FC Chemical Rxn Kinetics

→ use high current approximation

Electrochemical vs. **chemical rxn**

transferring free electrons ⇓ need a heterogeneous ◆ interface

electrode | electrolyte

e^- ← Ⓗ

interface

internal transfer ⇓ don't require a surface ~~can be~~ deals w/ Volume

current: $i = \frac{dQ}{dt}$ in $^C/_{sec}$

$\frac{dN}{dt}$ = reaction rate

$nF\frac{dN}{dt} = i = nF\,v$

example

5 sc cm H_2 gas at STP to fuel cell

(cm^3/min)

Assume 100% fuel utilization

5 cc/min →

0 ←

$n = 2$ $F \approx 96{,}000$

calculate how many atoms per second are ~~flowing~~ in $(\frac{moles}{s})$

~~that calculate the current in~~ use nFv to solve

$i = 0.66\,A$; solved in book

Charge is an "amount" $Q = \int i\,dt$

$Amps \cdot t = Q$

FC operates @ 2A for 1 hr. We change it to operate @ 5A for 2hr

# of moles H_2 needed? (or total volume)

$i_1 t_1 + i_2 t_2$

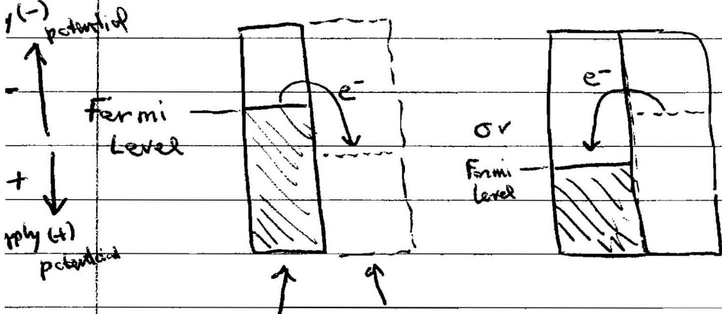
$2A \cdot 1hr + 5A \cdot 2hr = 12\ A/hr = 12 \cdot 3{,}600\ C = Q$

$N = \frac{Q}{nF} = 0.23$ moles $H_2 = \frac{12 \times 3{,}600\ C}{2 \times 96{,}000}$

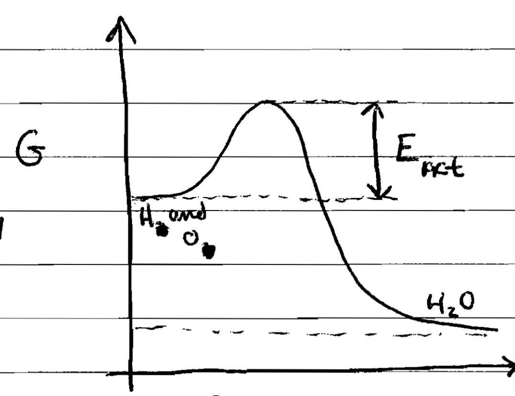
Current Density $j = \frac{i}{Area}$ A/cm^2

Area: planar surface area, not the true rxn site area

Potential controls electron energy

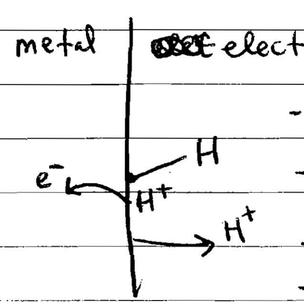


Reaction Barrier



$2H + O \longrightarrow H_2O$

$2H \longrightarrow 2H^+ + 2e^- \longrightarrow$ metal



- must first be absorbed and bond ①
- react and release ③A e^- M-H bond ②B
- transfer e^- ③
- release H^+ ④

limiting rate = slowest step

Suppose step ③ is slowest, (transfer of e^-)

must have enough free energy to tear off e^- from H

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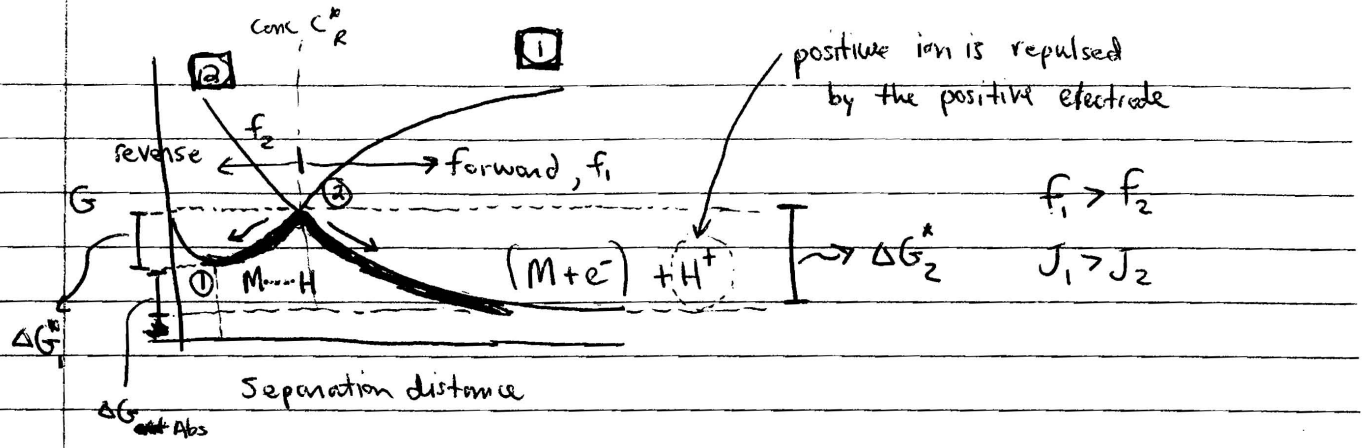


Probability of going from ① → ② $\sim \exp\left(-\frac{\Delta G_1^*}{RT}\right)$

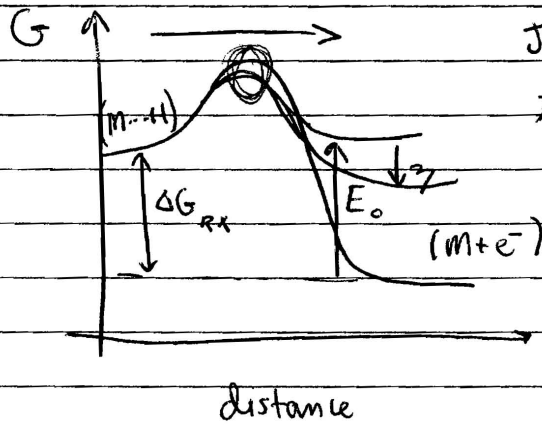
$P_{① \to ②} \cdot \left(f_1 / C\right) \cdot C_R^*$

$J_{net} \equiv J_1 - J_2$

$= C_R^* f_1 \exp\left(\frac{\Delta G_2^*}{-RT}\right) - C_R^* f_2 \exp\left(\frac{-\Delta G_1^*}{RT}\right)$

$\Delta G_2^* = \Delta G_1^* + \Delta G_{Abs}$

to lower ΔG_{act} we need to play with the M···H bonding
↳ lower the II curve.
Platinum is excellent for this.



$J_1 = J_2 = J_o \equiv$ exchange current

if $J_1 = J_2$: $I_{current} = 0$ ✓

E_o open circuit voltage ✓

To get current, reduce E_o by η