RDE. The semicircle corresponds to the fast oxidation and reduction kinetics, fitted with the Rs(RpCdl) part of the equivalent circuit.

At low frequencies, the impedance decreases with the increasing of the rotation rate, resulting in a finite-length diffusion which can be fit with the Warburg – shot circuit terminus element, WD in the equivalent circuit of Figure 5.

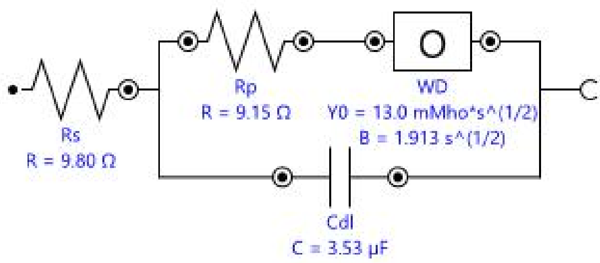


Figure 5. The equivalent circuit used to fit the data in Figure 3 and Figure 4.

CONTACT

Metrohm Viet Nam
Phan Dinh Giot
70000 Ho Chi Minh

info@metrohm.vn

CONFIGURATION

Autolab PGSTAT204

The PGSTAT204 combines the small footprint with a modular design. The instrument includes a base potentiostat/galvanostat with a compliance voltage of 20 V and a maximum current of 400 mA or 10 A in combination with the BOOSTER10A. The potentiostat can be expanded at any time with one additional module, for example the FRA32M electrochemical impedance spectroscopy (EIS) module.

The PGSTAT204 is an affordable instrument which can be located anywhere in the lab. Analog and digital inputs/outputs are available to control Autolab accessories and external devices are available. The PGSTAT204 includes a built-in analog integrator. In combination with the powerful NOVA software it can be used for most of the standard electrochemical techniques.

Autolab PGSTAT302N

This high end, high current potentiostat/galvanostat, with a compliance voltage of 30 V and a bandwidth of 1 MHz, combined with our FRA32M module, is specially designed for electrochemical impedance spectroscopy.

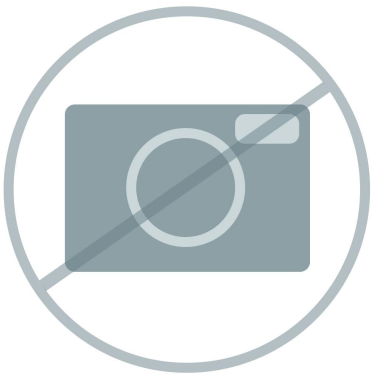
The PGSTAT302N is the successor of the popular PGSTAT30. The maximum current is 2 A, the current range can be extended to 20 A with the BOOSTER20A, the current resolution is 30 fA at a current range of 10 nA.

0.250 L Corrosion Cell

Complete cell for corrosion measurements, 250 mL.

Rotating disk electrode

The Autolab RDE is a high-end rotating disk electrode for measurements on systems where high rotation speed and low noise are required. The unit can go up to 10,000 rpm, a liquid Hg contact guarantees low noise. The PCTFE shaft has been designed to fit in Metrohm cell vessels, but also fits on most other electrochemical cells. The tip diameter is 10 mm, with an active surface diameter of 3 mm or 5 mm.
The rotation speed of the RDE is controlled manually with the button on the front of the motor control unit. The RDE can also be controlled remotely with the Autolab software. The rotation speed can be varied continuously between 100 and 10,000 rpm with a resolution of 1 rpm.



Advanced software for electrochemical research

NOVA is the package designed to control all the Autolab instruments with USB interface.

Designed by electrochemists for electrochemists and integrating over two decades of user experience and the latest .NET software technology, NOVA brings more power and more flexibility to your Autolab potentiostat/galvanostat.

NOVA offers the following unique features:

- Powerful and flexible procedure editor
- Clear overview of relevant real-time data
- Powerful data analysis and plotting tools
- Integrated control for external devices like Metrohm Liquid Handling devices