High Temperature Electrochemistry

The Search for Breakthroughs in Electrolysis

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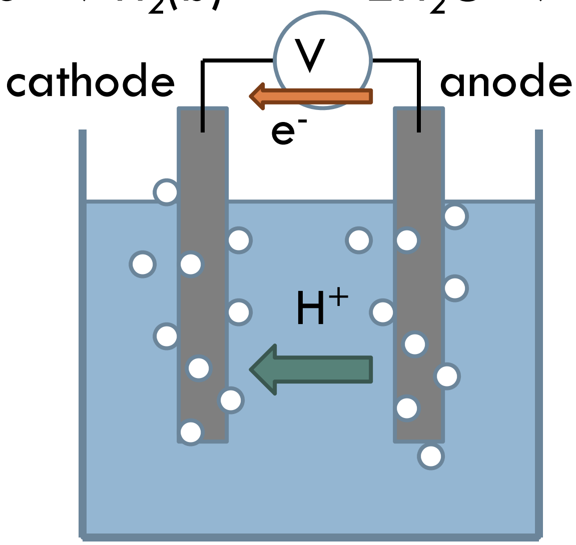
Electrolysis Schemes

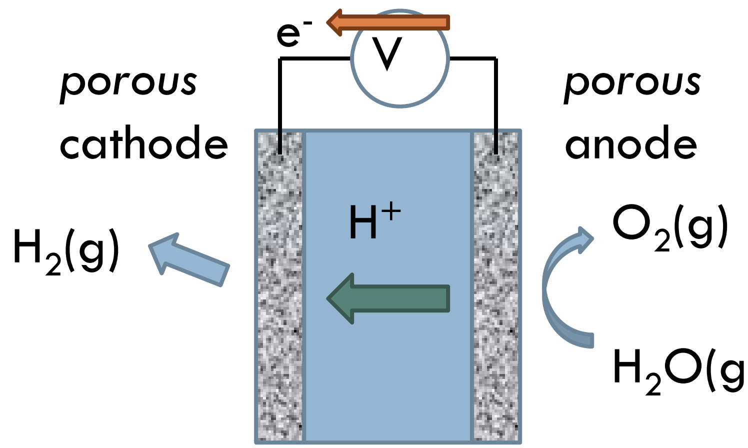
$H_2O \rightarrow H_2 + \frac{1}{2} O_2$

Low temperature (wet) | **High temperature (dry)**

$2H^+ + 2e^- \rightarrow H_2(b)$ $2H_2O \rightarrow 4H^+ + 4e^- + O_2(b)$



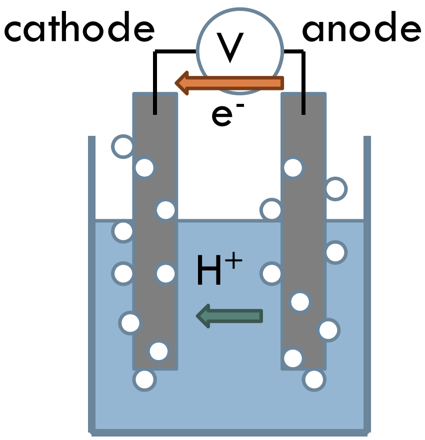
same global reactions



liquid or polymer electrolyte
aq. acid (H^+) or base (OH^-)
molten carbonate ($CO_3^{=}$)

solid electrolyte
proton (H^+) or oxide ion ($O^{=}$)
possible solid OH^- conductor

Voltage-Current Characteristics

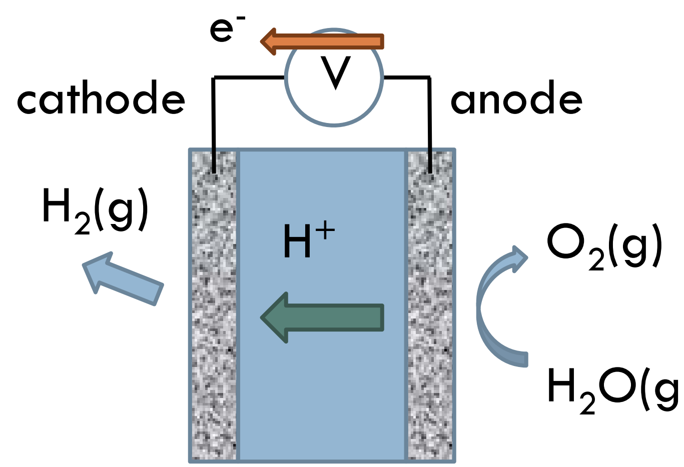


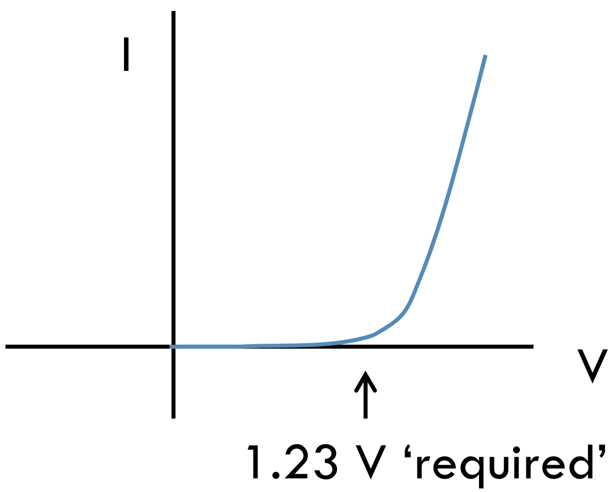
$$2H_2O \rightarrow 2H_2 + O_2$$

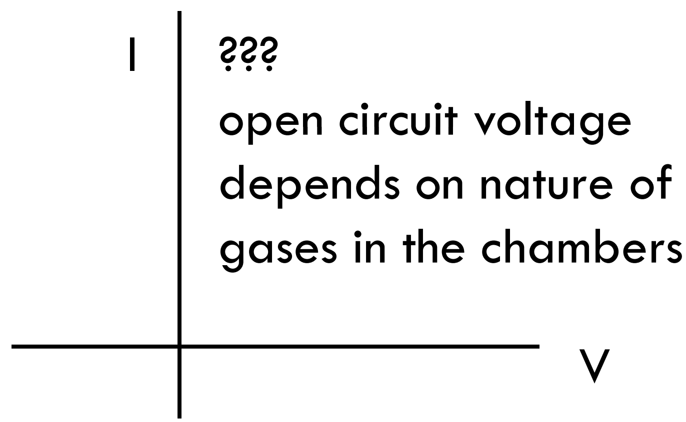
$$E^0 = \Delta G^0/nF = 1.23\ V$$

standard potential (E^0)

standard Gibbs energy of rxn (ΔG^0)

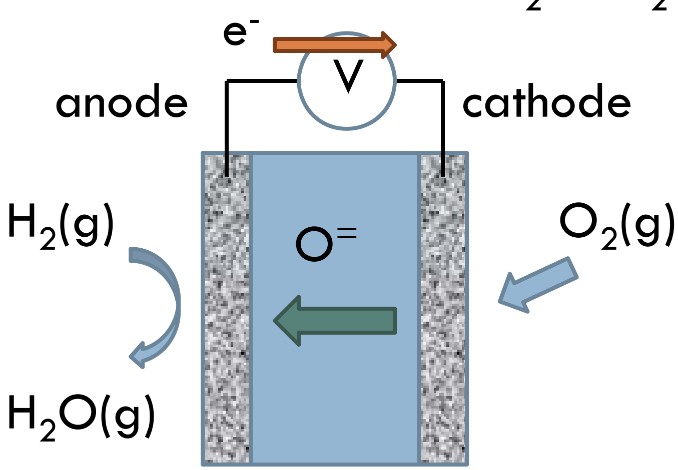






Consider a solid electrolyte FC

$2H_2 + O_2 \rightarrow 2H_2O$



At open circuit (& no leaks)

$\Delta G = \mu O_2(a) - \mu O_2(c) \neq \Delta G^0$

$\mu O_2 = \mu O_2^0 + RT\ln(pO_2)$

$$\Delta G = RT\ln\left\{\frac{pO_2(a)}{pO_2(c)}\right\}$$

$pO_2(a)$ fixed by equilibrium between H_2 and H_2O

$$\Delta G = \Delta G^0 + RT\ln\left\{\frac{pH_2O(a)^2}{pH_2(a)^2\, pO_2(c)}\right\}$$

$E = \Delta G/nF \quad (n = 4)$

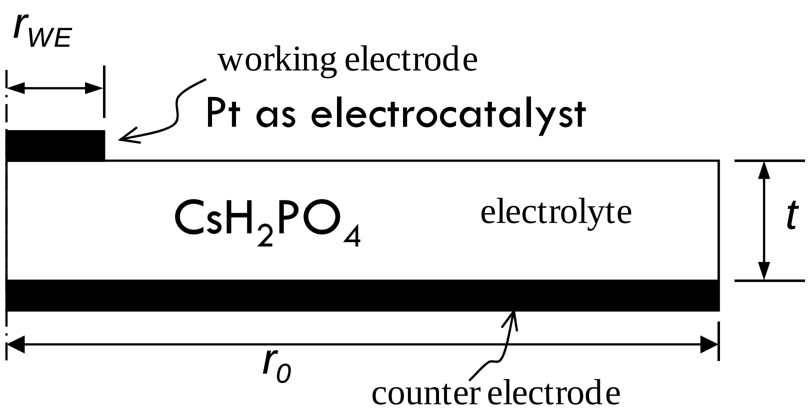
$$E = E^0 + \frac{RT}{4F}\ln\left\{\frac{pH_2O(a)^2}{pH_2(a)^2\, pO_2(c)}\right\}$$

(Nernst)

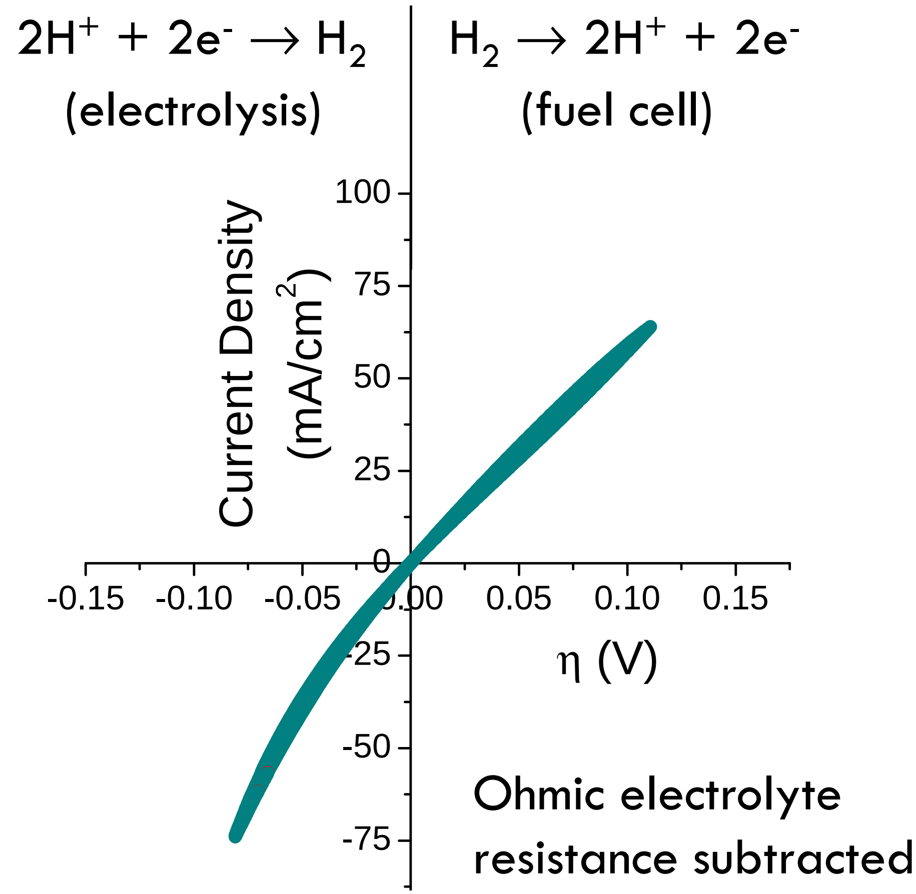
uniform gas composition $\Rightarrow$ zero V
fuel cell gas composition $\Rightarrow$ $E \neq E^0$

Example: Solid Proton Conductor

T = 240 °C; pH_2 = 0.57atm; pH_2O = 0.43 atm

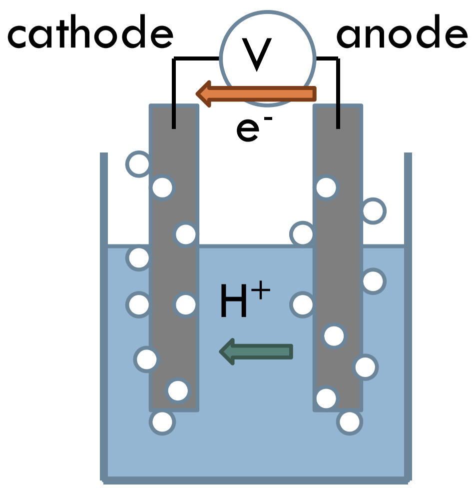


dimensions selected to render voltage drop across counter-electrode negligible



K. Sasaki et al., *Phys. Chem. Chem. Phys.* **11**, 8349-8357 (2009).

Liquid Electrolyte Cell



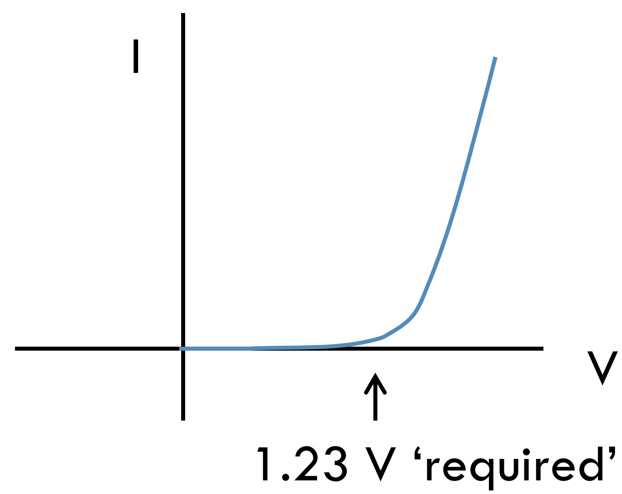
$2H_2O \rightarrow 2H_2 + O_2$

$E^0 = \Delta G^0/nF = 1.23$ V

standard potential

standard Gibbs energy of rxn

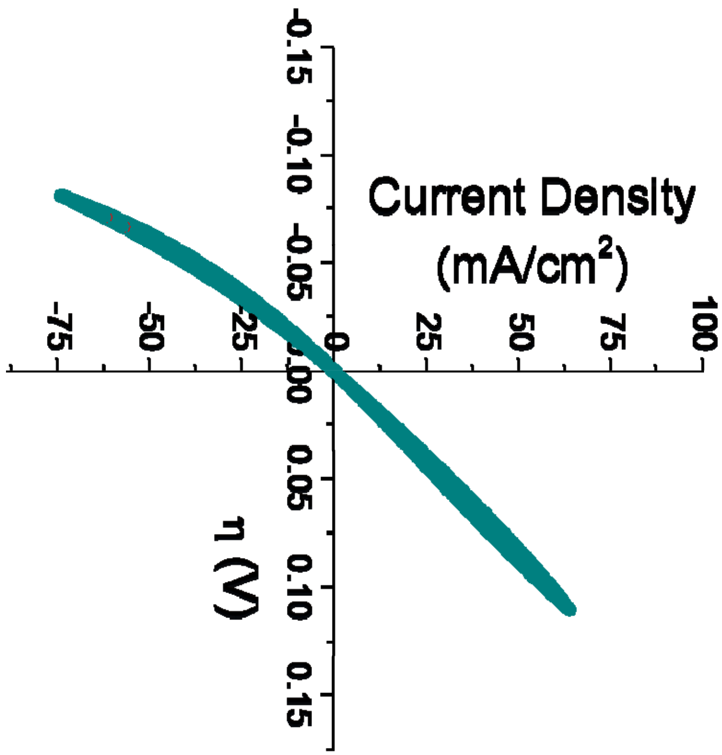
Why such a large overpotential??

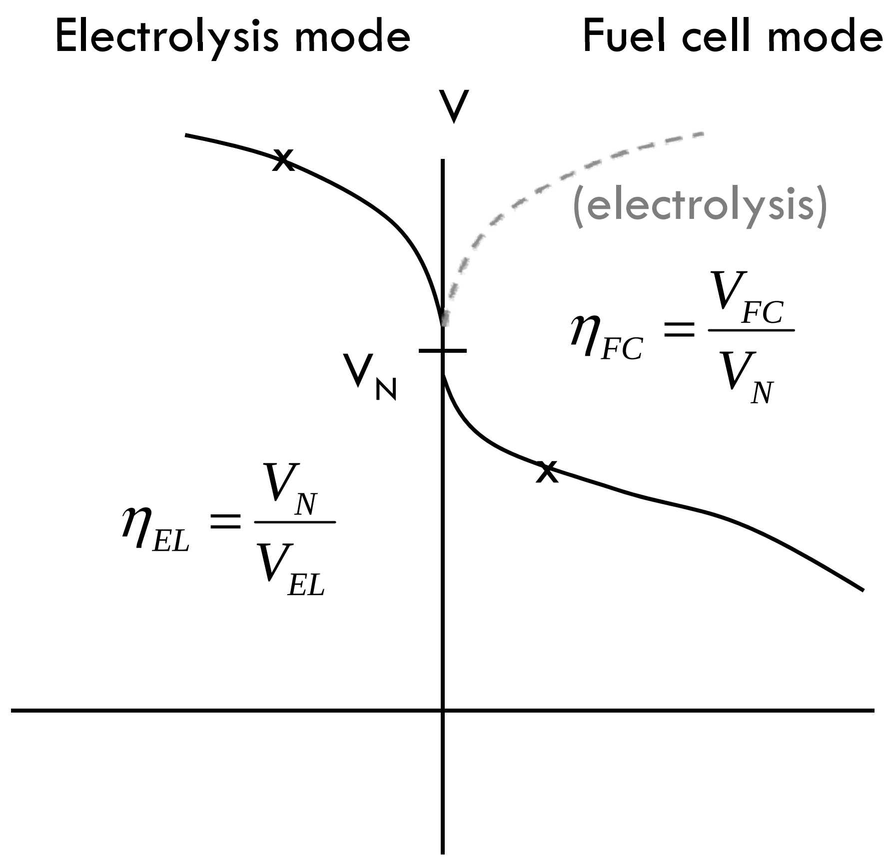


In fact, H_2 and O_2 generated are close to standard conditions: bubbles of pure H_2 and pure O_2. Can't use lesser voltage to generate less concentrated gases

Operation with gases (generally high T) $\Rightarrow$ greater voltage flexibility

Regenerative Cell (Electrolyzer/FC)

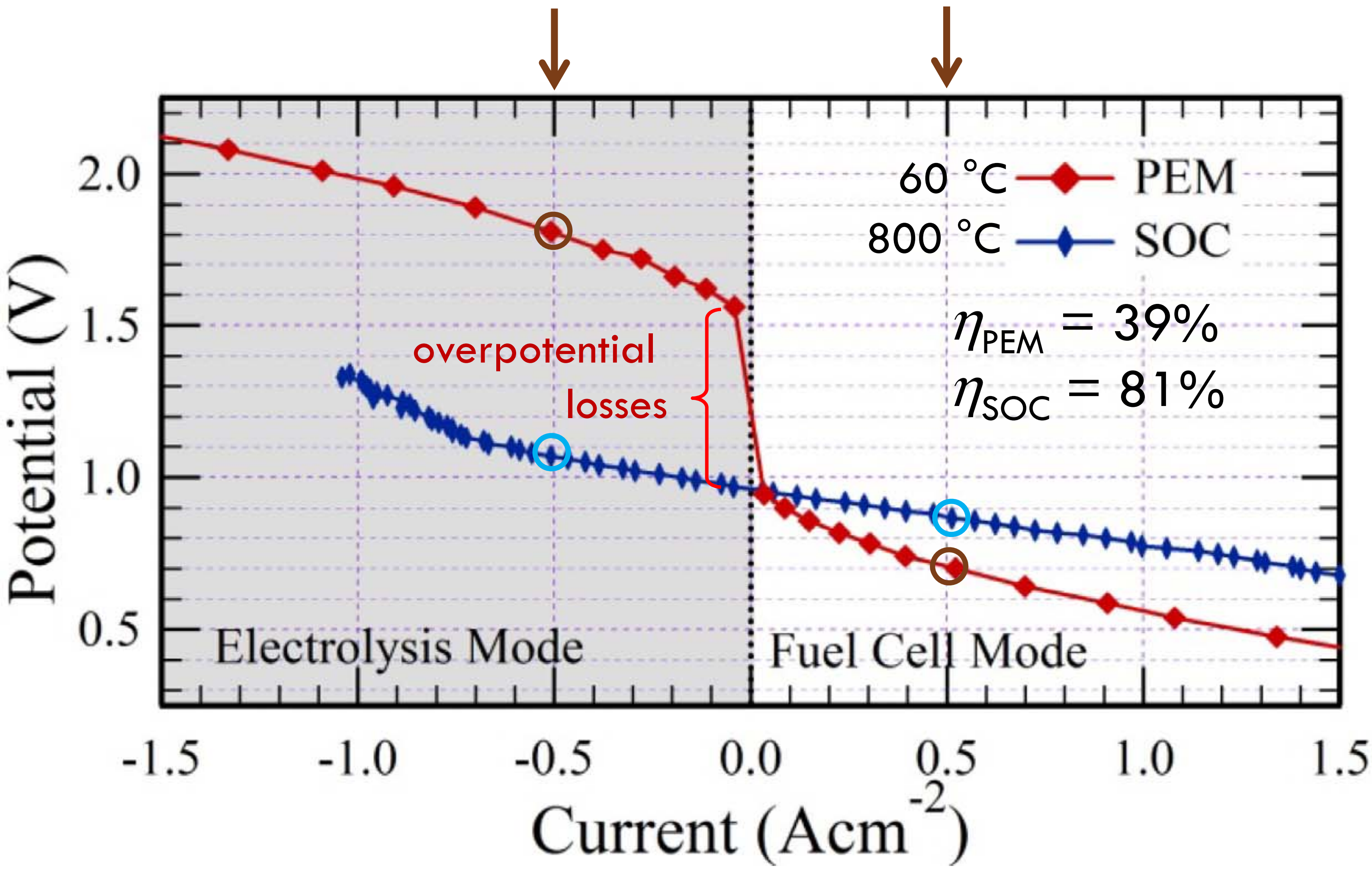




- Reorient previous plot
- Shift OCV due to non-uniform gases
- Change sign

Round trip efficiency: $\eta_{storage} = \frac{V_{FC}}{V_{EL}}$

State-of-the-Art in Lab Cells



After Bierschenk et al., *ECS Trans* **35** (2011) 2969, reproduced with permission of the Electrochemical Society

How to do Better

- Increasing temperature lowers E_N, therefore voltage requirement is reduced
  - $\Delta G = \Delta H - T\Delta S$, $\Delta S > 0 \Rightarrow \Delta G \downarrow$ as $T \uparrow$
  - For regenerative systems operated at single T, OCV is not important

$$\eta_{storage} = \frac{V_{FC}}{V_{EL}}$$

  - May be important when forming products as bubbles or solid components (unit chemical activities)
  - A bit of an accounting trick

$$\eta_{EL} = \frac{V_N}{V_{EL}} \qquad \eta_{EL} = \frac{V_N(RT)}{V_{EL}(HT)} > \frac{V_N(HT)}{V_{EL}(HT)}$$

would be okay if the heat were free

Thermoneutral Operation

Electrolysis is endothermic
To prevent cell from cooling,
require non-zero overpotential

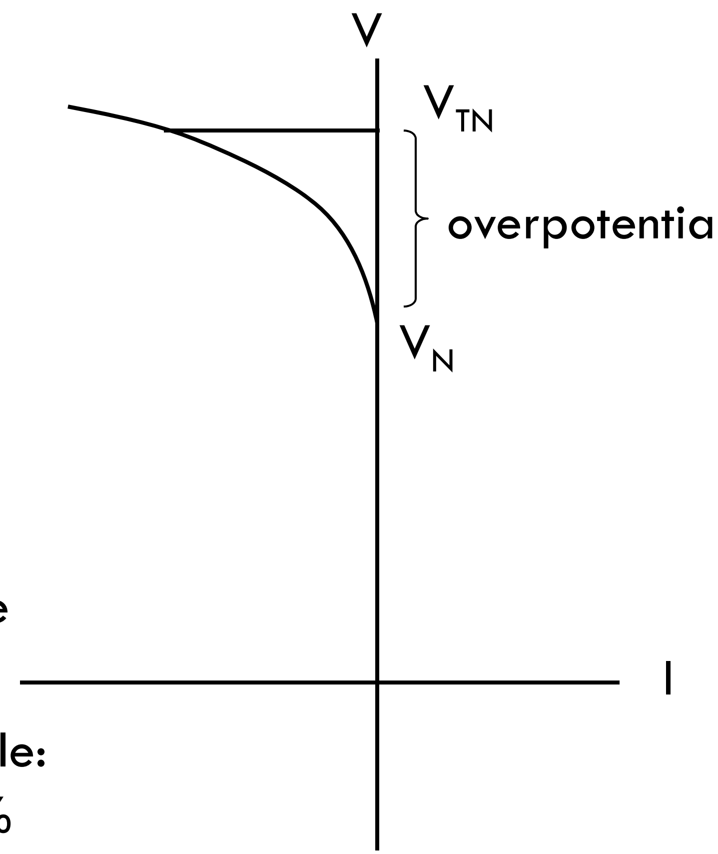
$$V_{\eta}^{\min} = T\Delta S / nF$$ min heat required

$$V_{TN} = \Delta H / nF$$ min operation voltage

maximum efficiency

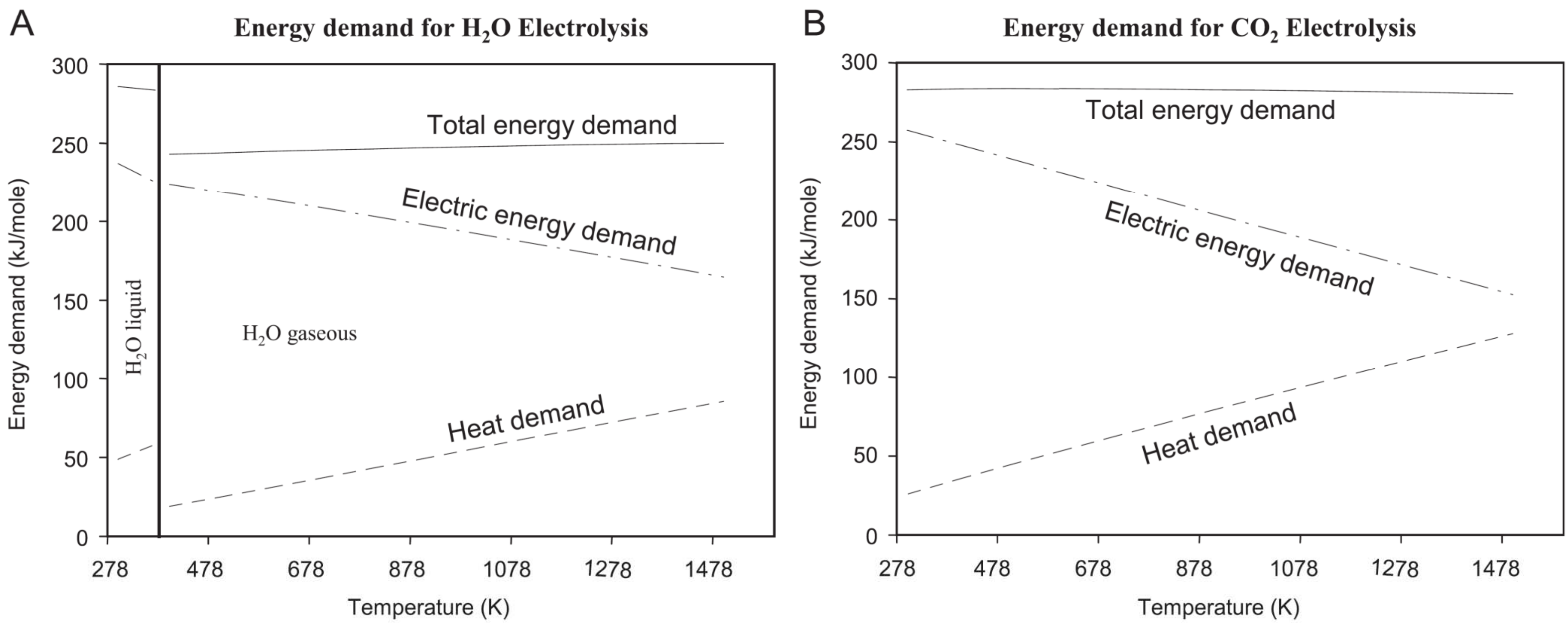
$$\eta_{EL} = \frac{V_N(HT)}{V_{TN}(HT)}$$

previous SOC example:
$\eta_{storage}$: 81% → 67%
η_{STEP}: 55% → 34 %



efficient electrodes of no benefit??

The Energy Trade-Off



If heat is free, CO_2 dissociation is preferable

Jensen et al., *Int. J. Hydr. Energy* **32** (2007) 3253, reproduced with permission of the International Assoc. of Hydrogen Energy.

Escaping the Trade-off?

- Goal: increase efficiency beyond limit set by V_{TN}
- To lower V_{TN} relative to V_N need to lower entropy content of the electrolysis products
- Barnett suggests CH_4 from coelectrolysis of CO_2 and H_2O
  - Can show that this modifies the entropy term such that V_{TN} is lowered and approaches V_N, particularly at lower temperatures (< 600 °C) or higher pressures (~ 10 atm)
  - Barnett *et al.*, *Energy & Env. Sci.* **4** (2011) 944.