Lecture #9

Methods involving forced convection-hydrodynamic methods.

Goal

This lecture provides an understanding of hydrodynamic electrochemical methods that utilize forced convection to control mass transfer. Students will explore the theoretical principles, experimental configurations, and analytical advantages of techniques such as rotating disk, rotating ring–disk, and channel flow electrodes.

Forced convection hydrodynamic methods are essential tools in electrochemistry for achieving controlled mass transport conditions, which are crucial for fundamental studies of reaction kinetics and for practical applications in electroanalysis, corrosion science, and energy conversion systems like fuel cells.

Methods involving forced convection-hydrodynamic methods in electrochemistry utilize external means such as pumps, fans, or mechanical rotation to induce a controlled flow of the electrolyte solution, thereby enhancing and controlling the rate of mass transport to the electrode surface. This allows for the study of reaction kinetics and mechanisms under well-defined, often steady-state, conditions.

Rotating Disk Electrode (RDE). In this widely used method, a disk electrode is rotated at a controlled rate, drawing the solution from the bulk towards the surface and ejecting products outwards. This creates a well-defined, predictable laminar flow and a concentration-diffusion layer of a specific thickness, which can be mathematically modeled using the **Levich equation**. By varying the rotation rate, researchers can control the mass transport rate and separate mass transfer effects from the electron transfer kinetics.

Rotating Ring-Disk Electrode (RRDE). This is an RDE with a concentric ring electrode surrounding the disk, separated by a thin gap. Products generated at the disk are transported by the forced convection flow to the ring, where they can be detected or further reacted. This allows for the detection of reaction intermediates and the study of complex multi-step reaction mechanisms, such as the oxygen reduction reaction (ORR).

Channel Flow Electrode. In this setup, the electrode is embedded in a channel, and the electrolyte solution is pumped through the channel under an applied pressure gradient. The flow dynamics are predictable under laminar conditions, allowing for quantitative analysis.

Wall-Jet Electrode. This method involves firing a jet of solution at an electrode surface. The high, localized flow rate enhances mass transfer and sensitivity, and the system can be modeled to provide kinetic and mechanistic information.

Vibrating Electrodes. The motion of the electrode itself induces forced convection in the surrounding solution.

Key advantages of forced convection techniques (FCT) are:

- FCT significantly increase the rate of mass transport to the electrode surface, leading to enhanced current and sensitivity in electrochemical measurements.
- FCT help to suppress the random and less predictable effects of natural convection (driven by density differences) by making the forced flow dominant and well-defined (laminar).
- FCT enable the study of fast electron transfer reactions by reducing the mass transport limitations.

Hydrodynamic voltammetry, such as RDE and RRDE methods, enables assessment of both kinetic parameters and the electrocatalyst reaction mechanism.

Compared to RDE, adding the ring electrode allows the user to collect species produced on the disk. In more detail, with Rotating Ring Disk Electrode, products generated at the disk are convectively transported to the ring, where they are directly detected (Figure 1).

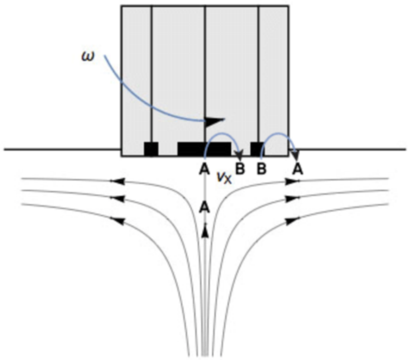


Figure 1. Redox reaction on a Rotating Ring Disk Electrode [1].

While reduction is occurring on the disc, a cycling potential at the ring can directly give the identity of, and information on, the generated product (intensity of peak current, peak potential, integrated charge).

Unlike static voltammetry, like cyclic voltammetry, where stationarity could be difficult to achieve, Rotating Disk Electrode enables steady state access easily and rapidly [2]. In static voltammetry, the diffusion layer thickness increases with time and there is no control over mass transfer (Figure 2). With a RDE, the convection of solution that is created compensates for this effect and a limiting current appears instead of a peak shaped current [3].

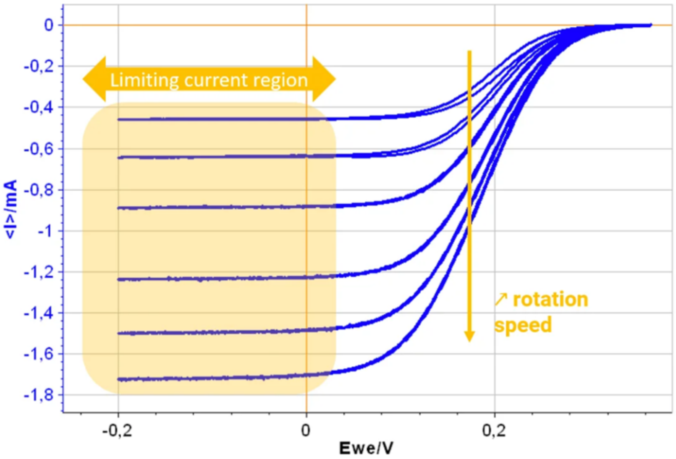


Figure 2. Results of the Levich plot experiment. The current plateaus occur at potentials for which the reaction is limited by mass transfer [2].

Figure 3 shows cyclic voltammograms of the discharge-ionization of indium on a glassy carbon electrode from a chloride electrolyte of the following composition 0.05M $InCl_3$ +2M NaCl. The reduction starts at E=−0.76V with an increase in cathodic current, followed by a limiting diffusion current at −0.83V.

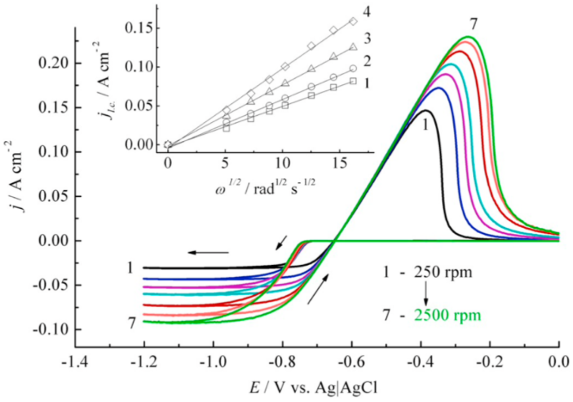


Figure 3. Cyclic voltammograms obtained at 25°C on GC electrode in 0.05M $InCl_3$ +2M NaCl solution for

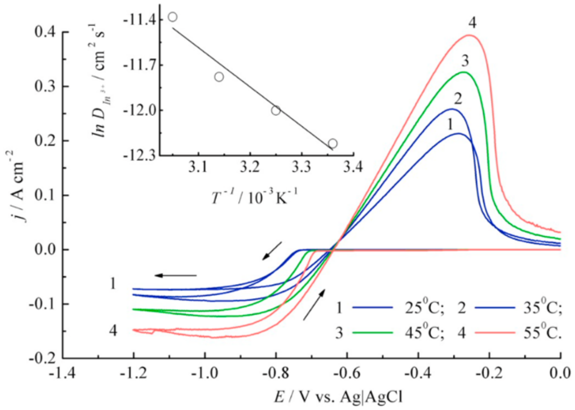


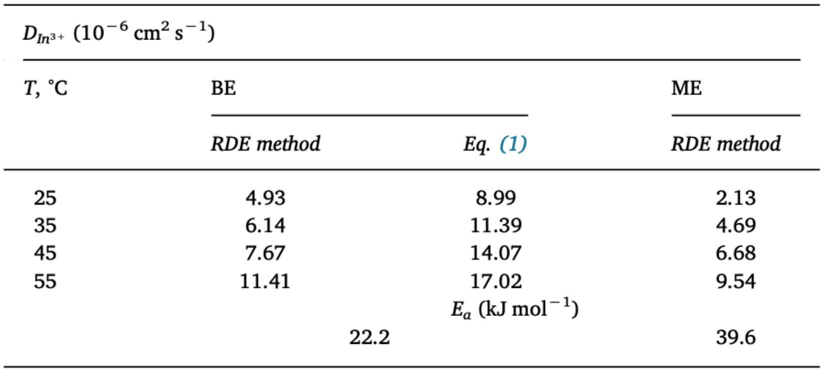
Figure 4. Cyclic voltammograms obtained at the rotation rate 2000 rpm on GC electrode in 0.05M $InCl_3$

various rotating rates (250, 500, 750, 1000, 1500, 2000 and 2500 rpm).
Scan rate of 10 mV s^{-1}. Inset: Levich plot performed at various temperatures: 1–25°C; 2–35°C; 3–45°C; 4–55°C.

+ 2M NaCl solution for various temperatures. Scan rate of 10 mV s^{-1}.
Inset: evolution of $D_{In}{}^{3+}$ versus T^{-1} (R^2 =0.97).

Varying the speed of rotation of the disk electrode allows establishing the limiting stage of the electrode process. The values of the limiting cathode currents grow with the increasing rotation speed. The growth of the area of the anode peak at different rotation rates is explained by the increase in the mass of the deposited indium. To determine the diffusion coefficient of In^{3+} ions, the dependence of the limiting cathode currents (j_{lc})on the square root of the angular velocity of rotation ($\omega^{1/2}$) was used. The diffusion coefficient of In^{3+} ions was calculated using Levich equation based on the dependence of the limiting cathode currents (j_{lc}) on the square root of the angular velocity of rotation ($\omega^{1/2}$) (Figure 3. Inset)

Table 1. The diffusion coefficients of In^{3+} ions and the activation energy of diffusion for a blank electrolyte (BE) and blank electrolyte containing 10^{-4} M tetrabutylammonium chloride solution (ME), respectively.



$D_{In^{3+}}$ (10^{-6} cm^2 s^{-1})			
T, °C	BE		ME
	RDE method	*Eq. (1)*	*RDE method*
25	4.93	8.99	2.13
35	6.14	11.39	4.69
45	7.67	14.07	6.68
55	11.41	17.02	9.54
		E_a (kJ mol^{-1})	
	22.2		39.6

It was found that the rate-determining stage of the electroreduction of indium on a glassy carbon electrode is diffusion. The above presented dependence (Figure 3. Inset) is characterized by a high correlation coefficient (in all cases $R^2 > 0.99$), which makes it possible to calculate the diffusion coefficient of In^{3+} ions at different. Temperatures (Table. 1). As the temperature increases, an increase in the limiting cathode currents is observed (Figure 4), which is associated with an increase in the diffusion coefficient ($D_{In}{}^{3+}$), obeying the Arrhenius equation (Figure 4. Inset).

Learning Outcomes

By the end of this lecture, students will be able to:

1. *Explain the principles of forced convection and its impact on mass transfer in electrochemical systems (related to LO 1.2).*
2. *Describe the operation and analytical use of rotating disk and rotating ring–disk electrodes (related to LO 1.3 and 2.1).*
3. *Interpret hydrodynamic voltammetric data to determine kinetic parameters and reaction mechanisms (related to LO 2.1 and 2.3).*

Questions and Self-study Assignments

1. *Define forced convection and explain how it differs from natural diffusion in electrochemical systems.*
2. *Derive the Levich equation and discuss its significance for rotating disk electrode experiments.*
3. *Describe the setup and working principle of a rotating ring–disk electrode and its use in detecting intermediates.*
4. *Calculate the diffusion coefficient of an electroactive species using given hydrodynamic voltammetry data.*
5. *Review a recent research article applying hydrodynamic methods in corrosion or fuel cell studies and summarize the main conclusions.*

References

1. https://www.biologic.net/topics/why-use-rde-and-rrde-method-to-characterize-electrocatalysts/
2. Bard, Allen J., Larry R. Faulkner, and Henry S. White. Electrochemical methods: fundamentals and applications. John Wiley & Sons, 2022.
3. CHAUHAN, Piyush, HERRANZ, Juan, WINZELY, Maximilian, et al. Interfacial pH and Product Selectivity Measurements during CO2 Reduction on a Rotating Ring-Disk Electrode. The Journal of Physical Chemistry C, 2023, vol. 127, no 33, p. 16453-16463.
4. Avchukir, Khaisa, et al. "Influence of tetrabutylammonium chloride on the electrodeposition of indium from chloride solution on a glassy carbon electrode." Journal of Electroanalytical Chemistry 842 (2019): 176-183.