

Lecture # 10



Electrolysis & Energy Storage

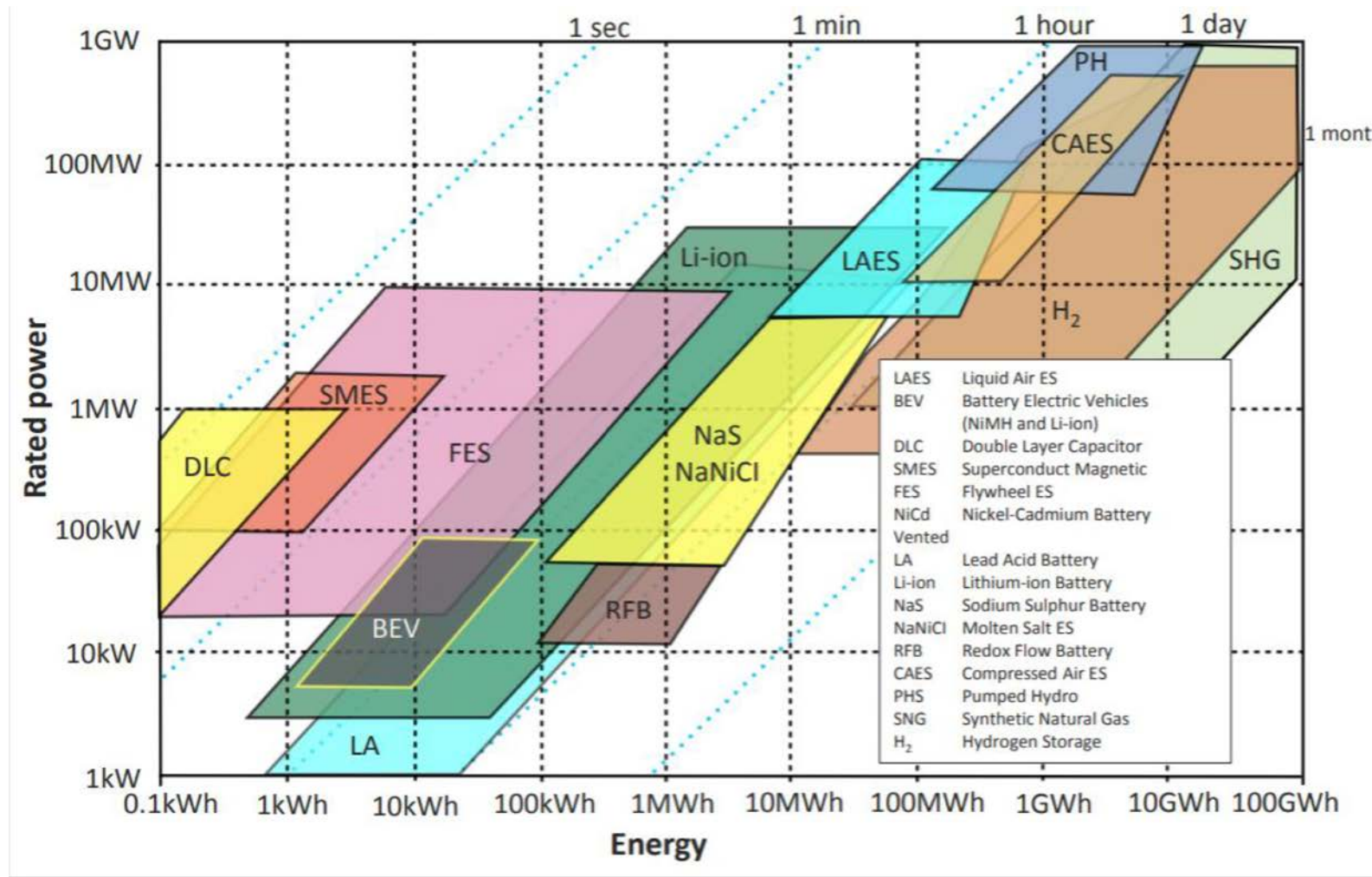
Ahmed F. Ghoniem

March 4, 2020

- Storage technologies, for mobile and stationary applications..
- Fuel Cells and Electrolysis, some more electrochemistry..
- CO₂ reduction/reuse via electrolysis

Shi, Yu et al in Literature/Luo Yu Electrolysis

Energy Storage Capacity

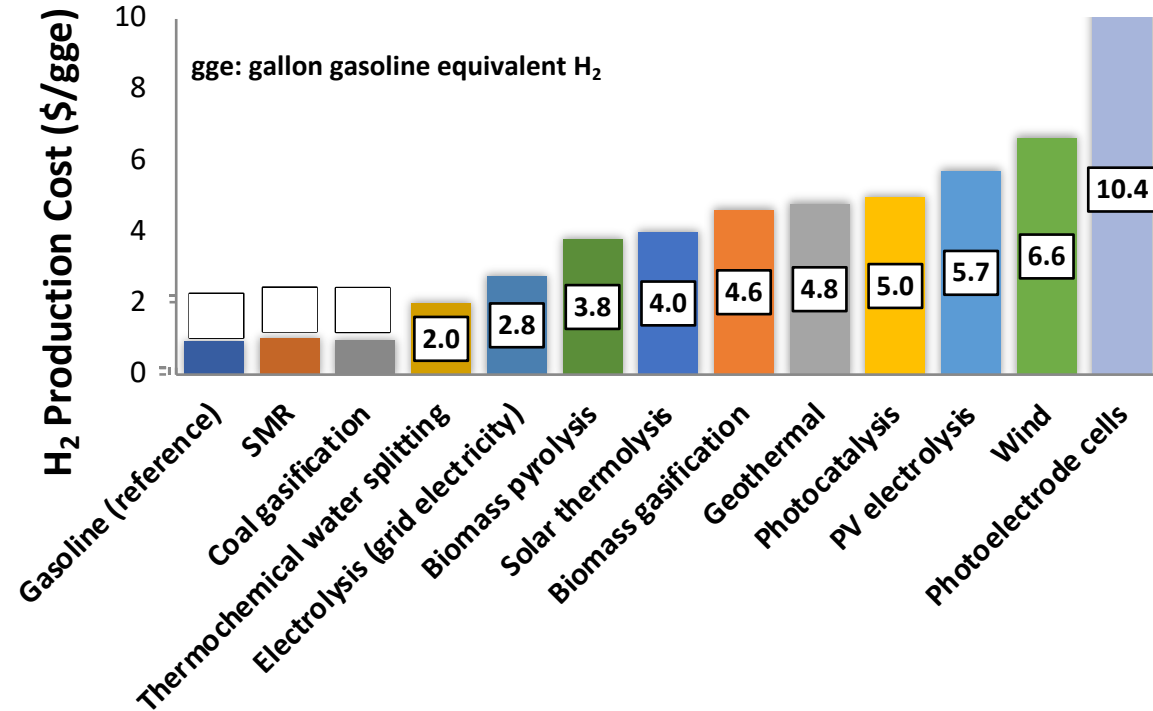


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Hydrogen Production

Hydrogen

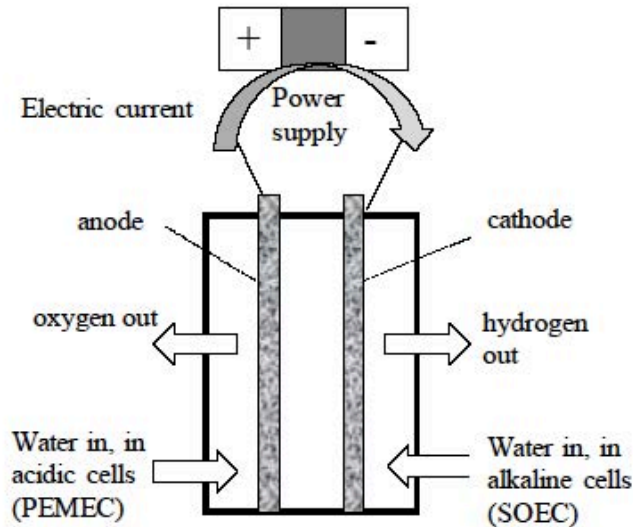
- Market of \$152.1B by 2021 ^[1]
- Important for oil refining especially heavy and sour crude
- Future clean fuel
- DOE threshold^[1] (by 2020): <\$2.00 /gge
- IEA suggests^[2] commercial cost target: \$0.3/gge



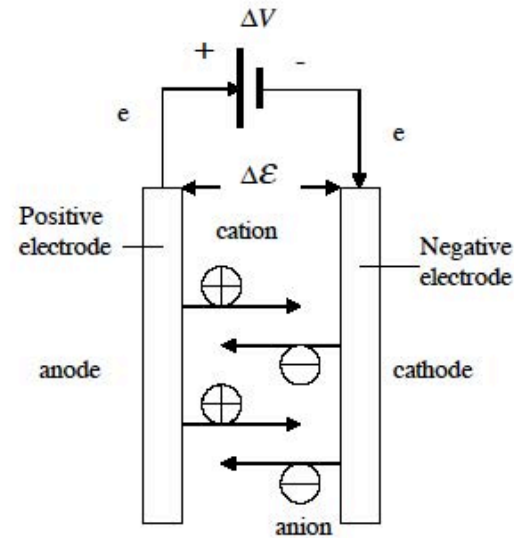
- Steam reforming has reached peak efficiency (70-85%)
- Novel technology needs to be developed to reach the goal
- Alternatives needed for zero CO₂ emissions

[1] Hydrogen production technical team roadmap, US DRIVE, June 2013.
 [2] Hydrogen production and storage: R&D priorities and gaps, IEA 2006
 [3] Hosseini (2016) Renew. Sust. Energ. Rev.
 [4] (Photon-based methods:) Dincer (2015) Int. J. Hydro. Energ.;
 [5] Geothermal: Yuksel (2016) Int. J. Hydro. Energ
 *All prices exclude compressing, storage, and dispensing costs

In an electrolyzer: a potential difference is externally imposed to force the reversal of the oxidation reactions and reduce water back to H_2 . Under finite current, a potential difference higher than the ideal/OC must be externally imposed to overcome the internal losses or overpotentials.

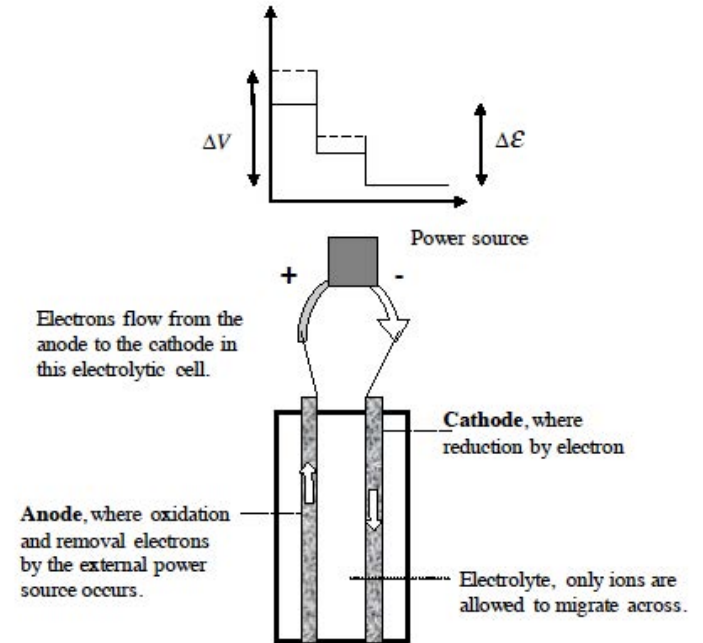


A schematic diagram of an electrolysis cell splitting water into pure oxygen and hydrogen. In an acidic (PEMEC) cell, the electrolyte conducts positive ions, water is introduced on the anode side and hydrogen leaves on the other side. In an alkaline (SOEC) cell, the electrolyte conducts negative ions, water is introduced on the cathode side and hydrogen leaves on the same side.



Electrolytic cell.

A source of electricity is connected to supply a potential to overcome the equilibrium potential of the reaction, $DV > D_e$. The cathode is now negatively charged, supplied externally with electrons, while the anode is positively charged.

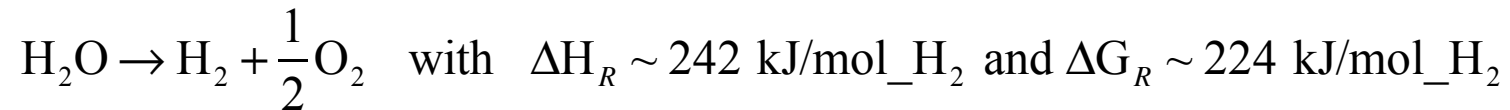


A simple electrolytic cell. Often neutral species are removed from both electrodes. The solid lines in the potential diagram show the equilibrium potential differences, and the broken lines show the case under finite current operation.

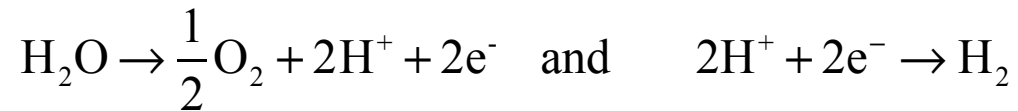
Electrolysis reduces water back to H₂

Can be used to store an “infinite” amount of energy (from electricity) in the form of chemical energy
Operates as the reverse of a fuel cell

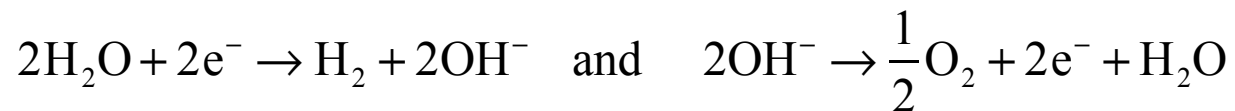
Overall Reaction:



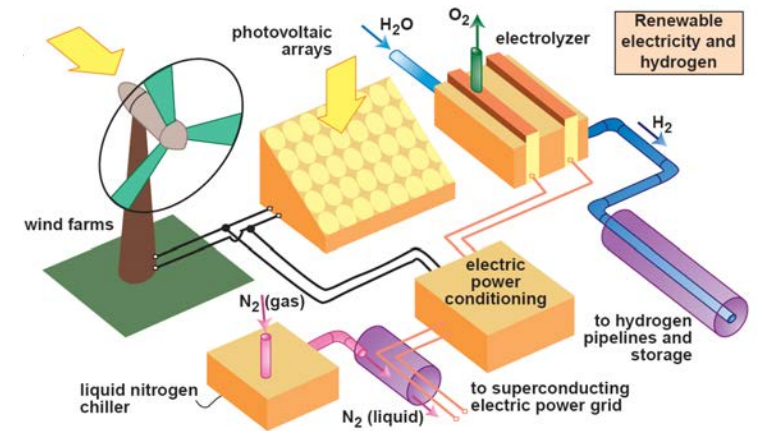
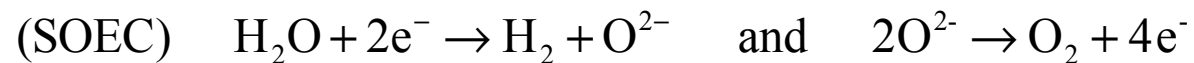
In an acidic (electrolyte transporting +ve ions) cell (PEM):



In an alkline (electrolyte transporting -ve ions) cell:

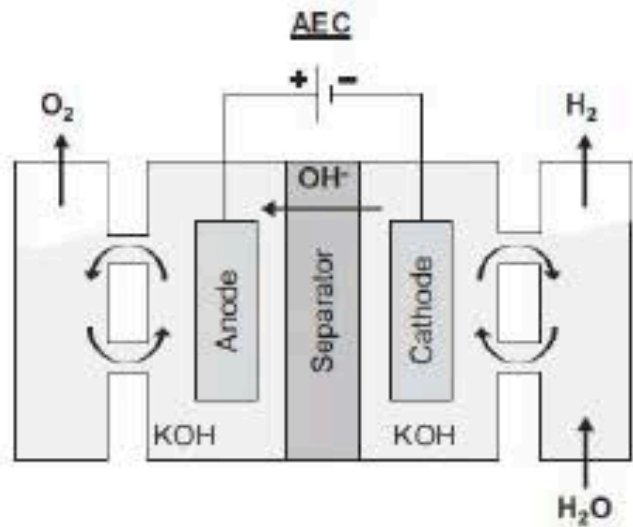
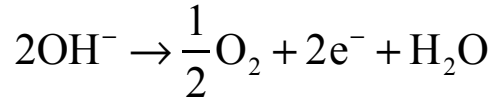
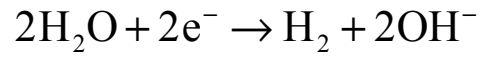


In Solid Oxide (electrolyte transporting -ve ions) cells:

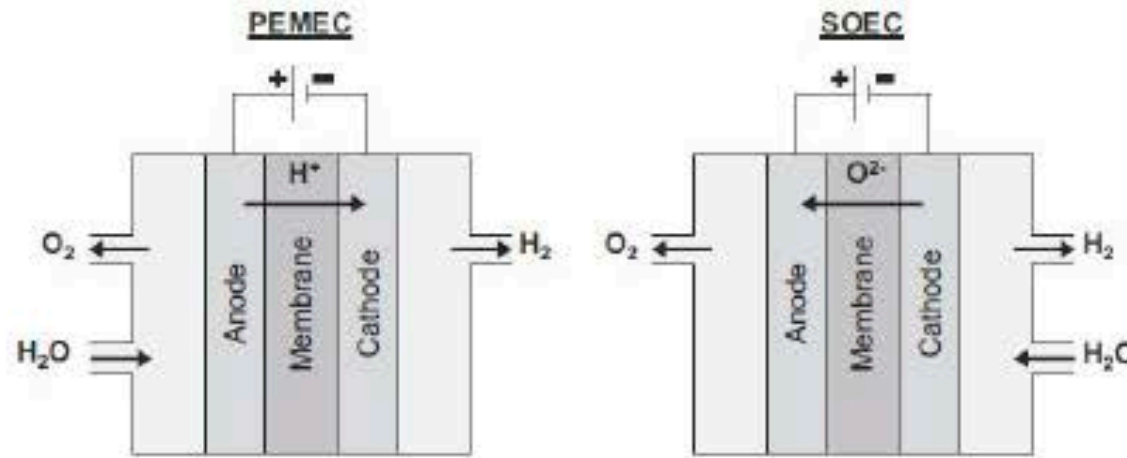
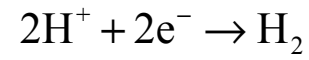
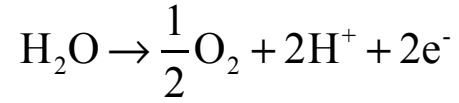


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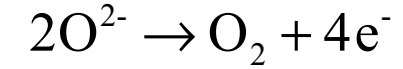
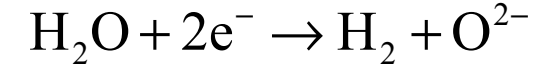
(AEC)



(PEM):



(SOEC)

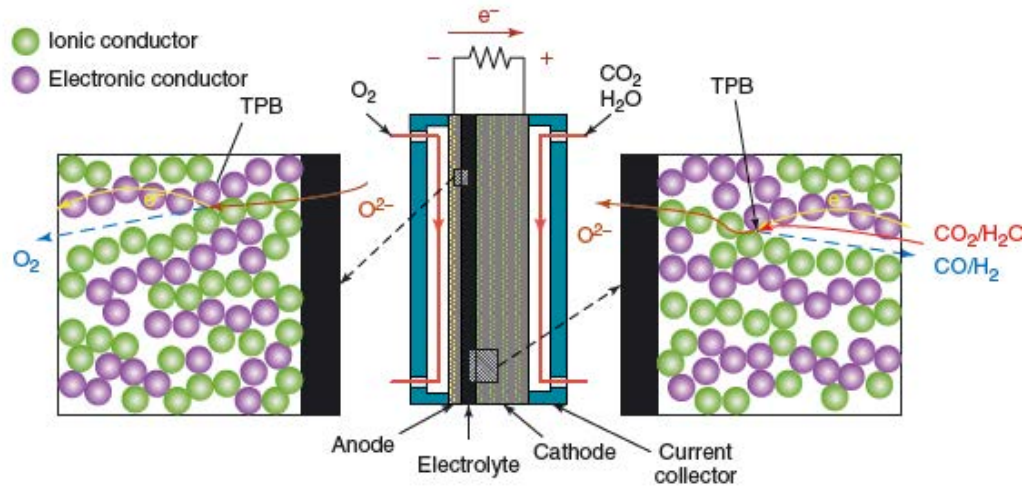


Schmidt, A. 2017, Int. J. Hydrog. Energy

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	Alkaline (AEC) (~\$1/W)	Polymer (PEMEC) (~\$2/W)	Solid Oxide (SOEC) (>\$2/W)
Pros	Widely Deployed No rare materials Long Life	High Pressure High Power Density Fast response	Least Electricity Required Fast Kinetics No rare materials
Cons	Low Power Density	Rare Materials (Pt, Ir)	Less deployed/ more risk

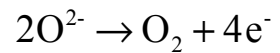
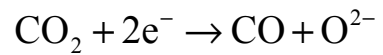
CO₂ Reuse



Electrolysis can be used to split water and/or CO₂
 But similar to SOFC's the high T solid oxide type is
 more compatible with CO₂ splitting



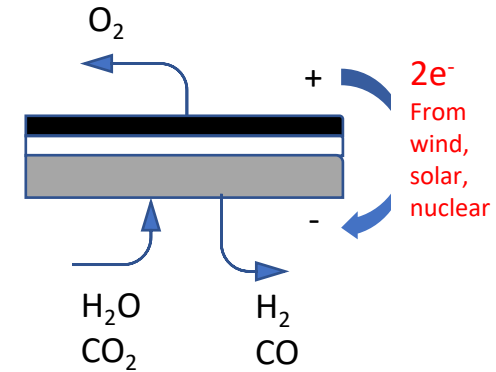
In an alkalyine (electrolyte transporting -ve ion) SOEC cell:



Solid Oxide Electrolysis and Fuel Cells

Oxygen electrode
 $\text{O}^{2-} \rightarrow \frac{1}{2}\text{O}_2 + 2e^-$

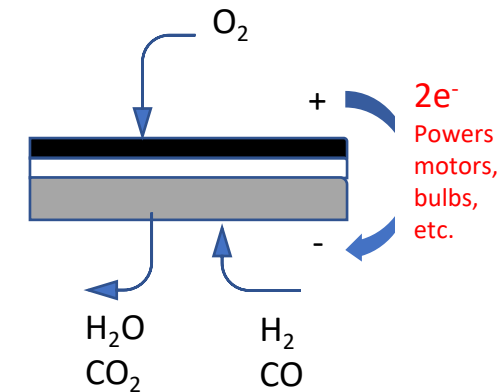
Fuel electrode
 $\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + \text{O}^{2-}$
 $\text{CO}_2 + 2e^- \rightarrow \text{CO} + \text{O}^{2-}$



SOEC

Oxygen electrode
 $\frac{1}{2}\text{O}_2 + 2e^- \rightarrow \text{O}^{2-}$

Fuel electrode
 $\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2e^-$
 $\text{CO} + \text{O}^{2-} \rightarrow \text{CO}_2 + 2e^-$



SOFC

Electrolysis reduces water back to H₂

Can be used to store an “infinite” amount of energy (from electricity) in the form of chemical energy
Operates as the reverse of a fuel cell

The thermodynamics are very similar to that of a fuel cell

$$Q - W = H_{out} - H_{in} = \Delta H_R \quad \text{and} \quad \frac{Q}{T^*} = S_{out} - S_{in} = \Delta S_R$$

$$-W = (H - TS)_{out} - (H - TS)_{in} = \Delta H_R - T\Delta S_R$$

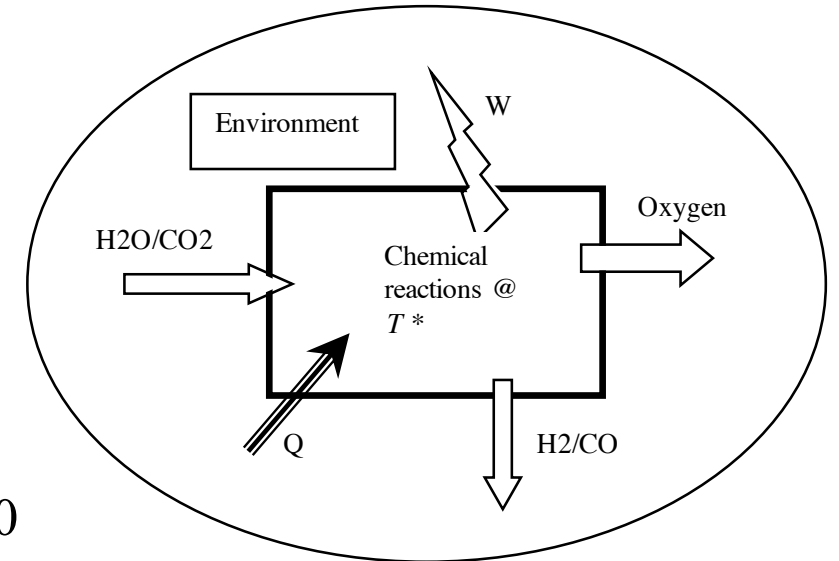
$$W = -\Delta G_R \quad \text{and} \quad Q = T\Delta S_R$$

$$Q = T\Delta S_R = \Delta H_R - \Delta G_R$$

reversing the original (FC) reaction, we have $\Delta H_R > 0$ and $\Delta G_R > 0$

In electrolysis, both work is added and heat is added (when $\Delta H_R > \Delta G_R$)

A fuel cell produces work and rejects heat, an electrolyzer needs both



$$W = -\Delta G_R \quad (\text{electricity})$$

$$Q = T\Delta S_R = \Delta H_R - \Delta G_R \quad (\text{heat})$$

In electrolysis, both work and heat are added

at 400 °K, $\Delta H_R \sim 242$ and $\Delta G_R \sim 224$ kJ/mol,
 thus, $W = -224$ and $Q = 18$ kJ/mol.

at 1000 °K, $\Delta H_R \sim 245$ and $\Delta G_R \sim 193$ kJ/mol,
 thus, $W = -193$ and $Q = 52$ kJ/mol

At higher temperature, need less work & more heat!

Open circuit voltage (similar to fuel cells),

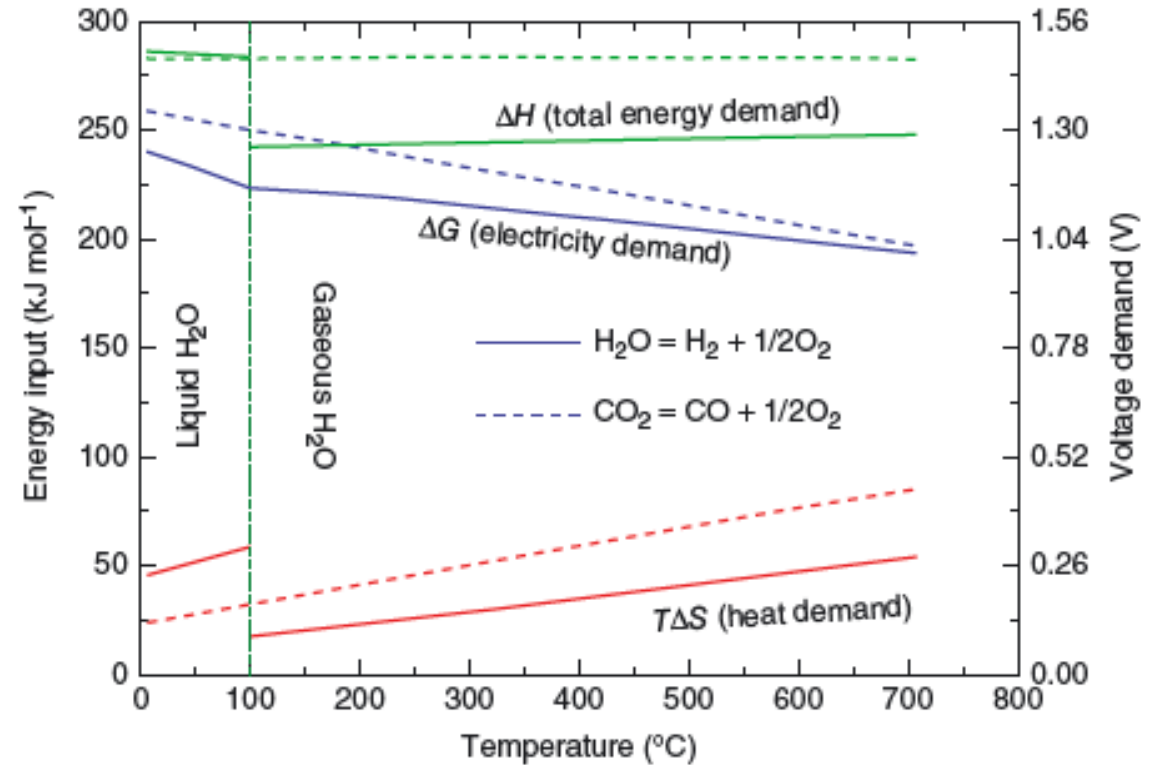
$$-W = \Delta G_R = -\Delta \mathcal{E} \zeta = -\Delta \mathcal{E} n_e \mathfrak{S}_a$$

$\mathfrak{S}_a = e^- N_a = 9.6485 \times 10^4$ Coulombs/mole
 for water splitting,

at 400 °K, $\Delta \mathcal{E} \sim 1.1$ V,

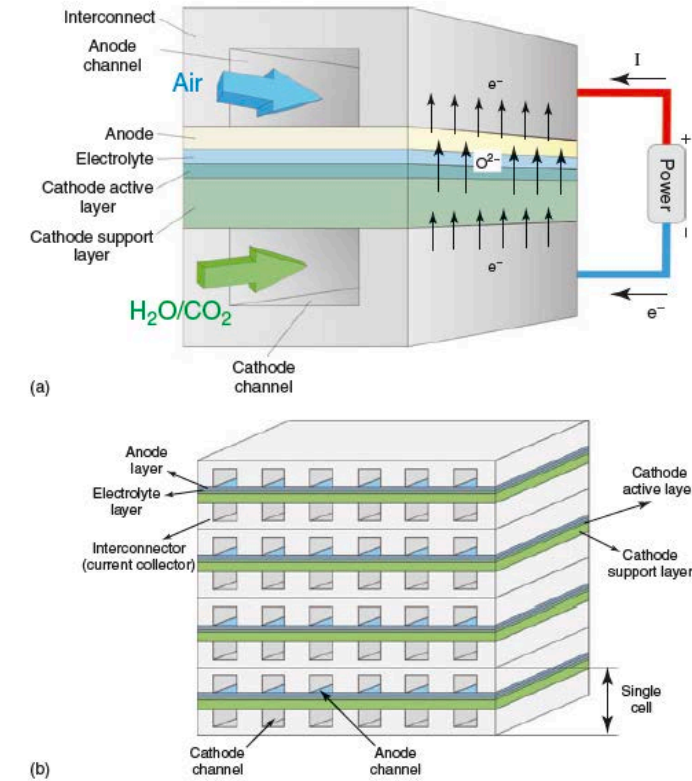
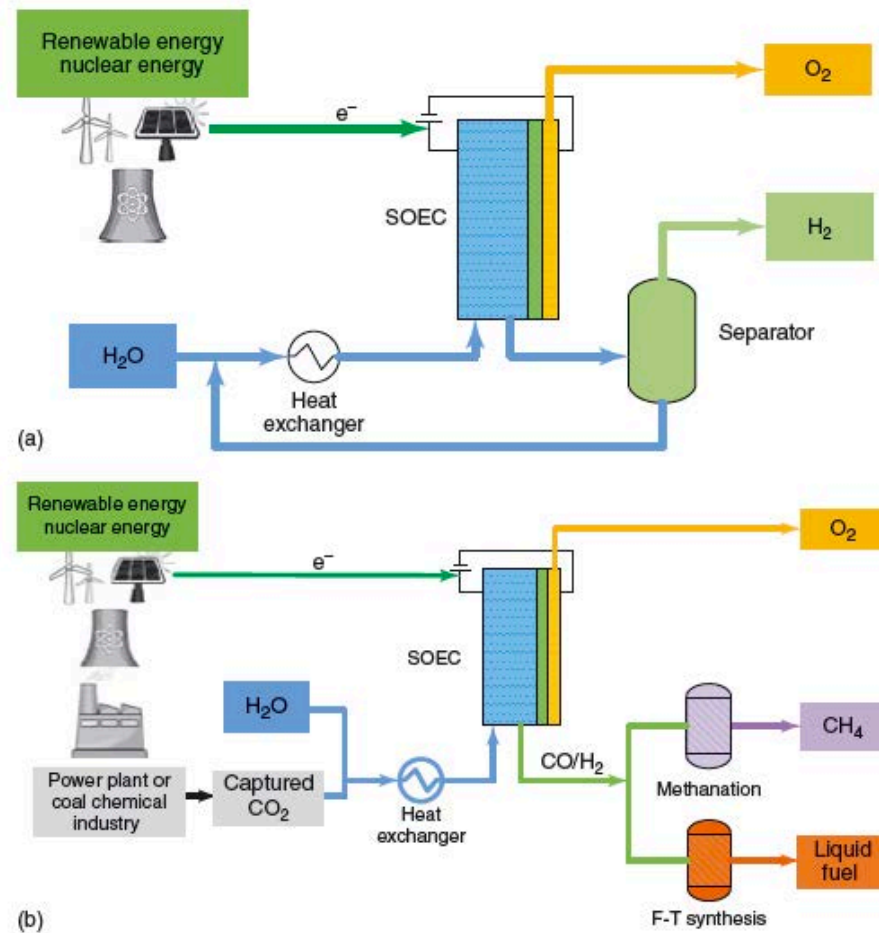
at 1000 °K, $\Delta \mathcal{E} \sim 0.86$ V.

Thermodynamics of Electrolysis



- In electrolysis, work demand decreases while heat demand increases with temperature
- Electrolysis can also be used to reduce CO₂ back to CO (but there are material challenges). The energy requirements are higher.

Electrolysis for production of H₂ and/or co-production of H₂/CO and synthesis fuels



(a) Single element
(b) A stack

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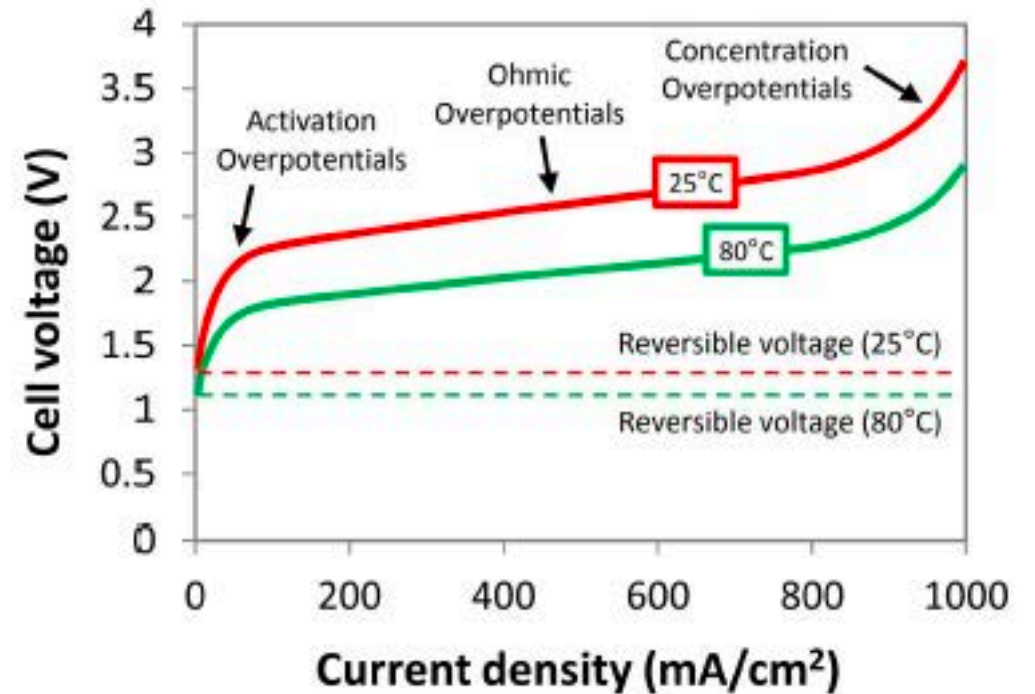
At finite current, an electrolyzer suffers from the same losses as a FC, generating positive internal voltage drop that must be compensated for externally,

$$\Delta \mathcal{E}_{EC} = \Delta \mathcal{E}^o + \tilde{\eta}_{a,act} + \tilde{\eta}_{a,conc} + \tilde{\eta}_{a,FU} + \tilde{\eta}_{el,oh} + \tilde{\eta}_{c,act} + \tilde{\eta}_{c,conc} + \tilde{\eta}_{a,FU}$$

$\tilde{\eta} \equiv$ (positive) overpotential

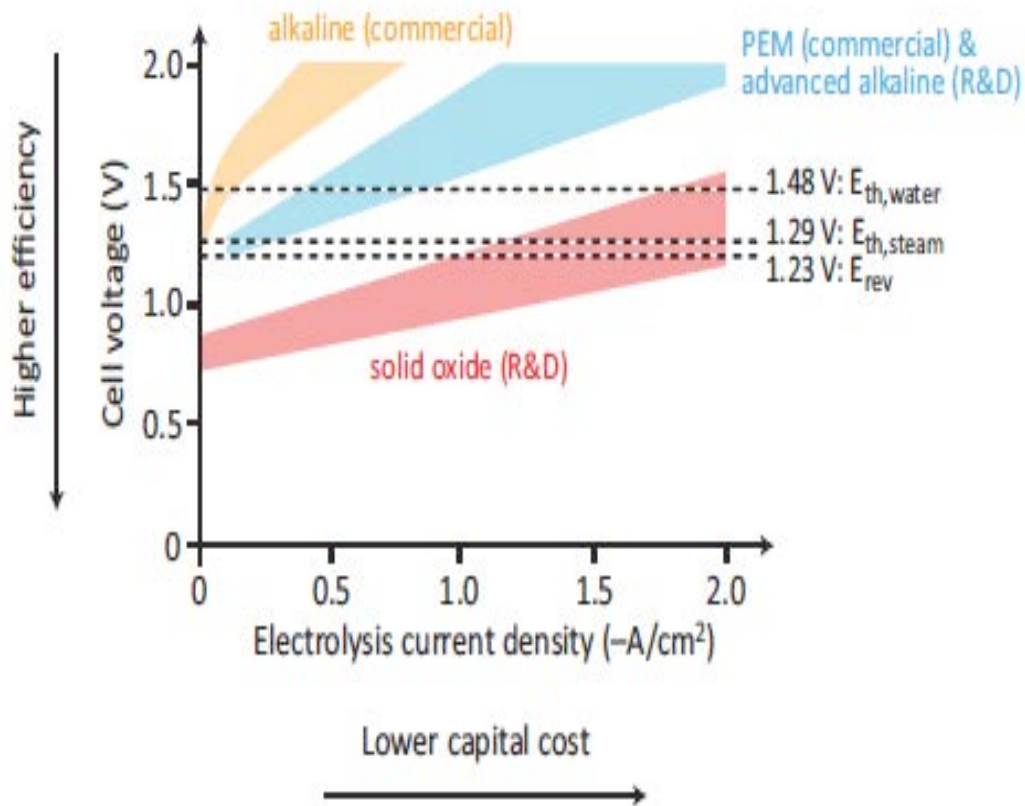
Therefore, the imposed external potential difference in electrolysis must be higher than the open circuit potential. The difference between the actual imposed potential difference and the open circuit values are expected to be of the same order of magnitude to those in fuel cells, at the same current (see two sides arrows in figure).

In this case, the difference between the ideal work and actual work is heat dissipated in the cell, which is typically the heat required by first law analysis.



B

Reversible voltage (zero current) and actual voltage of an electrolyzer at finite current at different T. Lower T reduces the OC voltage, but at finite current, kinetics are sluggish and diffusivity is lower leading to more losses and higher operating voltage



Typical I-V curve of a number of electrolyzers for water splitting, including low T commercial and advanced alkaline (PEM transporting OH⁻ ions) and solid oxide (SOEC). These are more complex than FC I-V curves, especially for SOEC because of the use of internal dissipation to supply thermal energy

From Luo et al. Applied Energy, 215 (2018).
Note the “negative” current increasing towards the left.

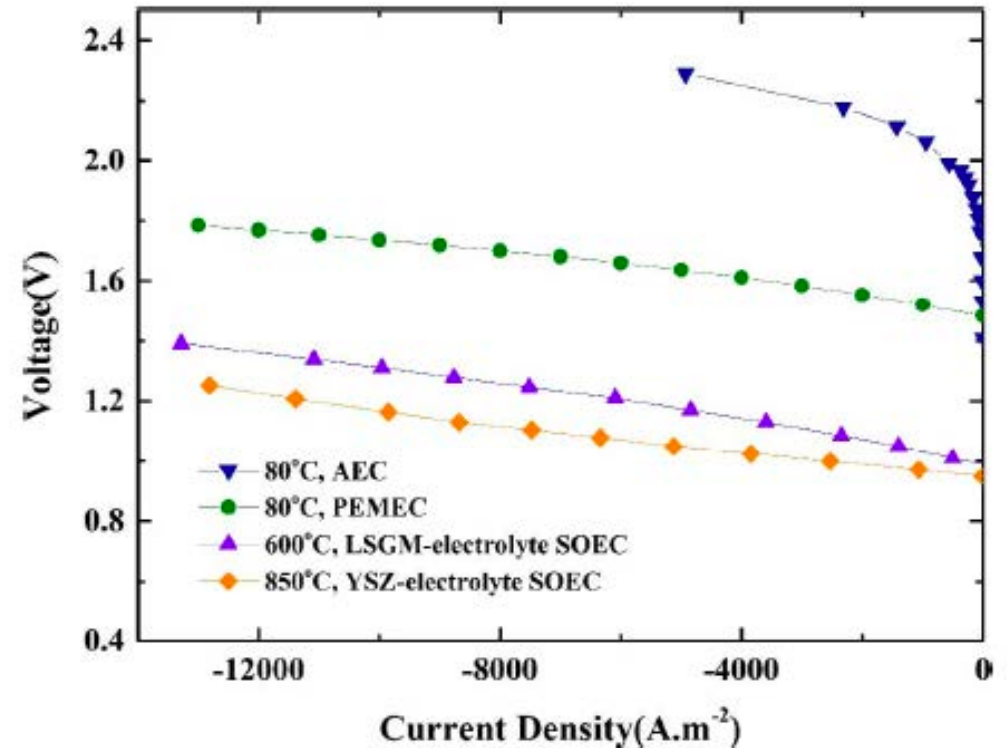


Fig. 3. Typical polarization curves of PEMEC, AEC, LSGM-electrolyte SOEC, and YSZ-electrolyte SOEC [32,33,35,36] for H₂O electrolysis.

- [32] Ebbesen SD, Graves C, Mogensen M. Int J Green Energy 2009;6:646–60.
- [33] Wendel CH, Gao Z, Barnett SA, Braun RJ. J Power Sources 2015;283:329–42.
- [35] Han B, Mo J, Kang Z, Zhang FY. Electrochim Acta 2016;188:317–26.
- [36] Miles MH, Kissel G, Lu PWT, Srinivasan SJ Electrochem Soc 1976;123:332–6.

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At finite current, it is *not* necessary to supply heat to the electrolysis cell externally, internal dissipation is sufficient to generate the necessary heat. Therefore only electricity is needed, at the *actual* potential (including the overpotentials) required to run the electrolysis reactions. The heat generation rate is $I(V-V_{oc})$.

Several efficiencies are usually defined: a second law efficiency, and a first law like efficiency which can be based on either the enthalpy or Gibbs free energy of the produced hydrogen:

$$\eta_{II} = \frac{\Delta \mathcal{E}_{OC}}{\Delta \mathcal{E}}$$

$$\eta_{thermal} = \frac{J_{H_2} \cdot \Delta \hat{h}_{R,H_2}}{i \cdot \Delta \mathcal{E}}$$

$$\eta_{work} = \frac{J_{H_2} \cdot \Delta G_{R,H_2}}{i \cdot \Delta \mathcal{E}}$$

Anode	Cathode	Electrolyte	T (C)	Cell Voltage (V)	η_{th}	η_{II}
IrO ₂					89.70%	74.55%
Ir _{0.6} Ru _{0.4} O ₂		Nafion 115	90	1.567	94.45%	78.49%
IrO ₂		Nafion 112	80	1.63	90.80%	
Ir _{0.5} Ru _{0.5} O ₂		Nafion 112	80	1.65	89.70%	
Ir		Nafion 112	80	1.72	86.05%	
Ru		Nafion 112	80	1.79	82.68%	
IrO ₂ nano film		Nafion 117	80	1.83	80.87%	
Ir Black		Nafion 115	90	1.7	87.06%	
Ir Black		Nafion 115	90	1.67	88.62%	
Ir Black		Nafion 115	90	2.45	60.41%	
Ir Black		Nafion 115	90	2	74.00%	
20%RuO ₂ /ATO (SnO ₂)						

Efficiency of a number of PEMEC. Note that the conditions at which these efficiency were determined could be very different, that is, the current or hydrogen production rate. The thermal efficiency is higher than the voltage efficiency because of the internal use of the heat generated by dissipation (Le Chang).

$$\eta_{II} = \frac{\Delta \mathcal{E}_{OC}}{\Delta \mathcal{E}}$$

$$\eta_{thermal} = \frac{J_{H_2} \cdot \Delta \hat{h}_{R,H_2}}{i \cdot \Delta \mathcal{E}}$$

$$\eta_{current} = \frac{J_{H_2}}{n_e \mathcal{S}_a i}$$

recall that under ideal conditions

$$J_{H_2} = n_e \mathcal{S}_a i$$

Anode Electrolyte Cathode	T°C	Voltage (V)	Current Density (A/cm ²)	Hydrogen Production Rate (umol/s cm ²)	$\eta_{current}$	η_{II}
YSZ Y ₂ O ₃ +Zr/YSZ LaMnO ₃				1.73		
Ni-YSZ YSZ LaCoO		1.31	0.13	0.35		
Y-ZrO ₃ ScSZ LSM		1.4	0.38	1.94		
Ni-CGO Y _{0.2} Ce _{0.8} O _{1.9} LSCF		1.22	0.4	2.04		
Ni+YSZ YSZ LSM+YSZ		1.3	0.32	1.58		
LSM-YSZ YSZ LSCM-YSZ		1.6	1.25	6.36		
Ni-YSZ YSZ LaSrCrMnO ₃						

Performance of solid oxide electrolysis cells, shown in terms of the current efficiency (less than 100% due to leakage, etc.), and the second law efficiency. Different values were determined under different conditions (not always defined clearly in publications). The “thermal” efficiency can be higher because more heat is generated and used in the reactions, but the values are somewhat arbitrary (Le Chang)!

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2.60J Fundamentals of Advanced Energy Conversion
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