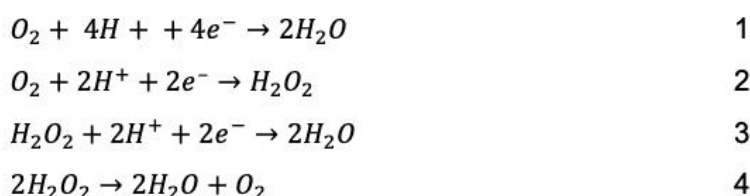


# 使用旋转环盘电极进行氧还原反应

The oxygen reduction reaction (ORR) is one of the most studied reactions in the field of electrocatalysis. The ORR in aqueous acidic electrolyte can proceed through different pathways depending on the reaction conditions. In most cases, the desired reaction is the 4-

electron process shown in **Equation 1**. Other possible reaction pathways include the combinations of **Equations 2** and **3**, where  $H_2O_2$  is formed as an intermediate, and **Equations 2** and **4**, where the reduction is incomplete.



## 概要

If hydrogen peroxide ( $H_2O_2$ ) is formed as a product or intermediate during the ORR, it can

be detected electrochemically through its oxidation reaction, **Equation 5**.



The ORR is generally studied in hydrodynamic conditions using a rotating working electrode (WE) to induce forced convection within the electrochemical cell. This strategy is applied to achieve a stable mass transfer limited current

density that may otherwise be difficult to maintain because of the slow kinetics of the reaction. In this application note, a rotating ring disk electrode (RRDE) set up is used to study the ORR.

## EXPERIMENTAL CONDITIONS

An Autolab PGSTAT302N potentiostat/galvanostat fitted with the BA module, a dual-mode bipotentiostat, was used in combination with the Autolab RRDE hardware. The measurements were carried out in a four electrode configuration using the Autolab RRDE electrochemical cell.

Since the electrochemical signals from Pt electrodes are sensitive to system impurities, all cell components in contact with the electrolyte were thoroughly cleaned. The cleaning procedure consists of soaking the components a diluted solution of  $\text{H}_2\text{SO}_4$  with  $\text{H}_2\text{O}_2$ , followed by rinsing several times with boiling water. The working electrodes were the Pt disk (WE1) and Pt ring (WE2), which are both built into a single RRDE tip. The RRDE tips have a theoretical collection efficiency of 24.9% based on the geometry of the disk and the ring. Determination of the experimental collection efficiency and the meaning of the theoretical collection efficiency value are outside the scope of this application note. The counter electrode (CE) was a platinum sheet and the reference

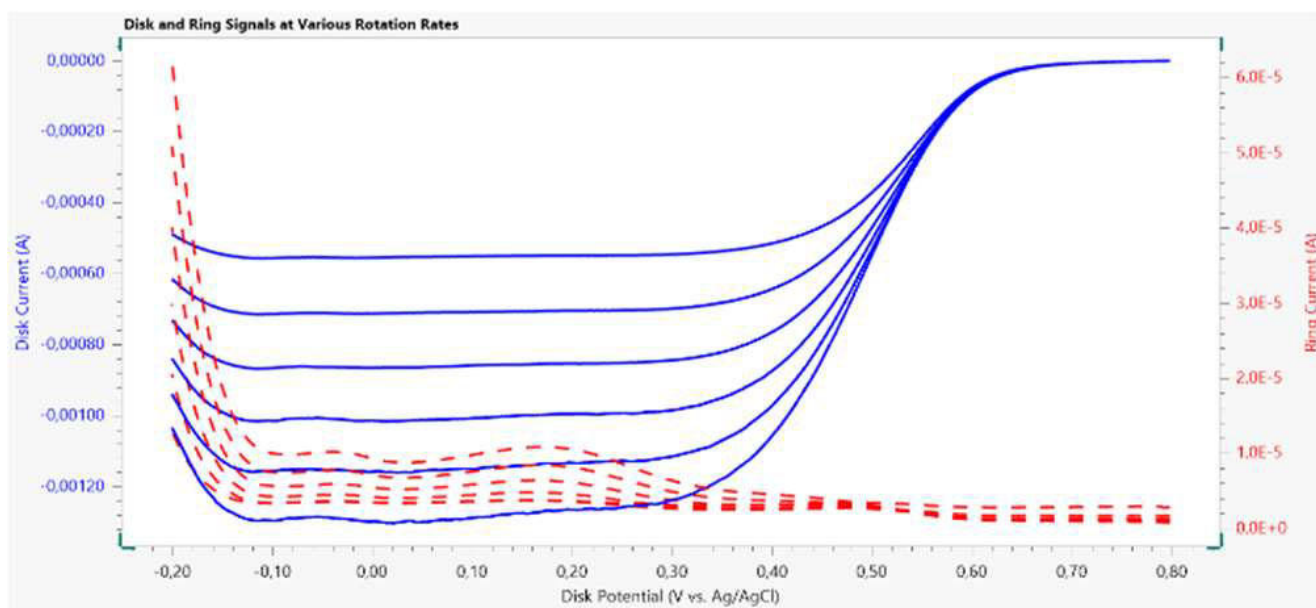
electrode (RE) was a double junction Ag/AgCl electrode with 3 M aqueous KCl solution in the inner compartment and the working electrolyte ( $0.5 \text{ M H}_2\text{SO}_4$ ) in the outer compartment. Both the CE and the RE were inserted into the cell at a height slightly above that of the bottom of the RRDE electrode tip in order to avoid disturbing the hydrodynamic flow profile. The  $0.5 \text{ M H}_2\text{SO}_4$  electrolyte was purged with high purity  $\text{O}_2$  gas for fifteen minutes prior to beginning the experiments in order to reach a saturated concentration of dissolved  $\text{O}_2$ . During the measurement, a blanket of  $\text{O}_2$  gas was maintained over the surface of the electrolyte to ensure that the concentration of dissolved  $\text{O}_2$  remained stable.

The experimental procedure *hydrodynamic linear sweep with RRDE* was applied using the NOVA software. At the disk, linear voltammetry staircase sweeps from 0.70 to  $-0.20 \text{ V vs. Ag/AgCl}$  were applied with various electrode rotation rates ( $\omega$ ). At the ring, the potential was fixed at 1.00 V and the current response was recorded.

## EXPERIMENTAL RESULTS

Figure 1 shows the results of a typical ORR RRDE experiment. The blue curves correspond to the current at the Pt disk (WE1) as the  $E$  is swept from 0.70 to  $-0.20 \text{ V}$  at a scan rate of  $50 \text{ mV s}^{-1}$

with various electrode rotation rates ( $\omega$ ). The red curves correspond to the current signal at the Pt ring (WE2), whose potential is fixed at a value of 1.00 V, at the same  $\omega$  values as the disk.



**Figure 1.** Plot of the disk (blue solid lines) and ring (red dashed lines) current data vs. the disk potential, collected during the hydrodynamic RRDE study of the ORR using a Pt disk and Pt ring.

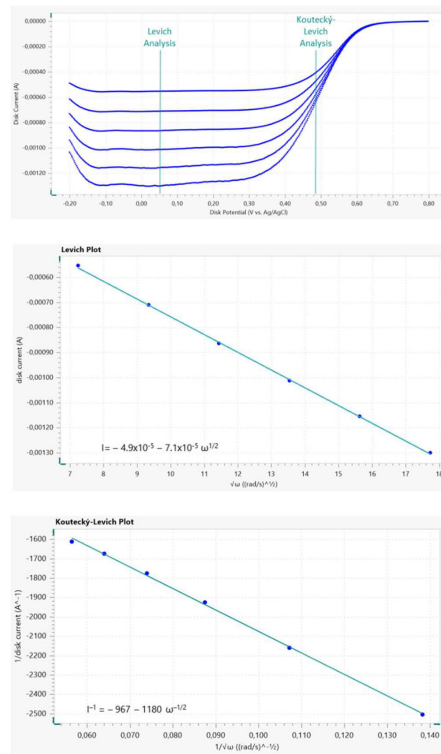
The  $\omega$  values varied between 500 and 3000 RPM; they were chosen with a square root relationship for intuitive representation on the Levich plot. As the potential at the disk is swept from high to low values, the onset of ORR gives rise to a negative (cathodic) signals that is observable at approximately 0.65 V.

The current increases with decreasing potential then reaches a plateau region at approximately  $E = 0.20$  V to  $-0.10$  V. This plateau is also known as the mass transfer limited region of the voltammetry profile where the rate of the ORR reaction is limited by the availability of oxygen at the electrode surface. The cathodic current increases in magnitude with increasing  $\omega$  according to the Levich relationship. At the lowest potential values (i.e., lower than  $-0.10$  V), cathodic current decreases in magnitude as the adsorption of hydrogen on the Pt electrode surface interferes with the ORR. The potential at the ring is fixed at 1.00 V, thus the X-axis of the graph in **Figure 1** does not apply to the ring data. Although the potential of the ring is fixed, the current signal at the ring changes as the

potential of the disk is swept. This is because the disk and the ring are in close proximity of each other (there is a separation of  $375\ \mu\text{m}$  between the disk and ring). Thus, the chemical environment at the disk influences the ring. As oxygen is reduced at the disk, reaction products, such as  $\text{H}_2\text{O}_2$ , diffuse from the disk to the ring and may undergo further reaction. The oxidation of  $\text{H}_2\text{O}_2$  gives rise to a positive (anodic) current signal and therefore the current at the ring is indicative of  $\text{H}_2\text{O}_2$  production at the disk. The anodic current at the ring increases as the potential of the disk is swept to low values that give rise to ORR at a significant rate. When the disk current is limited by mass transfer (plateau region of the blue curves), the current corresponding to  $\text{H}_2\text{O}_2$  oxidation at the ring continues at a relatively stable value. When the cathodic disk current decreases due to the presence of adsorbed hydrogen on its surface, the ring current increases sharply; this indicates a change in the ORR mechanism where a greater proportion of the reaction is now following a pathway that favors  $\text{H}_2\text{O}_2$  production.

Figure 2 shows the Levich and Koutecký-Levich plots for the ORR which demonstrate the

relationship between the current and the rotation rate at a fixed potential.



**Figure 2.** Linear sweep voltammetry profiles (top) from the disk electrode at various rotation rates; the potential value for the Levich and Koutecký-Levich analyses are indicated. Levich (middle) and Koutecký-Levich (bottom) plots.

When the potential value is selected within the mass-transfer limiting plateau of  $i$  vs.  $E$  curves, the

Levich plot follows a linear relationship according to **Equation 6**.

$$i_l = 0.62 \times AnFD^{2/3}v^{-1/6}C\sqrt{\omega} \quad 6$$

When the potential is selected from the region where the current is under a mixture of kinetic and mass

transfer control, the Koutecký-Levich plot is linear according to **Equation 7**.

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{0.62 \times AnFD^{2/3}v^{-1/6}C\sqrt{\omega}} \quad 7$$

For both **Equations 6** and **7**, the variables are defined as:

$A$  ( $\text{cm}^2$ ) is the geometric area of the disk  $F$  ( $= 96485$   $\text{C mol}^{-1}$ ) is the Faraday's constant  $D$  ( $\text{cm}^2\text{s}^{-1}$ ) is the diffusion coefficient of  $\text{O}_2$  in the electrolyte  $\nu$  ( $\text{cm}^2\text{s}^{-1}$ )

The Levich and the Koutecky-Levich plots can be fitted using linear regression to calculate the slopes and intercepts. For the Koutecky-Levich plot, the kinetic current  $i_k$  is calculated from the y-intercept which is equal to  $1/i_k$ . According to **Equation 8**, the  $i_k$

is the kinematic viscosity of the electrolyte  $C$  ( $\text{mol cm}^{-3}$ ) is the concentration of  $\text{O}_2$  in the electrolyte ( $\text{rad s}^{-1}$ ) is the angular frequency of rotation  $n$  is the number of electrons involved in the reaction

value can be related to the rate constant for electron transfer  $k$ . In order for **Equation 8** to be applied, the number of electrons involved in the reaction  $n$  must be known.

$$i_k = nFAkC$$

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## EXPERIMENTAL RESULTS

Information about the dominant mechanistic pathway at a given potential value can be elucidated based on the presence of  $\text{H}_2\text{O}_2$  detected at the ring (WE2). The data presented in **Figure 1** indicates that ORR proceeds via a mixture of the four-electron and two-electron pathways at potential values within the mass transfer limited plateau. At potential values less than  $-0.10$  V the two-electron mechanism becomes dominant, as evidenced by the increase in  $\text{H}_2\text{O}_2$  detected at the ring.

It is possible to calculate the diffusion coefficient of oxygen in the system using the slope value from the linear regression applied to the Levich plot in **Figure 2**. The variables relating to the system that are required for this calculation are listed in **Table 1**. The

concentration of  $\text{O}_2$  in the electrolyte is assumed to be equal to its solubility; in other words the solution is saturated. This experiment yields a diffusion coefficient value for oxygen in the electrolyte of  $7.6\text{E}5 \text{ cm}^2 \text{ s}^{-1}$  when assuming a four-electron process and  $2.2\text{E}5 \text{ cm}^2 \text{ s}^{-1}$  when assuming two electrons are transferred. In reality, both processes contribute to the measured electrochemical signal. The diffusion coefficient value is high when compared with a literature value of  $1.4\text{E}-5 \text{ cm}^2 \text{ s}^{-1}$  (see references). This property is sensitive to experimental parameters such as the concentration of  $\text{O}_2$  in the electrolyte, which is likely to be the most significant source of uncertainty in this measurement.

**Table 1.** System variables for the oxygen reduction reaction in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte at room temperature.

| Parameter                    | Value  | Unit                            |
|------------------------------|--------|---------------------------------|
| Kinematic viscosity          | 0.010  | cm <sup>2</sup> s <sup>-1</sup> |
| Solubility of O <sub>2</sub> | 1.1E-6 | mol cm <sup>-3</sup>            |
| Electrode geometric area     | 0.20   | cm <sup>2</sup>                 |

## CONCLUSIONS

In this application note, the Autolab RRDE system was used to study the oxygen reduction reaction with a Pt disk/Pt ring electrode. The H<sub>2</sub>O<sub>2</sub> formed at the disk electrode during ORR was detected at the ring electrode; its presence was used as an indicator of the reaction pathway. The Levich and Koutecky-

Levich plots were fitted using linear regression. The resulting equations can be used to calculate the diffusion coefficient O<sub>2</sub> in the electrolyte, the number of electrons transferred during the reaction, and the rate constant for electron transfer.

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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。



### Autolab RRDE

Autolab RRDE 池是一个完整的电化学池,针对采用 Autolab RRDE(或 Autolab RDE2)的强制对流试验而设计。该套件包括容积为 300 mL 的玻璃容器,配有恒温外套用于温度调节。

所有可能与溶液接触的部件,均可在腐蚀性条件下进行清洁,因此该池适用于典型的电催化试验或敏感界面的电化学测量。



Autolab RRDE 是低噪音的旋转环盘电极,可用于在受控流体力学条件下进行电化学测量。环和盘电极组件可通过收集实验检测反应中间体原位。

Autolab RRDE 旋转环盘电极使用 2 个相同的低摩擦汞触点确保低噪音测量,并可与任何配备 BA-双模双恒电位仪模块的 Autolab 恒电位仪/恒电流仪联用。

RRDE 旋转环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 RRDE 旋转环盘电机。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
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- 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

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