Instrumental Technique

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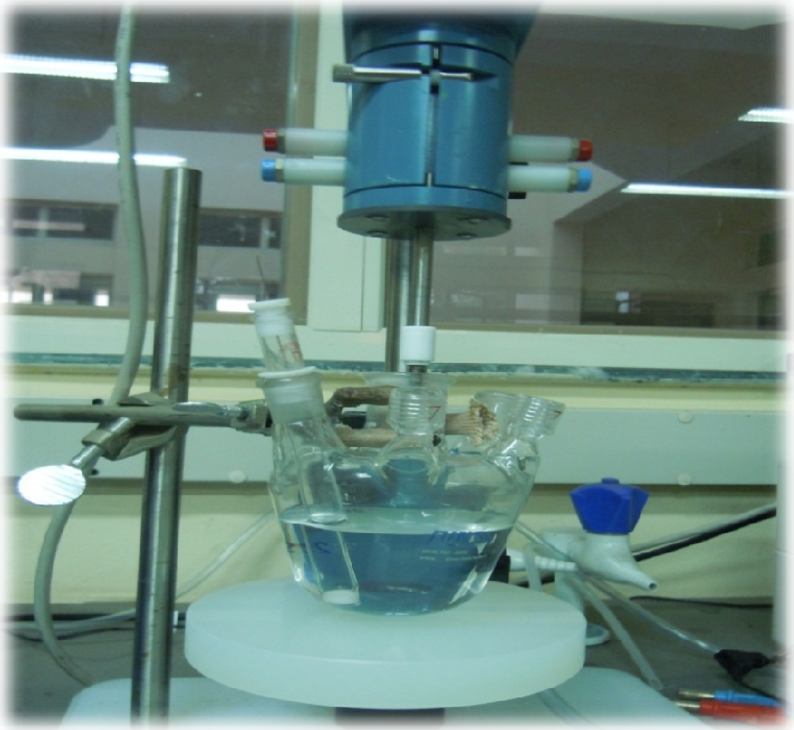
Rotating Disk Electrode (RDE)

- A rotating disk electrode (RDE) is a hydrodynamic working electrode used in a three electrode system.

- The rotating disk electrode (RDE) method has been widely used for electrochemical analysis and evaluation, as it can ensure an electrode reaction under well-defined hydrodynamic conditions.

- An RDE is a polished disc surrounded by an insulating sheath of substantially larger diameter. The structure is rotated about an axis perpendicular to the surface of the disc electrode.

- The disk like working electrode is generally made of a noble metal or glassy carbon, however any conductive material can be used based on specific needs.



Theoretical Concepts

- Heterogeneous chemical reactions that usually involve the transfer of electrons across the interface between a solid and an adjacent solution phase.

- The continuous conversion of reactant to product requires the supply of reactant to the electrode surface and the removal of product.

- In the case of dilute solutions usually mass transport becomes dominant . Three forms of mass transport can be important in electrochemistry:

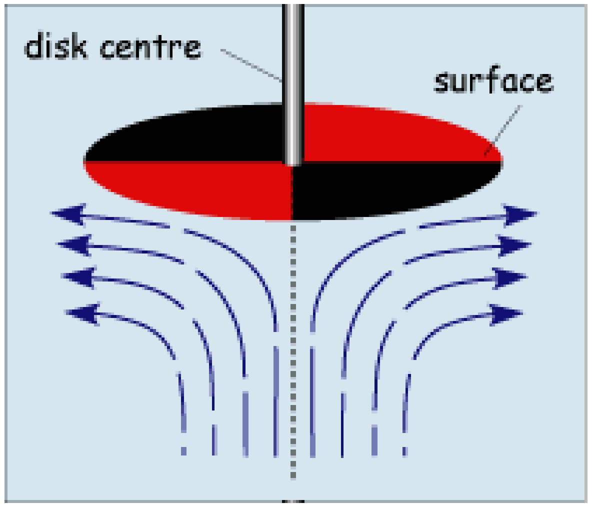
  (i) diffusion, defined as the movement of a species due to a concentration gradient

  (ii) convection, in which the movement is due to external mechanical energy—for example, electrode rotation

(iii) migration due to a potential gradient—that is, only the charged species is affected

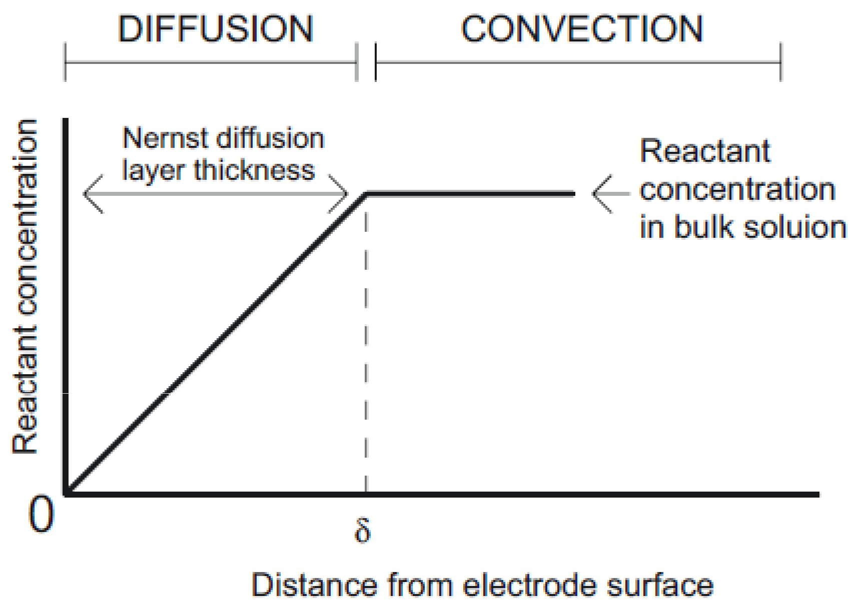
- A rotating disk electrode (RDE) is a device that creates a totally defined solution flow pattern in which the mass transport of the species is almost completely due to convection.

- This property allows the RDE to be used to calculate parameters related to mass transport, such as the diffusion coefficient of the various electroactive species (Di)



Solution movement caused by rotation of an RDE

• According to the Nernst diffusion layer model, the electrolyte can be divided into two zones



• A first region close to the surface of the electrode with thickness δ, where it is assumed that there is a totally stagnant layer and thereby diffusion is the only mode of mass transport.

•A second zone outside the first region where a strong convection occurs, and all species concentrations are constant

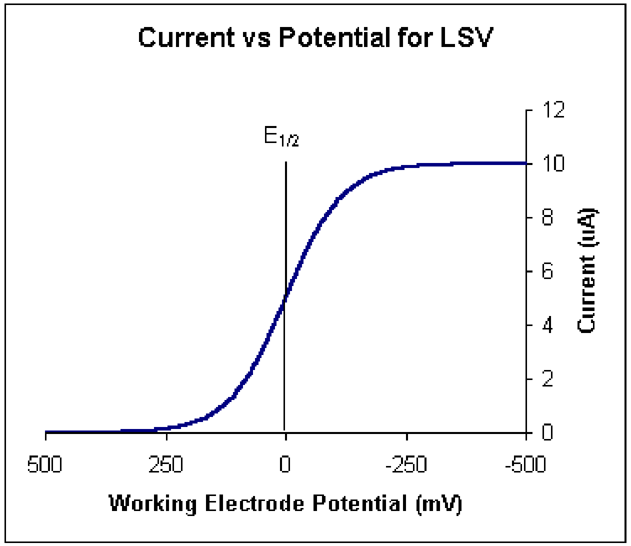
The Levich Equation

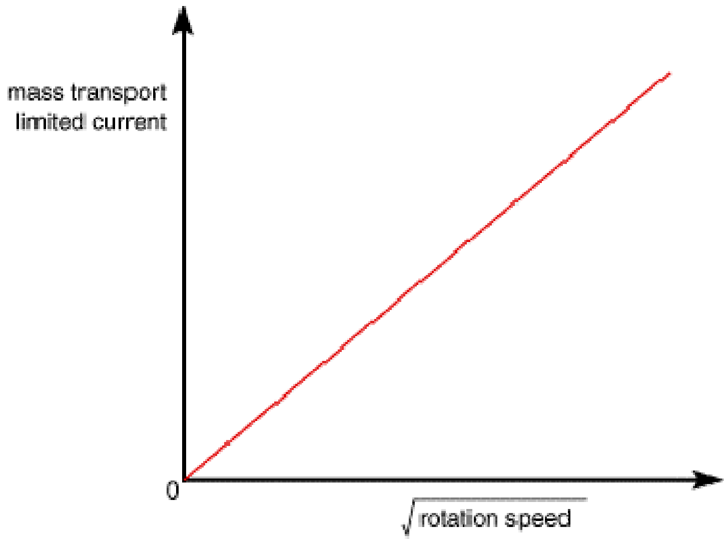
$$i_L = (0.620)\ n\ F\ A\ D^{2/3}\ w^{1/2}\ v^{-1/6}\ C$$

W- angular rotation rate of electrode

V- kinematic viscosity of solution

N- number of electrons involved in electrode reaction



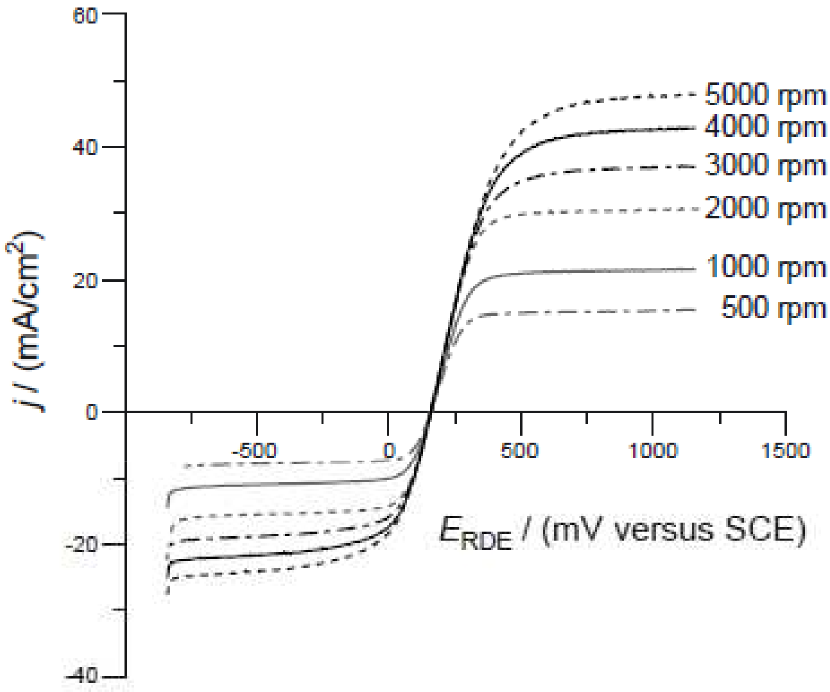


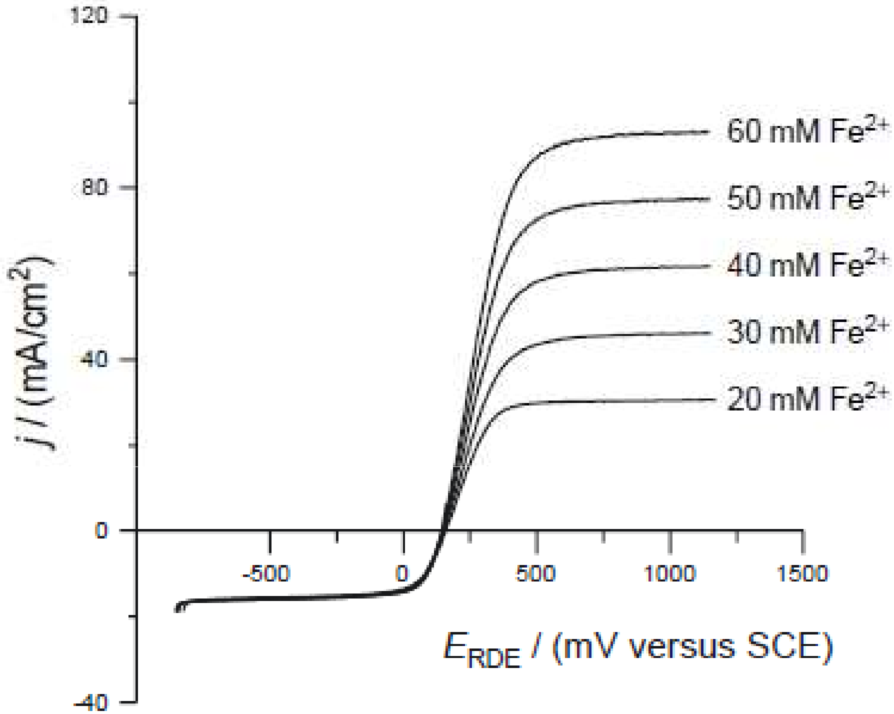
Applications

• The current is monitored with respect to the applied potential at a known sweep rate and the information is recorded on an *X–Y plotter.*

•Important parameters to consider when using linear sweep voltammetry are shown in Table

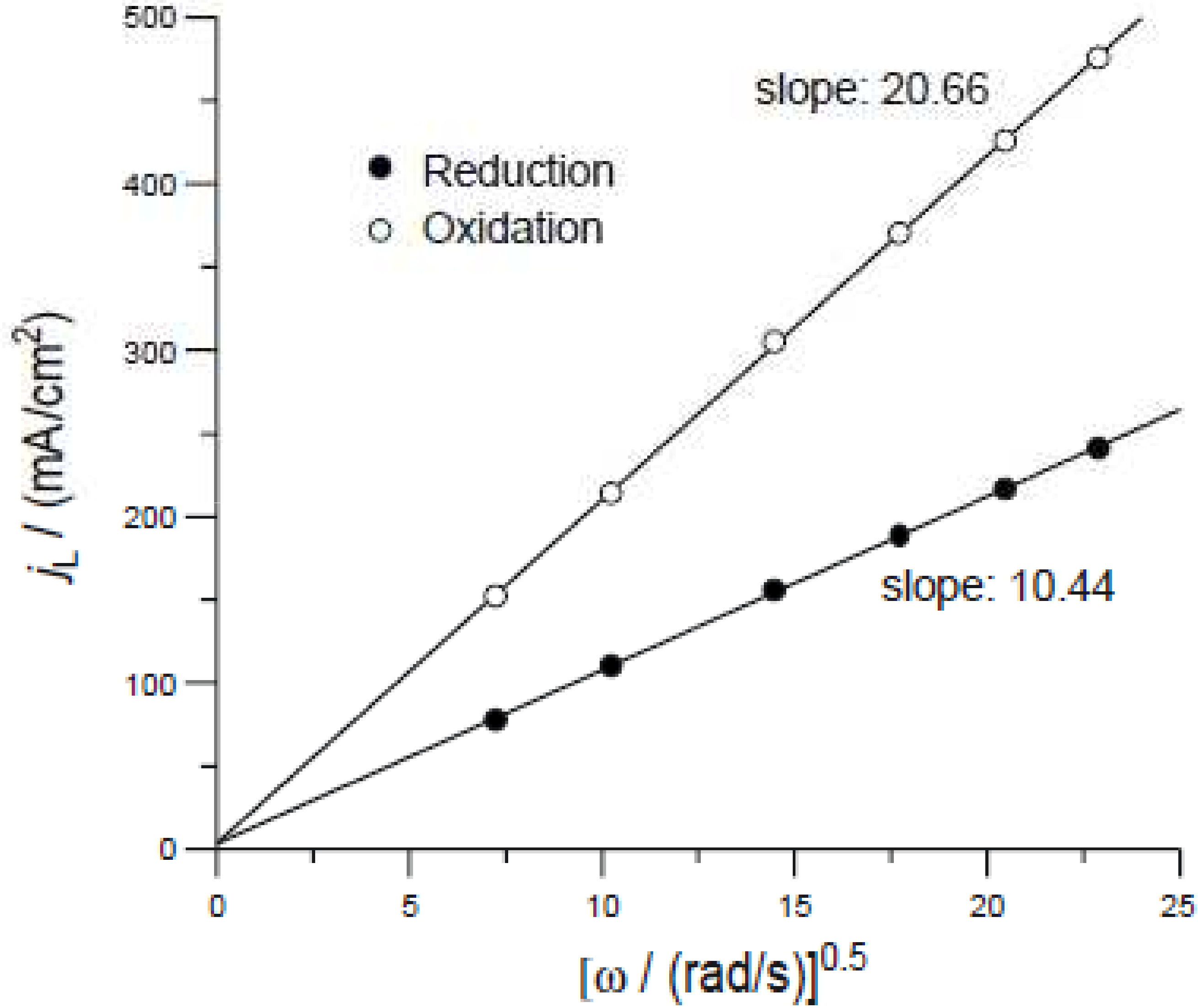
Parameter	Value
Bulk solution	10 mM $K_3Fe(CN)_6$, 20 mM $K_4Fe(CN)_6$, 0.1 M Na_2SO_4
Volume	150 mL
Initial sweep direction	positive
Initial potential	-800 mV vs SCE
Final potential	1200 mV vs SCE
Scanning rate	5 mV s^{-1}
Rotation speed	210 rad s^{-1}, fixed or variable value





Current density vs potential curves as a function of rotation rate for a solution of $K_3Fe(CN)_6$ (10 mM) + $K_4Fe(CN)_6$ (20 mM) in Na_2SO_4 (0.1 M) at a vitreous carbon RDE. Sweep rate: 5 mV s^{-1}

Current density vs potential curves as a function of K4Fe(CN)6 concentration at a vitreous carbon RDE. Rotation rate: 2000 rpm. Sweep rate: 5 mV s^{-1}



slope: 20.66
Reduction
Oxidation
slope: 10.44
0
100
200
300
400
500
j_L / (mA/cm^2)
0
5
10
15
20
25
[ω / (rad/s)]$^{0.5}$

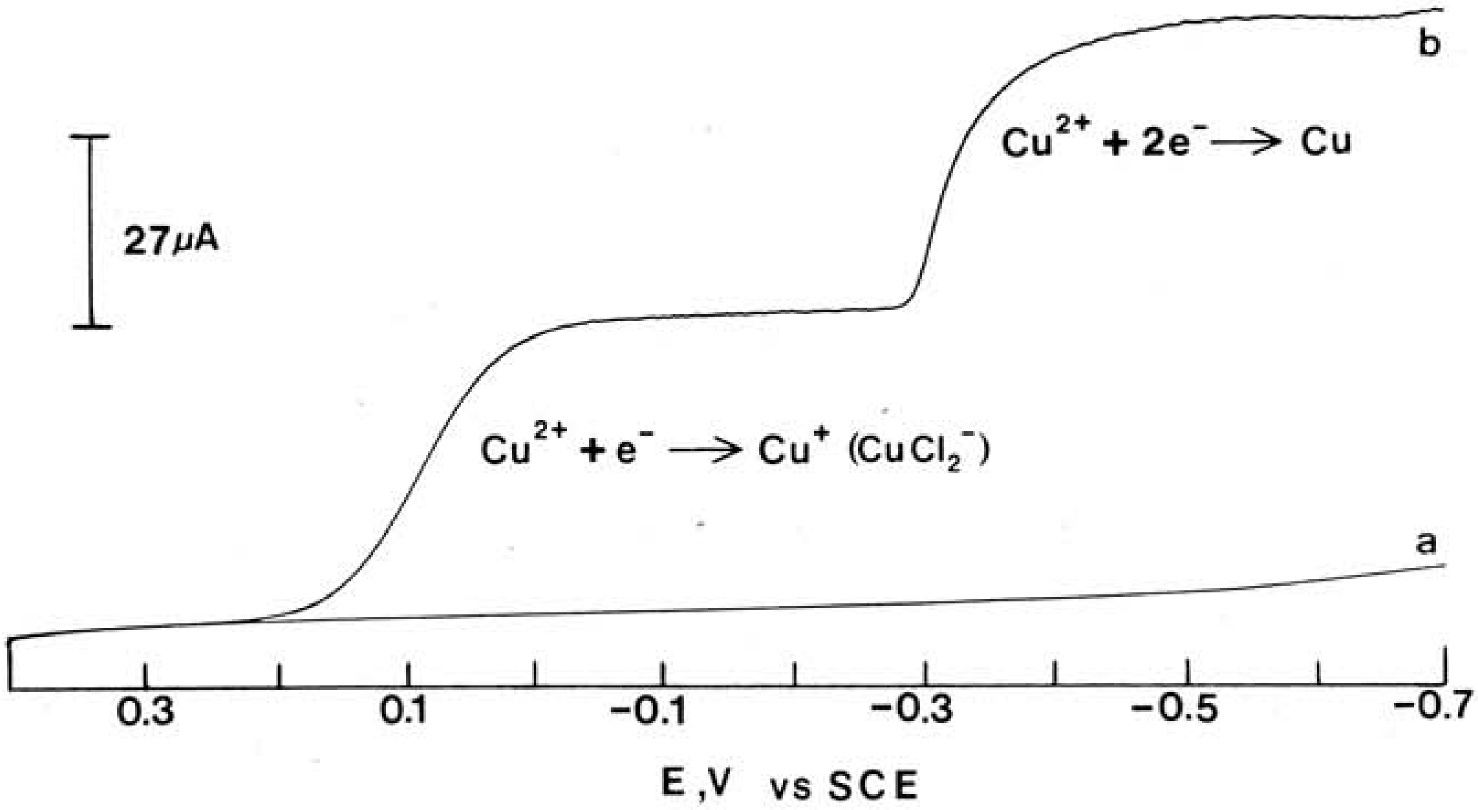


Figure 4. Rotating disk voltammograms of 1 mM $CuCl_2$ in 0.1 M KCl. Glassy carbon electrode. Scan rate: 100 mV s^{-1}. Rotation rate: 1000 rpm. (a) 0.1 M KCl supporting electrolyte. (b) Reduction of Cu^{2+}.

THANK YOU