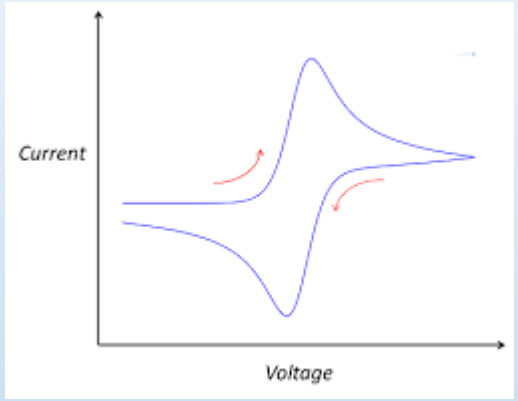
Fundamentals of Electrochemistry



Course: CSO 203
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Department of Chemistry, IIT Kanpur

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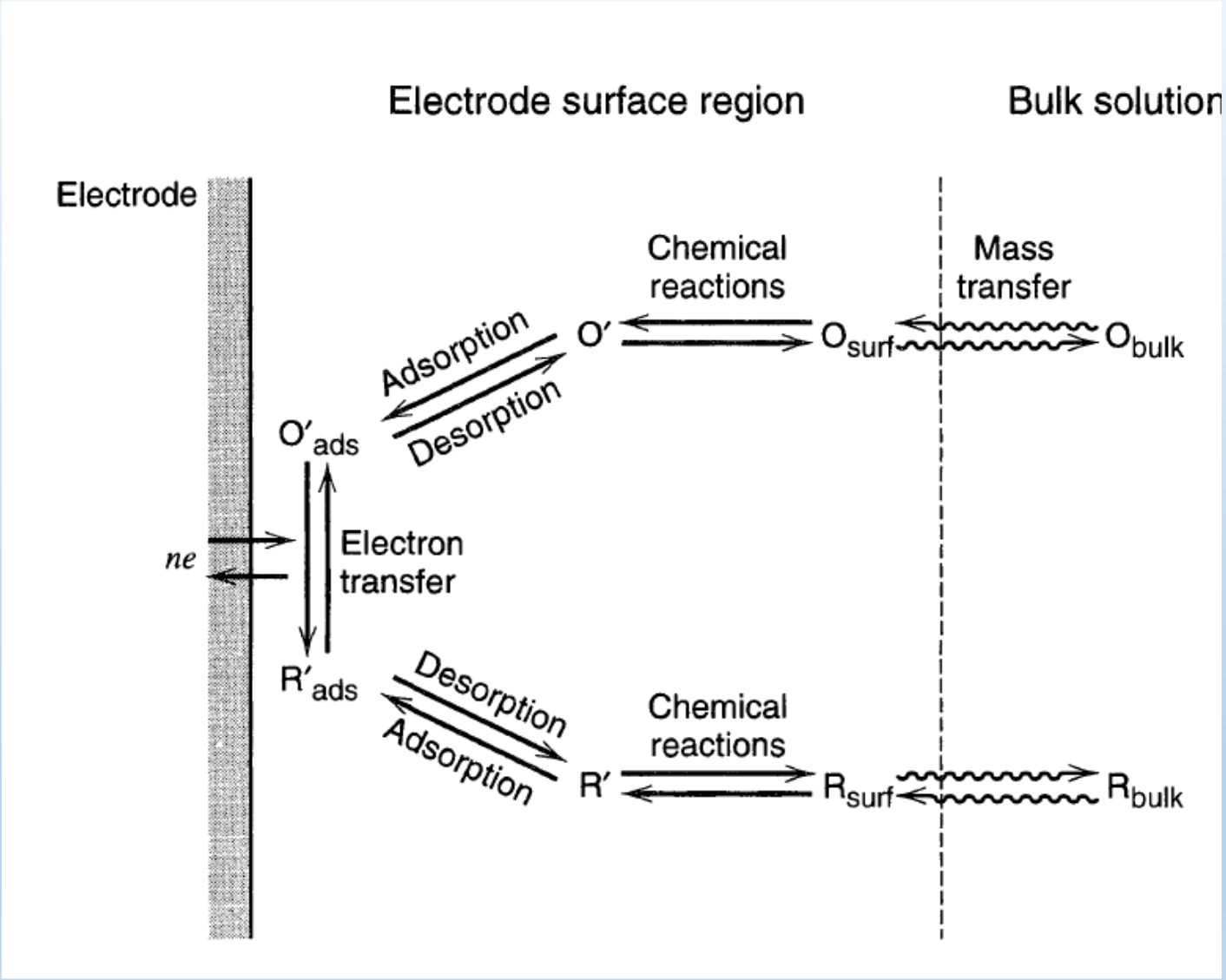
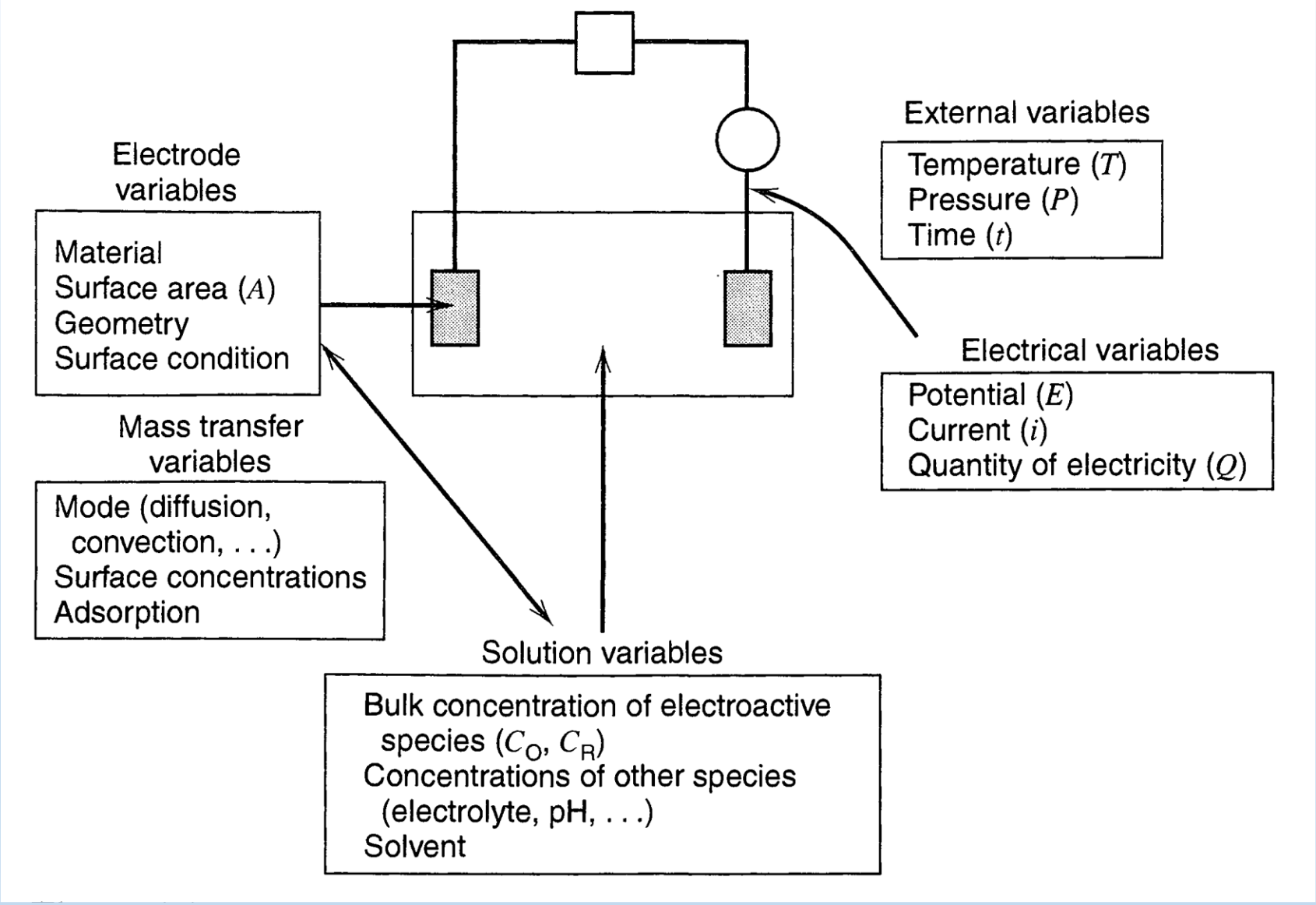
Pathway of a general electrochemical reaction



Factors Affecting the Electrochemical reactions



Electrochemical Cells—Types and Definitions

Electrochemical cells in which faradaic currents are flowing are classified as either *galvanic* or *electrolytic* cell

A galvanic cell is one in which reactions occur spontaneously at the electrodes when they are connected externally by a conductor

These cells are often employed in converting chemical energy into electrical energy

Galvanic cells of commercial importance include primary (non-rechargeable) cells, secondary (rechargeable) cells, and fuel cells

Lead-acid batteries

For discharging,

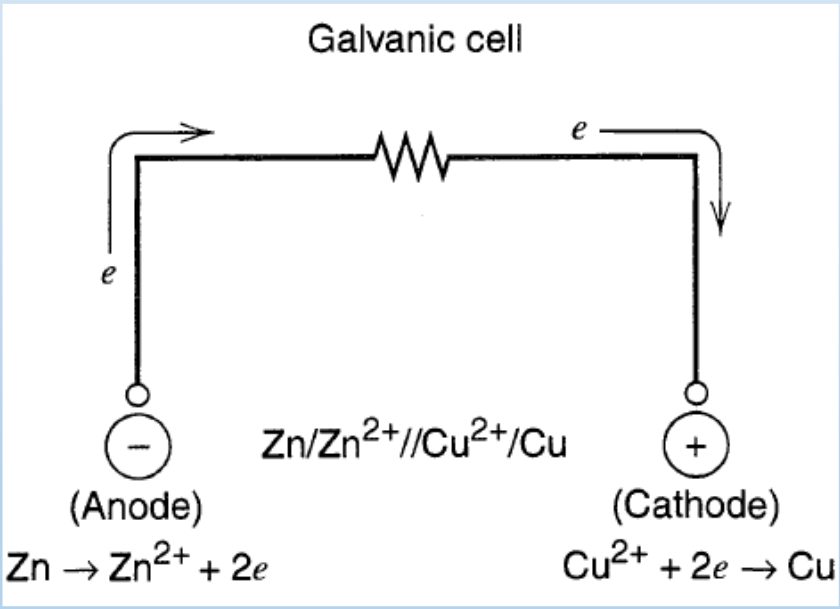
Negative plate reaction: $Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^-$

Positive plate reaction: $PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

overall reaction:

$Pb(s) + PbO_2(s) + 2H^+(aq) + 2HSO_4^-(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

For charging?



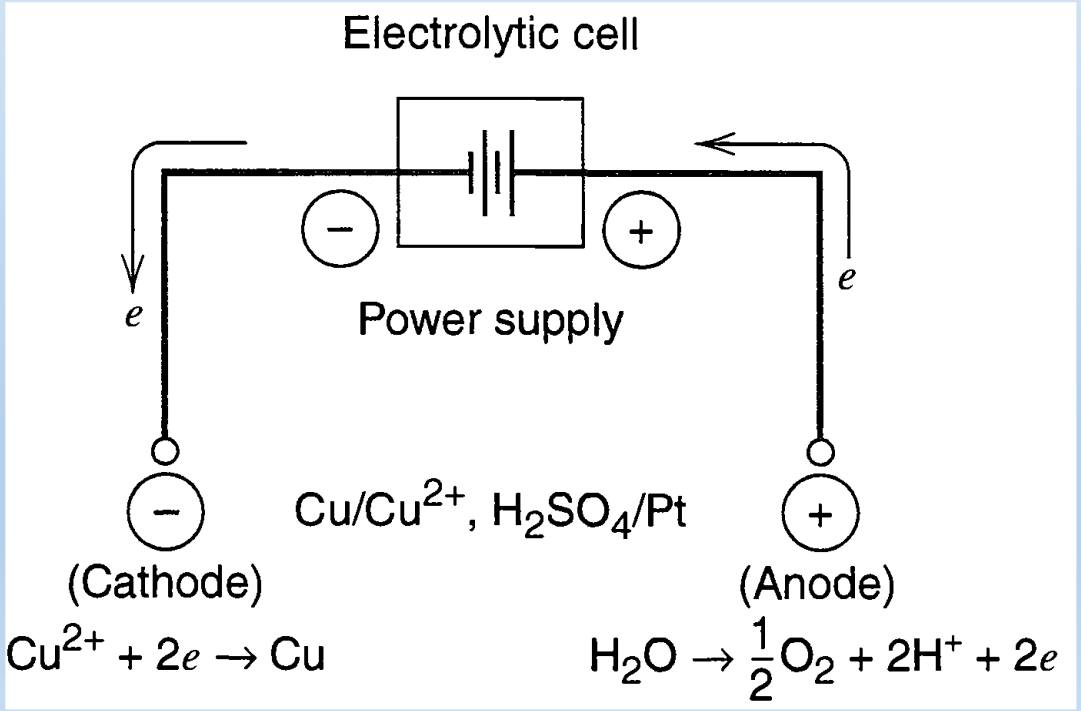
Electrochemical Cells—Types and Definitions

An electrolytic cell is one in which reactions are occurred by the imposition of an external voltage greater than the open-circuit potential of the cell

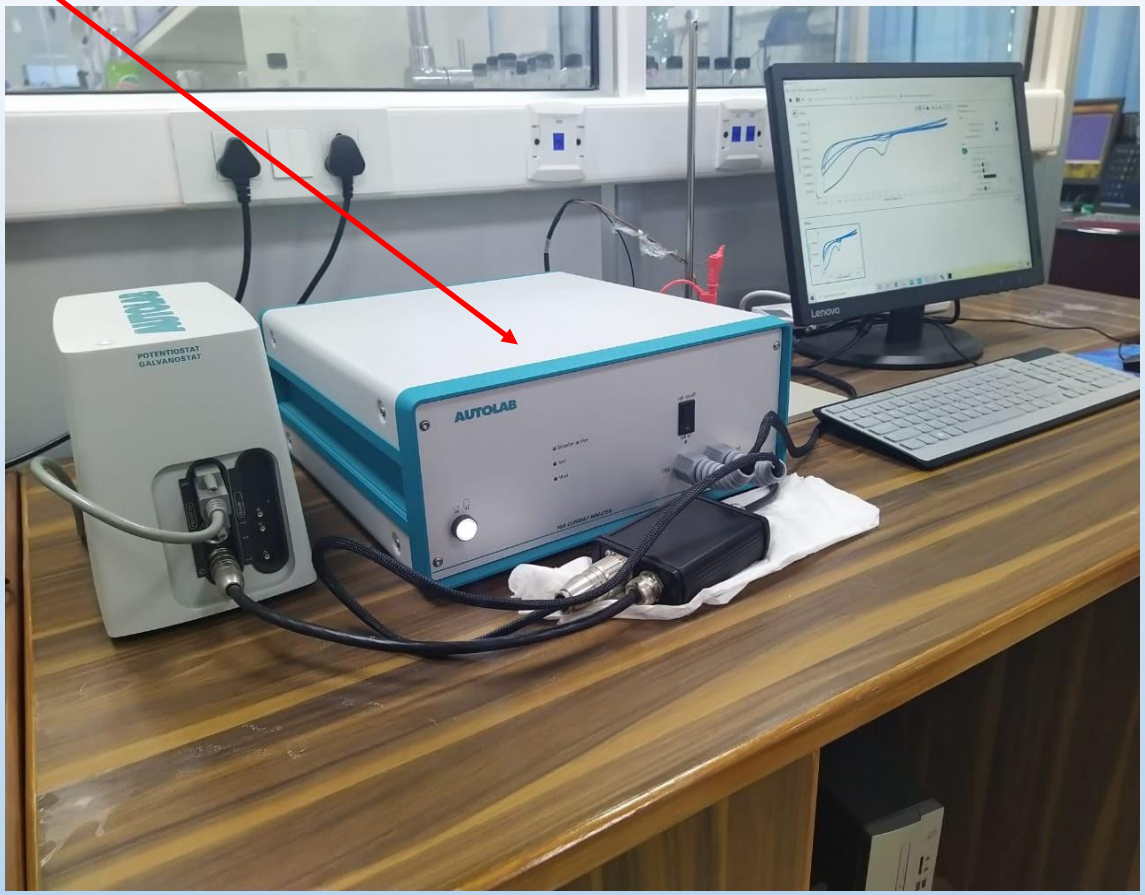
These cells are frequently employed to carry out desired chemical reactions by expending electrical energy

Commercial processes involving electrolytic cells include electrolytic syntheses (e.g., the production of chlorine and aluminum), electrorefining (e.g., copper), and electroplating (e.g., silver and gold)

***Electrolysis** can be defined broadly to include chemical changes accompanying faradaic reactions at electrodes in contact with electrolytes*

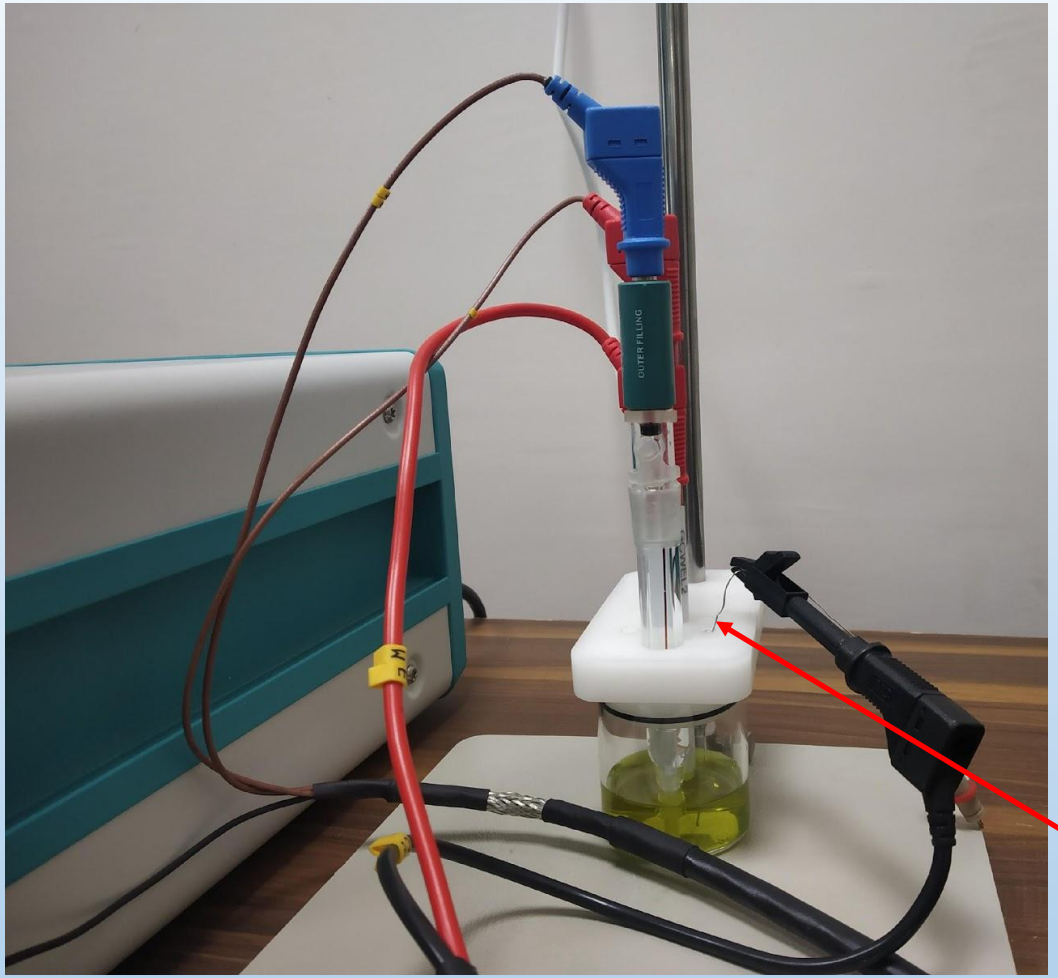


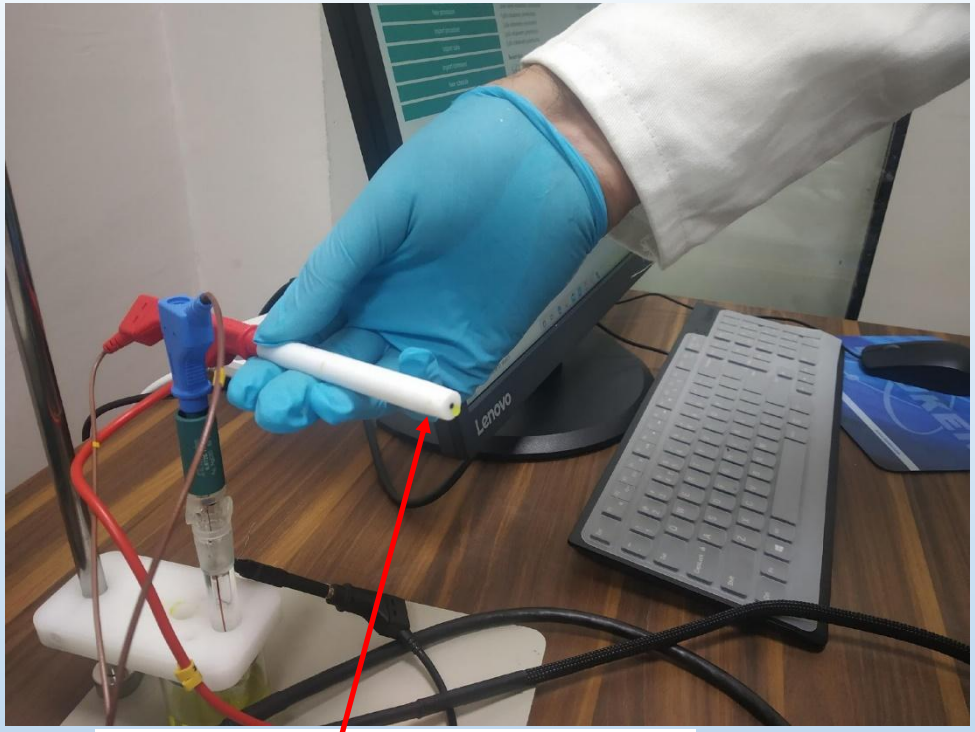
Know your Potentiostat

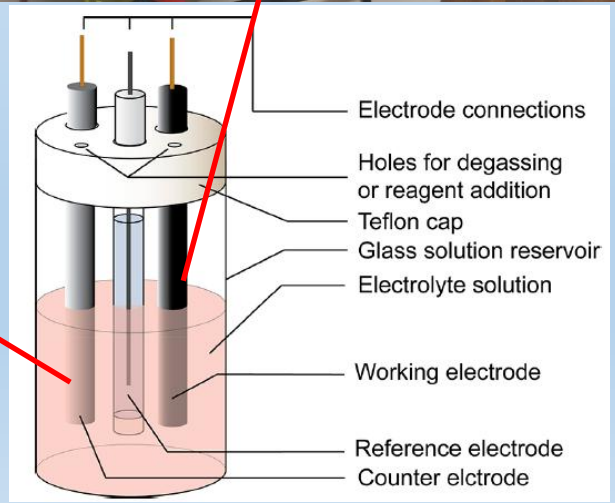


- *A potentiostat is the electronic device used to apply a desired potential/current and measure the current/potential response in electroanalytical experiments*
- *The system functions by maintaining the potential of the working electrode at a constant level with respect to the reference electrode by adjusting the current at an auxiliary electrode*

Know your three electrodes



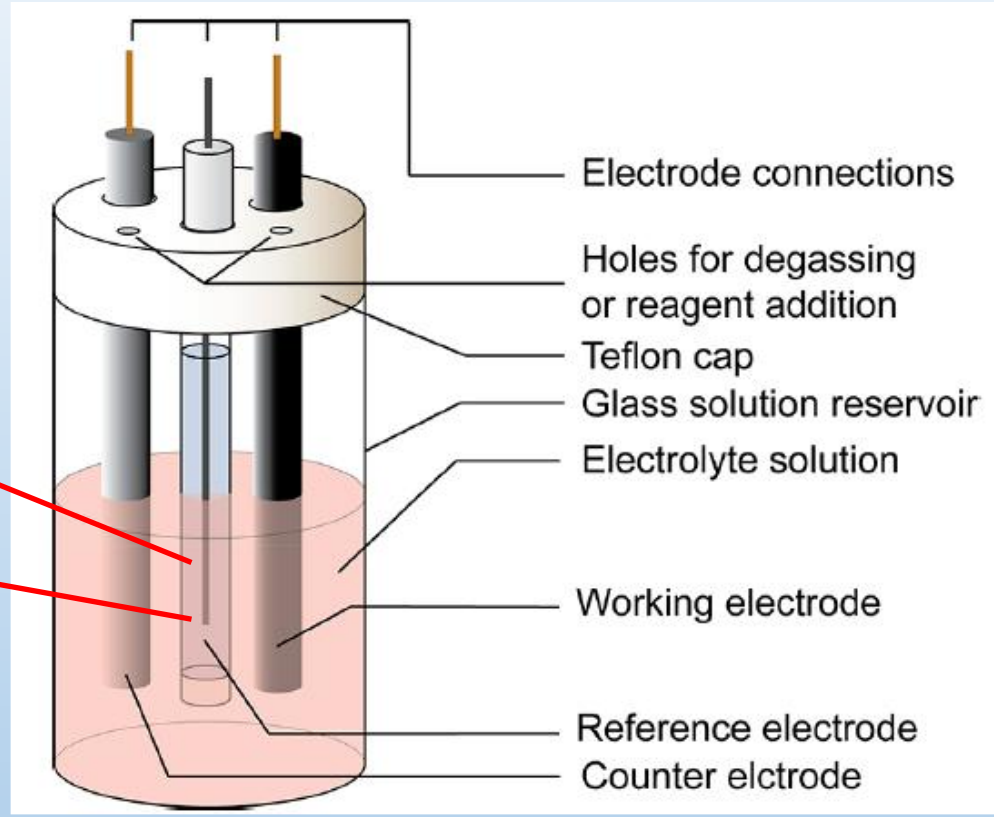




Know your reference electrodes

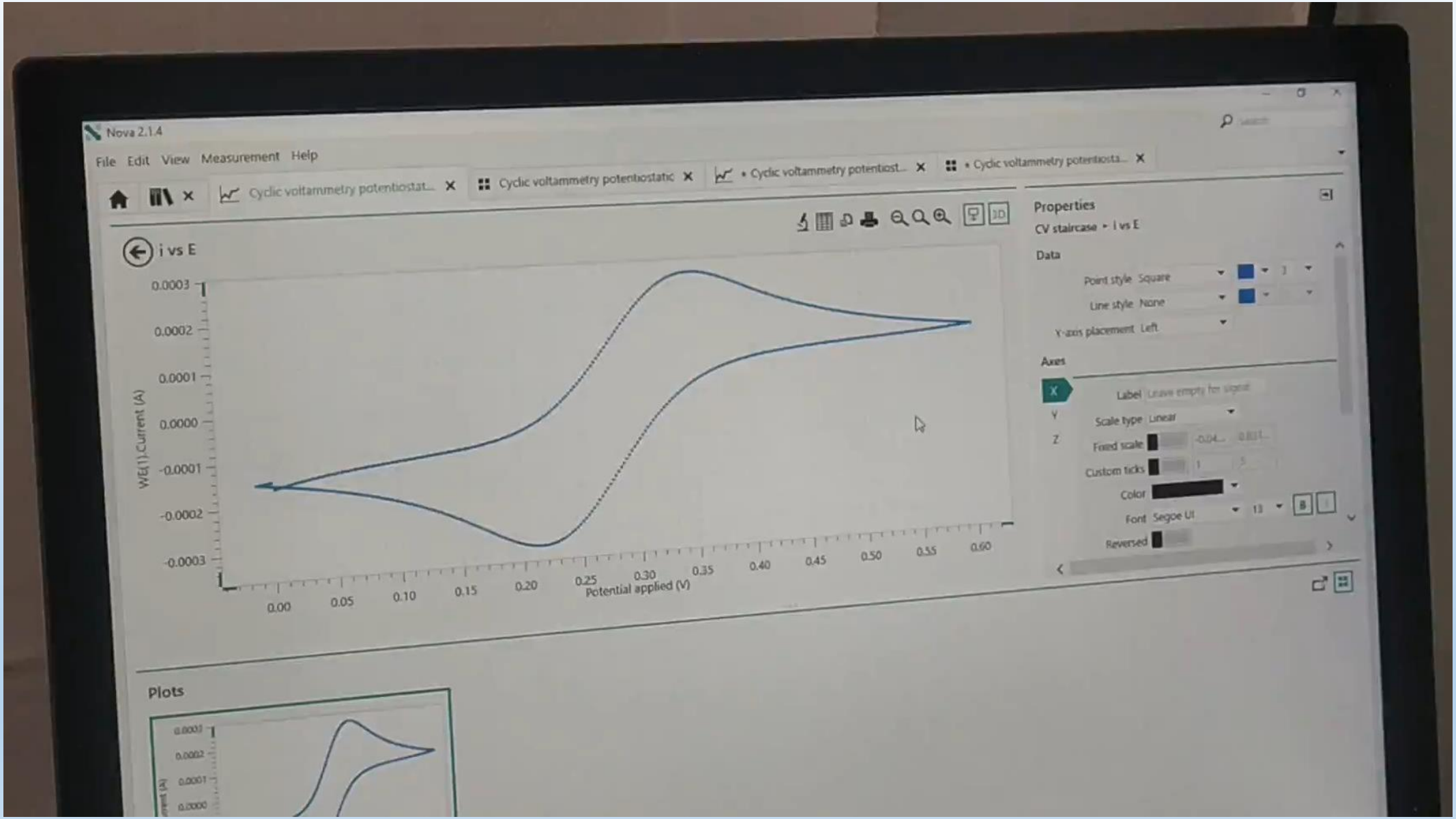
Non aqueous reference electrode

Aqueous reference electrode (Ag/AgCl in KCl (3M or saturated)



Demonstration of cyclic voltammogram of $K_3Fe(CN)_6$/ $K_4Fe(CN)_6$

Cyclic Voltammogram of Fe^{2+}/Fe^{3+}



CV of Ferrocene (10 mM in CH_3CN with 0.1 M $TBAPF_6$)

Nova 2.1.4

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Search

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Commands

- Control
- Measurement - gen...
- Measurement - cycl...
- Measurement - volt...

Cyclic voltammetry potentiostatic

AUT51966

Autolab control | Apply 0 V | Cell on | Wait 5 s | Ferrocene test | Cell off

Properties

CV staircase

Command name	Ferrocene test
Start potential	0 V_{REF}
Upper vertex poten...	0.32 V_{REF}
Lower vertex potent...	-0.2 V_{REF}
Stop potential	0 V_{REF}
Number of scans	1
Scan rate	0.05 V/s
Step	0.00244 V
Interval time	0.048828 s
Estimated number...	410
Estimated duration	20.02 s
Number of stop cro...	2

More

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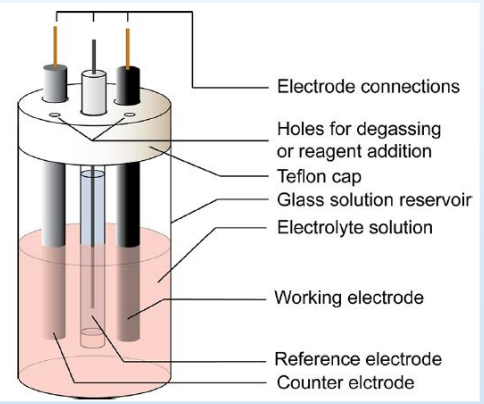
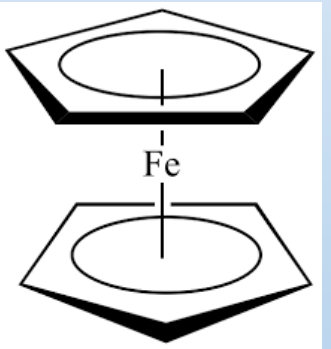
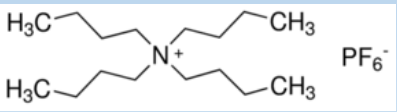
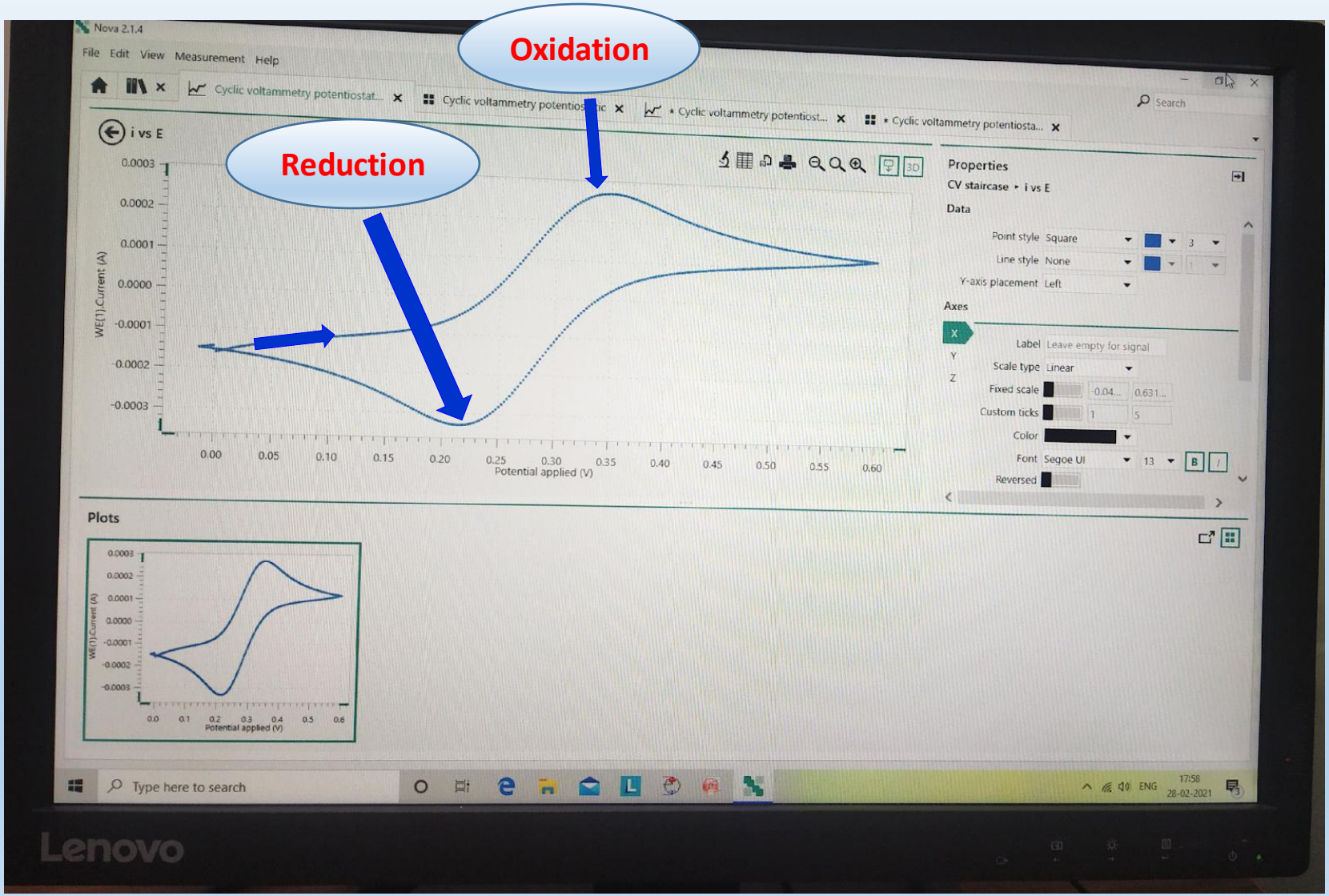


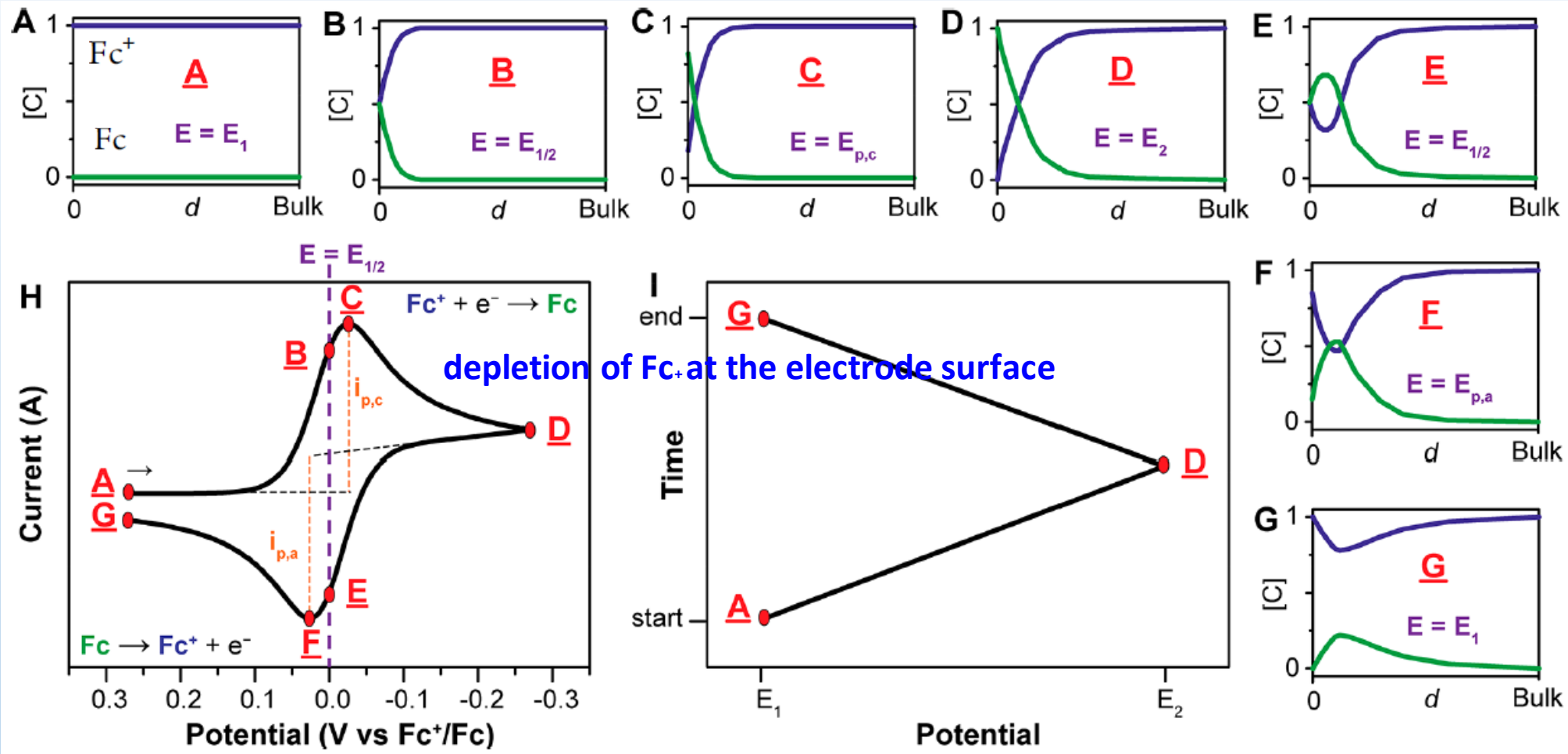




Explanation of a cyclic voltammogram



Understanding the "Duck" Shape behavior in CV



Why are there peak(s) in a cyclic voltammogram?