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.

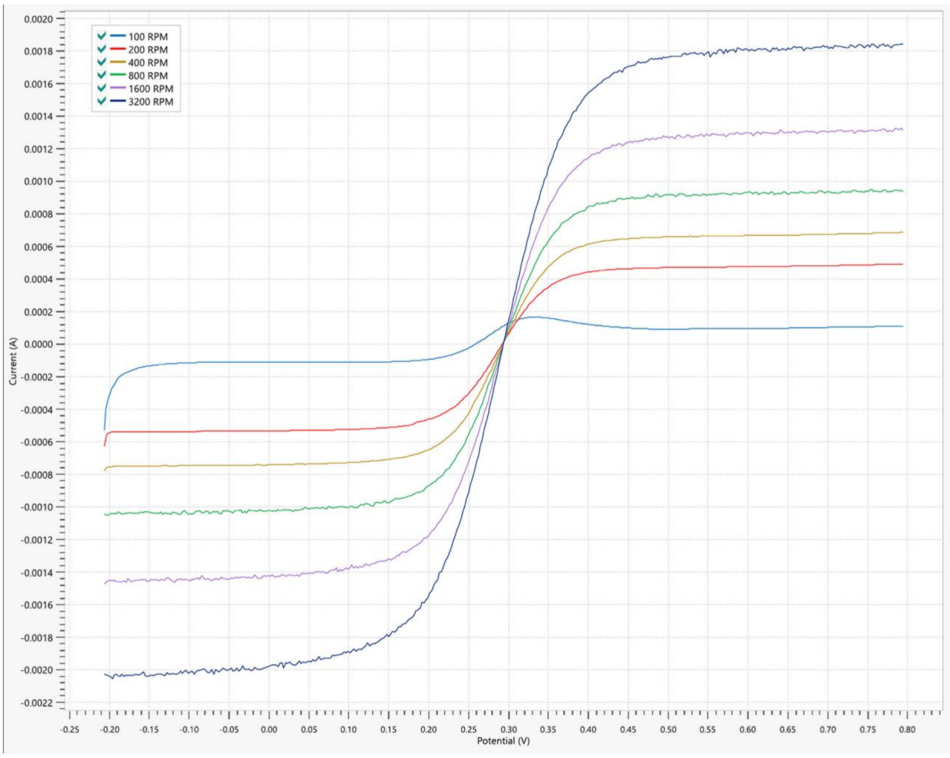

Figure 1. Overlay of the LSV curves recorded at different rotation rates using the Autolab RDE. Light blue: 100 RPM; red: 200 RPM; yellow: 400 RPM; green: 800 RPM; purple: 1600 RPM; dark blue: 3200 RPM.

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.

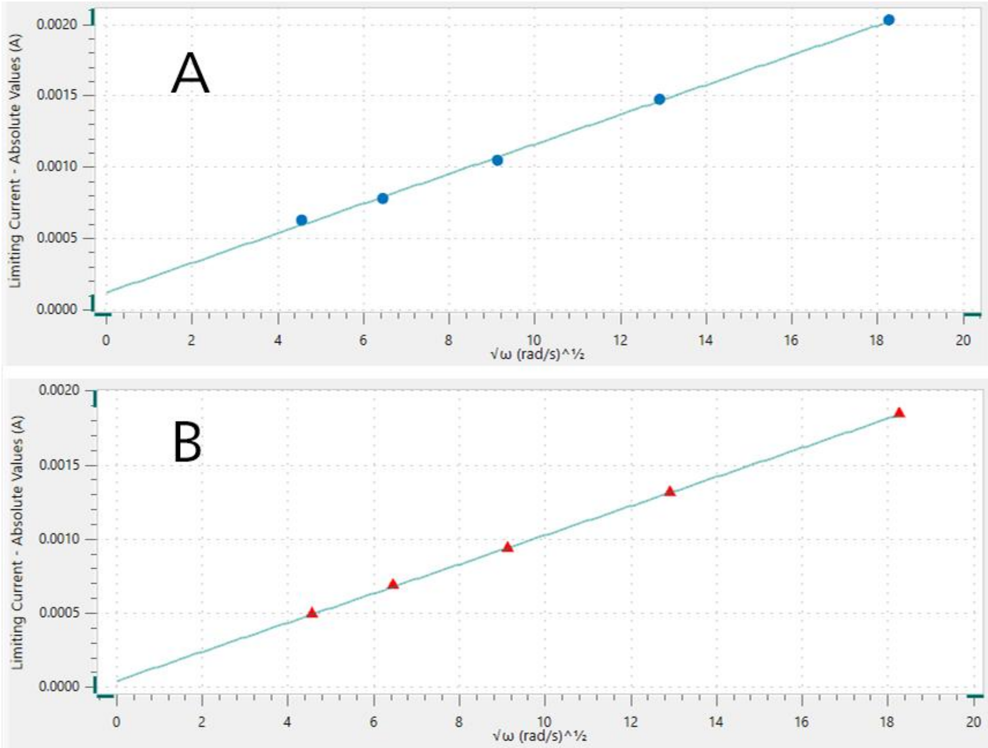

Figure 2. The Levich plots obtained by plotting the absolute values of the limiting currents versus the square root of the angular frequency. A - blue dots: anodic limiting currents. B - red triangles: cathodic limiting currents.

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

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

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.

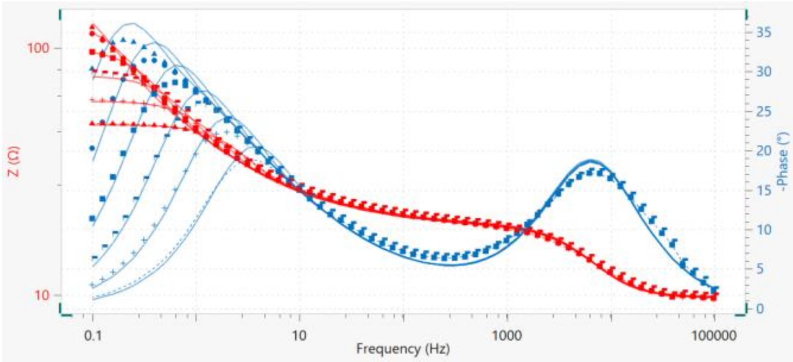

Figure 3. Bode plot (phase shift in blue data and module of the impedance in red data) for each rotation rate. Triangles: 100 RPM; circles: 200 RPM; squares: 400 RPM; flags: 800 RPM; crosses: 1600 RPM; dotted lines: 3200 RPM. The solid lines are the fit results.

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

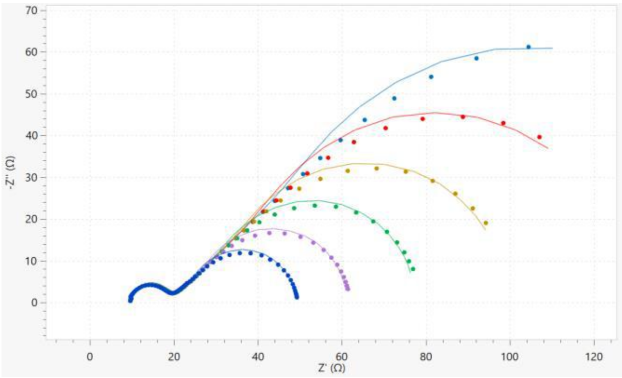

Figure 4. Nyquist plot for each rotation rate. Data are in points and the fit results are in solid lines. Light blue: 100 RPM; red: 200 RPM; yellow: 400 RPM; green: 800 RPM; purple: 1600 RPM; dark blue: 3200 RPM.

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**.

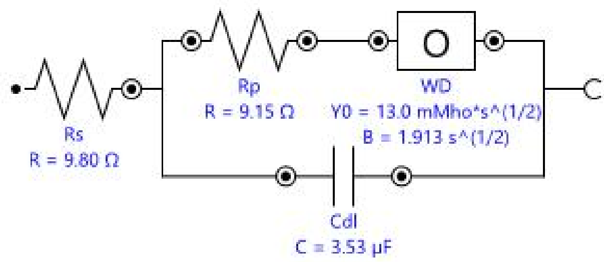

Figure 5. The equivalent circuit used to fit the data in Figure 3 and Figure 4.

CONTACT

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CONFIGURATION

Autolab PGSTAT204

PGSTAT204 合了小巧格和模化。器包括基本恒位/恒流,其从 20 V,最大流 400 mA 或 10 A,与 BOOSTER10A 合使用。此恒位可随用附加模行展,例如 FRA32M 化学阻抗(EIS)模。
PGSTAT204 是一款惠的器,可置于室的任何位置。具有模和数字入/出,可控制 Autolab 附件和外部。PGSTAT204 包括内置模分器。与高性能的 NOVA 件用,可用于大多数准化学技。

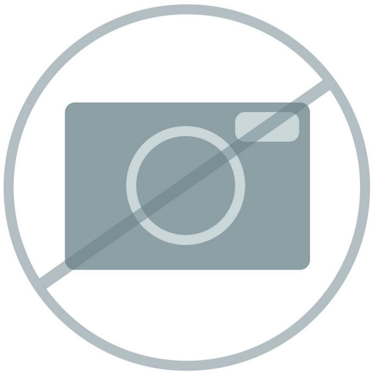
Autolab PGSTAT302N

高端高流恒位/恒流,具有 30 V 从, 1 MHz,可与我的 FRA32M 模用,化学阻抗而。
PGSTAT302N 是流行的 PGSTAT30 的后款型。最大流 2 A,借助 BOOSTER20A 流范可展至 20 A,当流范 10 nA 流分辨率 30 fA。

0.250 L

完整的腐量池,250 mL。

Autolab RDE 是一个高端旋,用于在需要高速和低噪音的系上行量。装置可到 10,000 rpm,液汞触点能保噪音低。PCTFE 棒的用于安装到万通解池中,但也可以安装到大多数化学池上。端直径 10 mm,有效面直径 3 mm 或 5 mm。
RDE 旋的旋速度可手通机控制元正面的按行控制。也可使用 Autolab 件程控制 RDE 旋。旋速度可在 100 和 10,000 rpm 之以 1 rpm 的幅度改。



NOVA 是通 USB 接口控制所有 Autolab 器的件包。由化学家化学而,集成了超二十余年的用体和最新的 .NET 件技,NOVA 使的 Autolab 恒位/恒流有更性能和活性。
NOVA 提供了以下的独特功能:

- 功能大且活的程序器
- 重要数据一目了然
- 大的数据分析和工具
- 集成化控制外器,如万通 LQH 液体理