Potentiostat Experiments
(DC)
Potentiostat Picture

- Potentiostat (DC measurement)
- Frequency Response Analyzer (AC Measurement)
Potentiostat/Galvanostat

- **Potentiostat** (control E)
  - Electronic instrument
  - Controls “electrical potential” between the WE & RE
  - Forces whatever current is necessary to flow between WE & RE to keep the desired potential
  - As long as needed current NOT exceed limit

- **Galvanostat** (control I)
  - An electronic instrument
  - Controls “current” through an electrochemical cell
  - As long as needed cell voltage NOT exceed limit
1. **H₂ Crossover (CO) Experiment**

   = “Linear Sweep Voltammetry” (LSV)

\[
\begin{align*}
H₂ & \rightarrow 2H^+ + 2e^- \\
\frac{1}{2}O₂ + 2H^+ + 2e^- & \rightarrow \frac{1}{2}H₂O \\
H₂ + H₂O + \text{Air (or } O₂\text{)} & \rightarrow 2H^+ + 2e^- \\
\end{align*}
\]

Normal Fuel Cell

Telling How Much “little” H₂ is
H$_2$ Crossover Experiment
= “Linear Sweep Voltammetry” (LSV)

• Potential Sweep – One Direction (low to high)
• Input function: $E_{\text{start}}$, $E_{\text{final}}$, sweep rate
• SLOW Fixed sweep rate: 1-4 mV/s
  – Slow for “insignificant” V from double layer capacitance
  – Slow for not significant H$_2$ adsorption peak
• Faradaic current monitored
• Use a “Potentiostat”
Crossover Curve

- Measure “Transport Rate (Limiting Current)” of Hydrogen (H₂) through Membrane
- Tell Hydrogen Crossover Rate
- (By product) Tell Whether short circuit or not

Faradaic Current of H₂ Oxid. Rxn.
At WE

\[ V = iR \]
\[ R_{\text{short}} = \frac{V}{I} \]
\[ \text{Cond.}_{\text{short}} = \frac{I}{V} = \text{slope} \]
→ Steeper, Worse Short

Increasing Potential (increase)
Set by potentiostat
H₂ Crossover Experiment (Short Circuit)

Electrically Conductive Path

Telling How Much “little” H₂ is
2. Effective Catalytic Area (ECA) Experiment

- **Cyclic Voltammetry** (CV)

\[ H_2 + H_2O + H_2 + H_2O \rightarrow 2H^+ + 2e^- \]

Telling How Much Catalytic Area is “active” for Hydrogen Adsorption

Normal Fuel Cell

Little H₂
2. ECA Catalytic Area Experiment

- **“Cyclic Voltammetry” (CV)**
  - Reversible Process
- **Input function**: $E_{\text{start}}$, $E_{\text{final}}$, sweep rate, #cycles
- **MODERATE** Fixed sweep rate: 20-30 mV/s
  - Faster than LSV to see significant $H_2$ adsorption peak
  - NOT to be too fast → Too much double layer capacitance
  - NOT to be too fast → Becomes semi-reversible (irreversible)
- Faradaic current monitored
- Use a “Potentiostat”
Cyclic Voltammetry Curve

Peak height scales as \((\text{sweep rate} - \text{mV/s})^{0.5}\)

Hydrogen Adsorption Peak: \(\ce{H2} \rightarrow \ce{H2,ads}\)

\(\ce{H2} \rightarrow 2\ce{H^+} + 2\ce{e^-};\) Oxidation (as \(E\) \(\rightarrow\) more positive)

\(2\ce{H^+} + 2\ce{e^-} \rightarrow \ce{H2}\) Reduction (as \(E\) \(\rightarrow\) more negative)

Hydrogen Desorption Peak: \(\ce{H2,ads} \rightarrow \ce{H2}\)
Calculating Effective Catalytic Area

Crossover Current
+ Double Layer Capacitance Current
(\alpha \text{ Surface Area, Cdl, scan rate})

ASS: Known H\textsubscript{2} adsorption on flat Pt
210 \, \mu\text{C/cm}^2\cdot\text{Pt}

= Area \rightarrow \text{Charge} \rightarrow \text{Pt-surface area}
- Active for hydrogen adsorption *
- (Might not be same as in cell)

Order of 20 – 100 m\textsuperscript{2}/g

Ex-situ Methods Verification
1. Chemisorption (CO adsorption)
2. XRD

\[ \text{ECA} = \frac{\text{charge} \, [\mu\text{C/cm}^2 \cdot \text{Pt}]}{210 \, [\mu\text{C/cm}^2 \cdot \text{Pt}] \times \text{electrode loading} \, [\text{g Pt/cm}^2]} \]
CV Parameters

- Peak Ratio
- Active Peak: 2\textsuperscript{nd} = Pt (110)
- Possible 5 faces of Pt – see 2
- Double layer capacitance
  - Interfaces (Nafion/Pt/C)
- Adsorption with CO Poisoning
- Reversibly of reaction ($E_{ads}$ vs. $E_{des}$)
- Pt & C Oxidation at high Potential
Cyclic Voltammetry

Calculation of Electrochemical Surface Area
Cathode - Alfa Aesar: 40% Pt/C - 25% Nafion
Raw Data (CO vs. CV - STD SCale

B48D2R3CO.cor
B48D2R3CV.cor
Cathode - Tanaka: 46% Pt/C - 35% Nafion
Raw Data (CO vs. CV) - STD Scale

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B536D2R1CO.cor
B536D2R1CV-200ccmin.cor
Cathode - Tanaka: 46%Pt/C - 35%Nafion
GOOD - Different Loading

E (Volts) vs. I (Amps/cm²) graph showing two peaks.
Cathode - Tanaka: 46%Pt/C - 35%Nafion BAD

I (Amps/cm²)

E (Volts)
Anode - Alfa Aesar: 40% Pt-Ru (1:1) - 25% Nafion
Anode - Alfa Aesar: 36% Pt-Ru (1:1) - 25% Nafion
(Old Lot vs. New Lot) 0.4 mg/cm² Pt-Ru
Anode_Tanaka_High S.A.

Anode - Tanaka: Pt 30.1%, Ru 23.3% - 35% Nafion