



Voltammetry and Polarograph

- Electrochemistry techniques based on current (*i*) measurement as function of voltage (*E*_{appl})
- Voltammetry—Usually when the working electrode is solid, e.g., Pt, Au, GC.
- Polarograph—A special term used for the voltammetry carried out with a (liquid) MURCURY electrode.
- Voltammogram—The plot of the electrode current as a function of potential.









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Advantages of 3- over 2-electrode Cell System

<u>Remember:</u> In 3-electrode cell system, electrochemical cell current passes between WE and Counter electrode

3-electrode system

- Provides great flexibility in location of the reference and the working electrodes and minimizes the effect of solution *iR* drop.
- 2. Virtually has no current passing through the reference electrode.

Potentiostat

- Voltage (E) source that drives the cell
- Supplies whatever *E* needed between WE and CE to maintain specific *E* between WE and Ref. electrode
- Very high impedance (so that *i* passes though the ref. electrode is minimized)



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Working Electrodes

- Mercury electrodes (liquid)—dropping mercury electrode, hanging mercury drop electrode...
- Solid electrodes: mm in diameters, Pt, Au, GC.
- Micro(Ultramicro) electrodes: μm in diameter: Pt, Au, carbon fiber.
- Solid/liquid electrode: Mercury film electrodes, carbon paste electrode.
- Chemically modified electrodes
- ITO electrode (Transparent glass coated with ${\rm In-SnO_2}$
- Screen printing electrodes





















































Hydrodynamic Voltammetry

- Voltammetry in which analyte solution is kept in continuous motion.
- Two ways: Stirring the solution, and rotating the electrode.







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Chapter 23 Summary

- Voltammetry, polarography, voltammogram
- Potentiosat, electrochemical cell, 2 vs 3electrode, types of working electrodes
- Voltammetric signals: excitation vs response
- Processes at the surfaces of working electrodes, mass transfer/transport
- Pulse/linear/cyclic/stripping/hydrodynamic voltammetry

