使用 AUTOLAB RDE 研究 K₃[Fe(CN)₆]/ K₄[Fe(CN)₆]氧化和还原反应的质量传输特性

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.

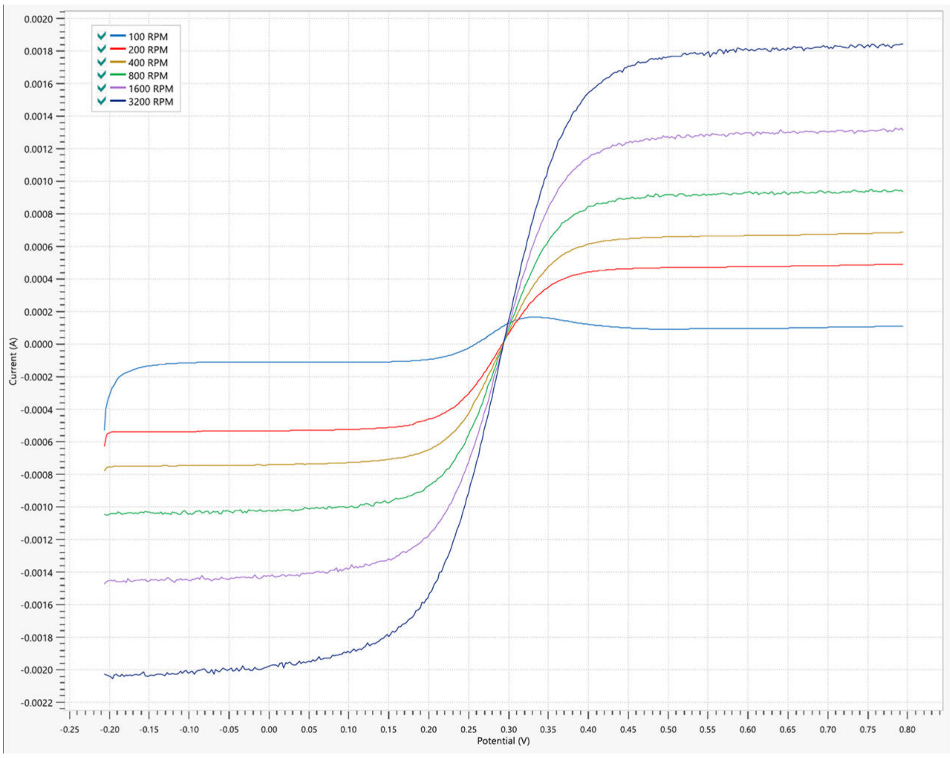

Figure 1. Overlay of the LSV curves recorded at different rotation rates using the Autolab RDE. Light blue: 100 RPM; red: 200 RPM; yellow: 400 RPM; green: 800 RPM; purple: 1600 RPM; dark blue: 3200 RPM.

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.

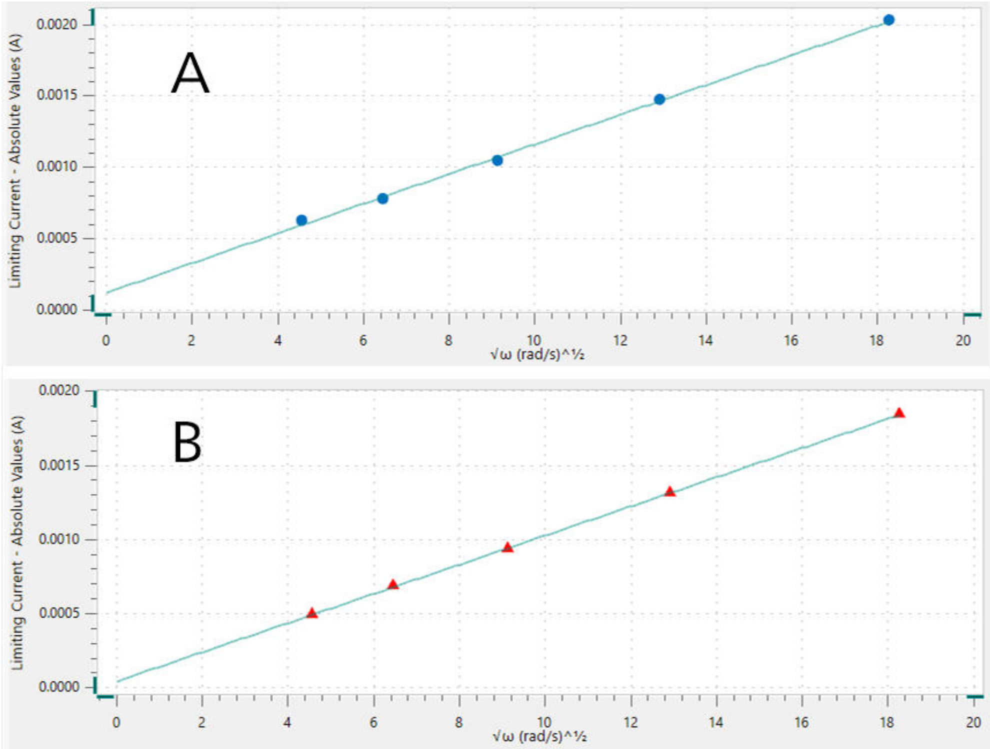

Figure 2. The Levich plots obtained by plotting the absolute values of the limiting currents versus the square root of the angular frequency. A - blue dots: anodic limiting currents. B - red triangles: cathodic limiting currents.

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.

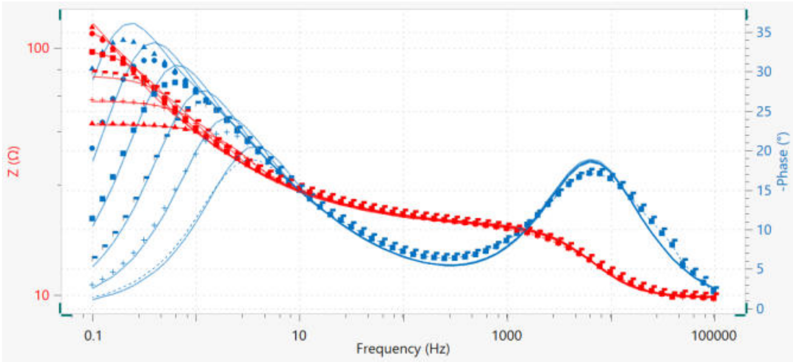

Figure 3. Bode plot (phase shift in blue data and module of the impedance in red data) for each rotation rate. Triangles: 100 RPM; circles: 200 RPM; squares: 400 RPM; flags: 800 RPM; crosses: 1600 RPM; dotted lines: 3200 RPM. The solid lines are the fit results.

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

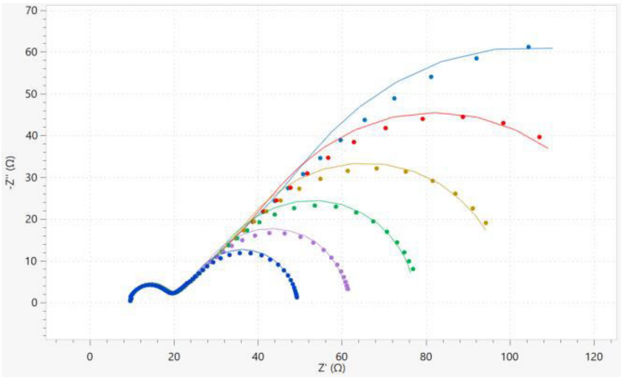

Figure 4. Nyquist plot for each rotation rate. Data are in points and the fit results are in solid lines. Light blue: 100 RPM; red: 200 RPM; yellow: 400 RPM; green: 800 RPM; purple: 1600 RPM; dark blue: 3200 RPM.

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**.

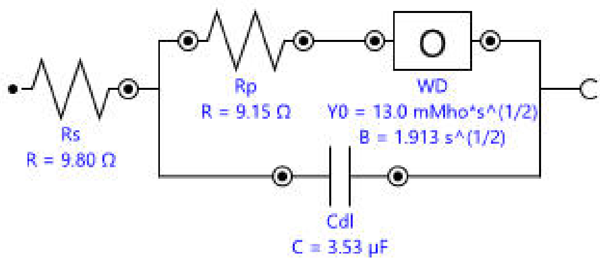

Figure 5. The equivalent circuit used to fit the data in Figure 3 and Figure 4.

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CONFIGURATION

Autolab PGSTAT204

PGSTAT204 结合了小巧规格和模块化设计。该仪器包括基本恒电位仪/恒电流仪,其顺从电压为 20 V,最大电流为 400 mA 或 10 A,与 BOOSTER10A 组合使用。此恒电位仪可随时用附加模块进行扩展,例如 FRA32M 电化学阻抗谱(EIS)模块。

PGSTAT204 是一款经济实惠的仪器,可置于实验室的任何位置。具有模拟和数字输入/输出,可控制 Autolab 附件和外部设备。PGSTAT204 包括内置模拟积分器。与高性能的 NOVA 软件联用,可用于大多数标准电化学技术。

Autolab PGSTAT302N

该恒电位仪/恒电流仪,具有 30 V 顺从电压,带宽为 1 MHz,可与我们的 FRA32M 模块联用,专门针对电化学阻抗谱而设计。

PGSTAT302N 是流行的 PGSTAT30 的后继款型。最大电流为 2 A,借助 BOOSTER20A 电流范围可扩展至 20 A,当电流范围为 10 nA 时电流分辨率为 30 fA。

0.250 L

完整的腐蚀测量池,250 mL。

Autolab RDE 是一个高端旋转圆盘电极,用于在需要高转速和低噪音的系统上进行测量。该装置可达到 10,000 rpm,液态汞触点能够确保噪音低。PCTFE 棒的设计适用于安装到万通电解池中,但也可以安装到大多数电化学池上。端头直径为 10 mm,有效面直径为 3 mm 或 5 mm。
RDE 旋转圆盘电极的旋转速度可手动通过电机控制单元正面的按钮进行控制。也可使用 Autolab 软件远程控制 RDE 旋转圆盘电极。旋转速度可在 100 和 10,000 rpm 之间以 1 rpm 的幅度连续改变。

NOVA 是设计为通过 USB 接口控制所有 Autolab 仪器的软件包。

由电化学家针对电化学而设计,集成了超过二十余年的用户体验和最新的 .NET 软件技术,NOVA 使您的 Autolab 恒电位仪/恒电流仪拥有更强性能和灵活性。

NOVA 提供了以下的独特功能:
- 功能强大且灵活的程序编辑器
- 重要实时数据一目了然
- 强大的数据分析和绘图工具
- 集成化控制外围仪器,诸如万通 LQH 液体处理设备

下载最新版本的 NOVA