Fuel Cells

Lots of Solid Oxide Fuel Cells Though Since I am Biased

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Lecture 4.5 – 2018 Edition

Fuel Cells Part 1

Non-SOFC Cells

Polymer Electrolyte Membrane (PEM)
Proton Exchange Membrane (PEM)

Note still have unspent fuel leaving

Electrons released with high potential

H+ (protons) transported through porous membrane

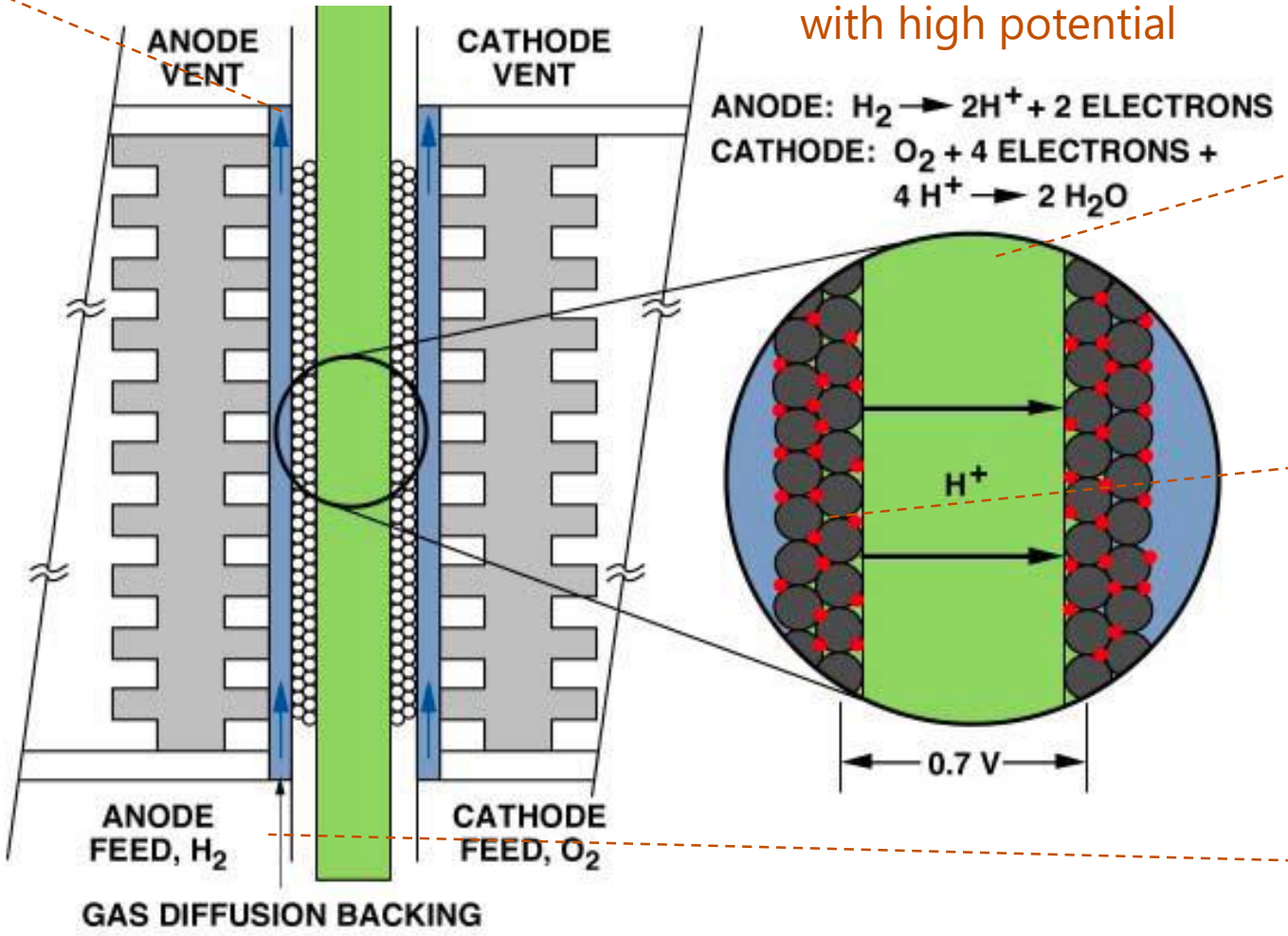
Means that other stuff can get in too.

Usually Platinum Catalyst

Susceptible to poisoning from CO, CH_4, sulfur, etc.

Need ultra-clean H_2.

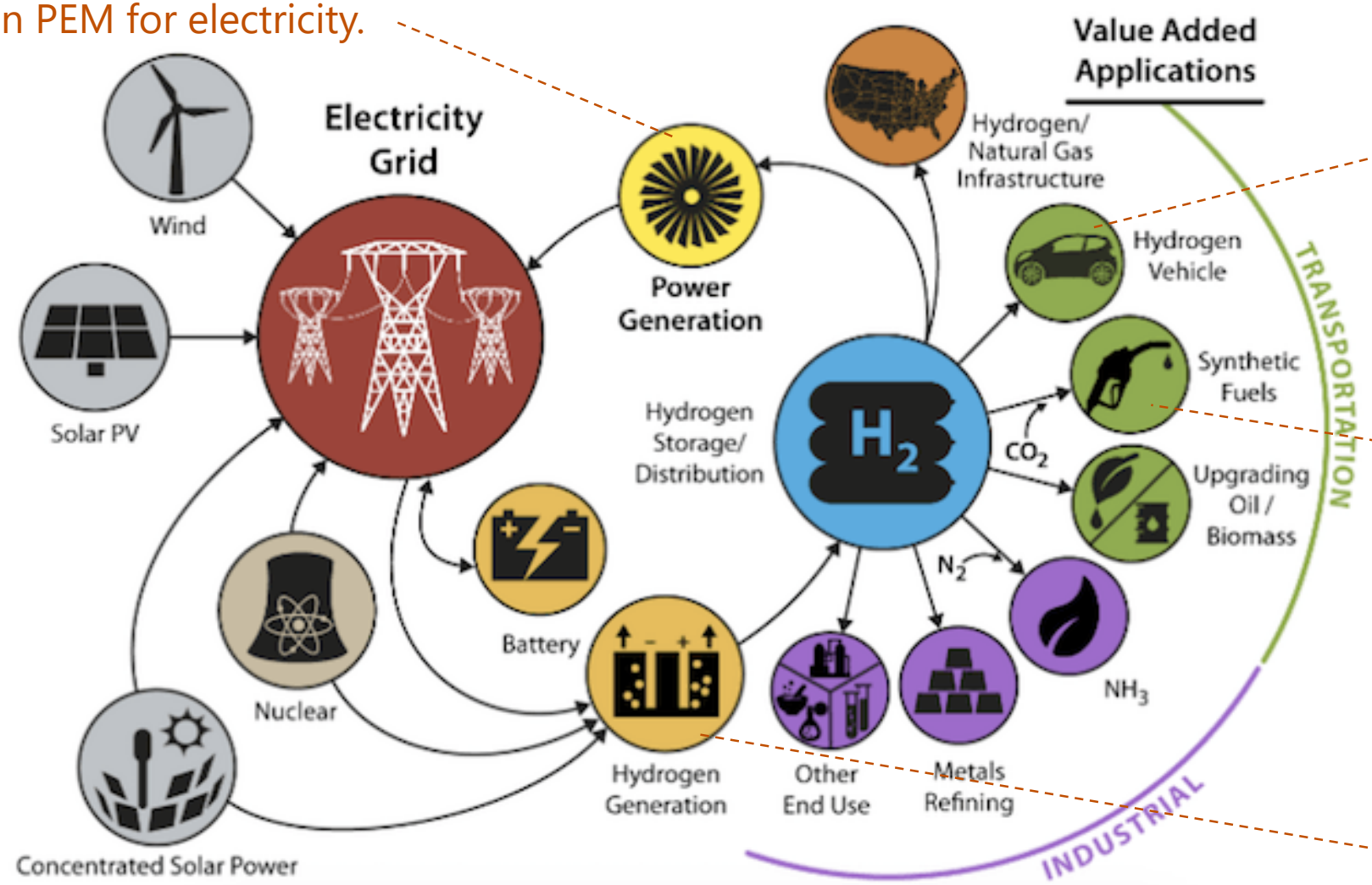
Low Temperature!
60-120°C



Sources: EG&G. Fuel Cell Handbook, 7th Ed. (2004)

Key Value: Role in Hydrogen Economy

Stored H_2 used in PEM for electricity.



Carbonless, Smogless emissions from Cars using PEMs

Consume CO2!
Needs carbonless energy to make sense.
(or unicorns)

Key step is power-to-hydrogen

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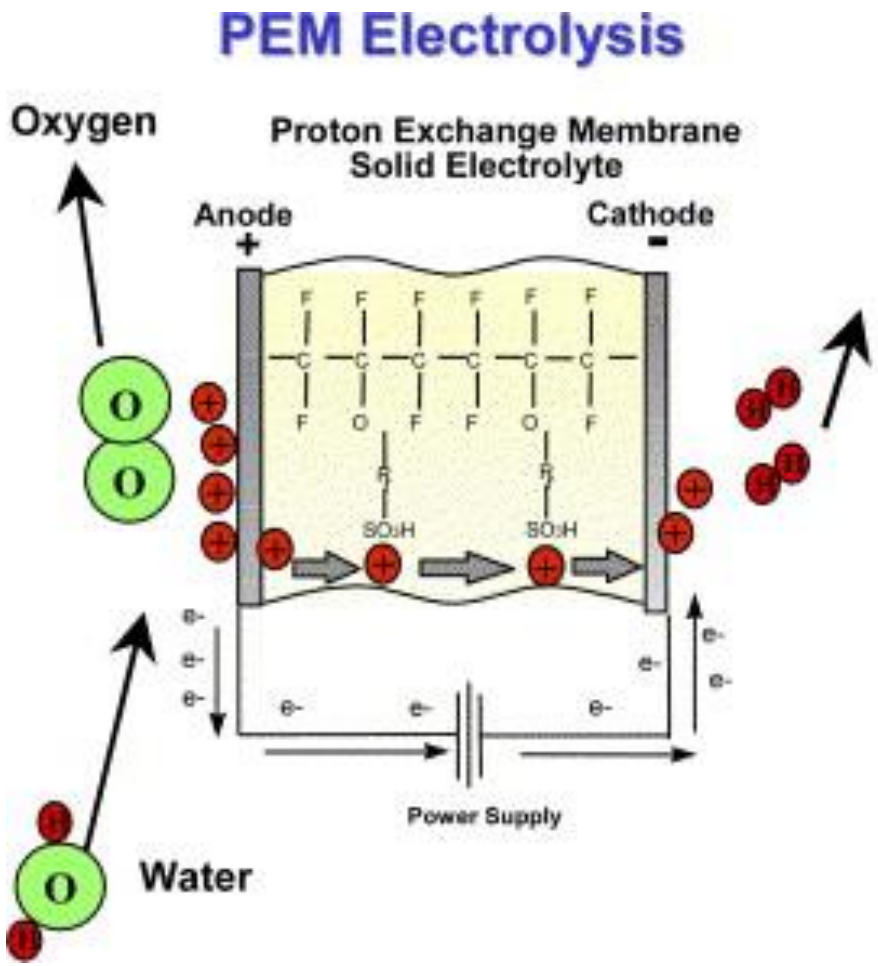
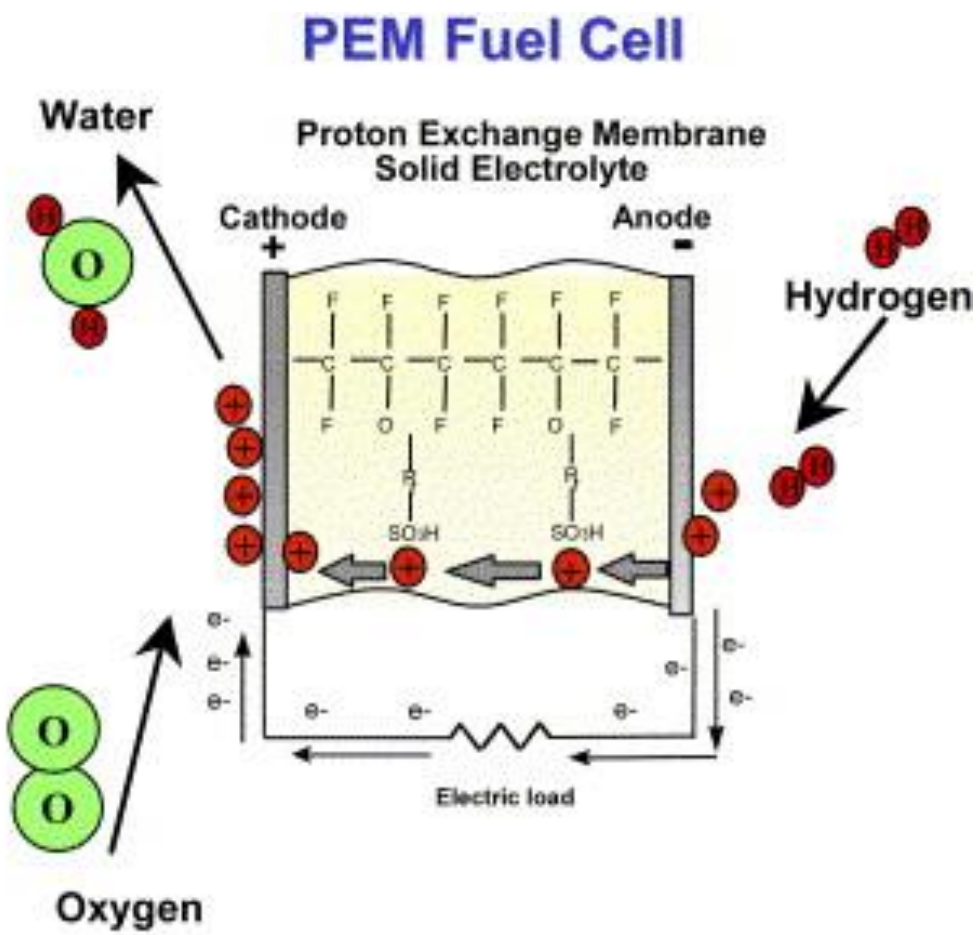
Sources: Casey T. .S. Pumps $30 Million More Into Hydrogen Economy. TriplePundit.com (Oct 2016)

Electrolysis (Backwards Fuel Cells)





Sources: Barbir F. PEM Electrolysis for production of hydrogen from renewable energy source. *Solar Energy* 78:5:661-669 (2005)

Copper Chloride Cycle

Copper is O carrier, Chlorine is H carrier

Key Step (splits H from O from water)

$$2CuCl_2(s) + H_2O(g) \rightarrow CuO \cdot CuCl_2(s) + 2HCl(g) \text{ at } 400\ ^\circ\text{C}.$$

$$CuO \cdot CuCl_2(s) \rightarrow 2CuCl(l) + \tfrac{1}{2}O_2(g) \text{ at } 500\ ^\circ\text{C}.$$

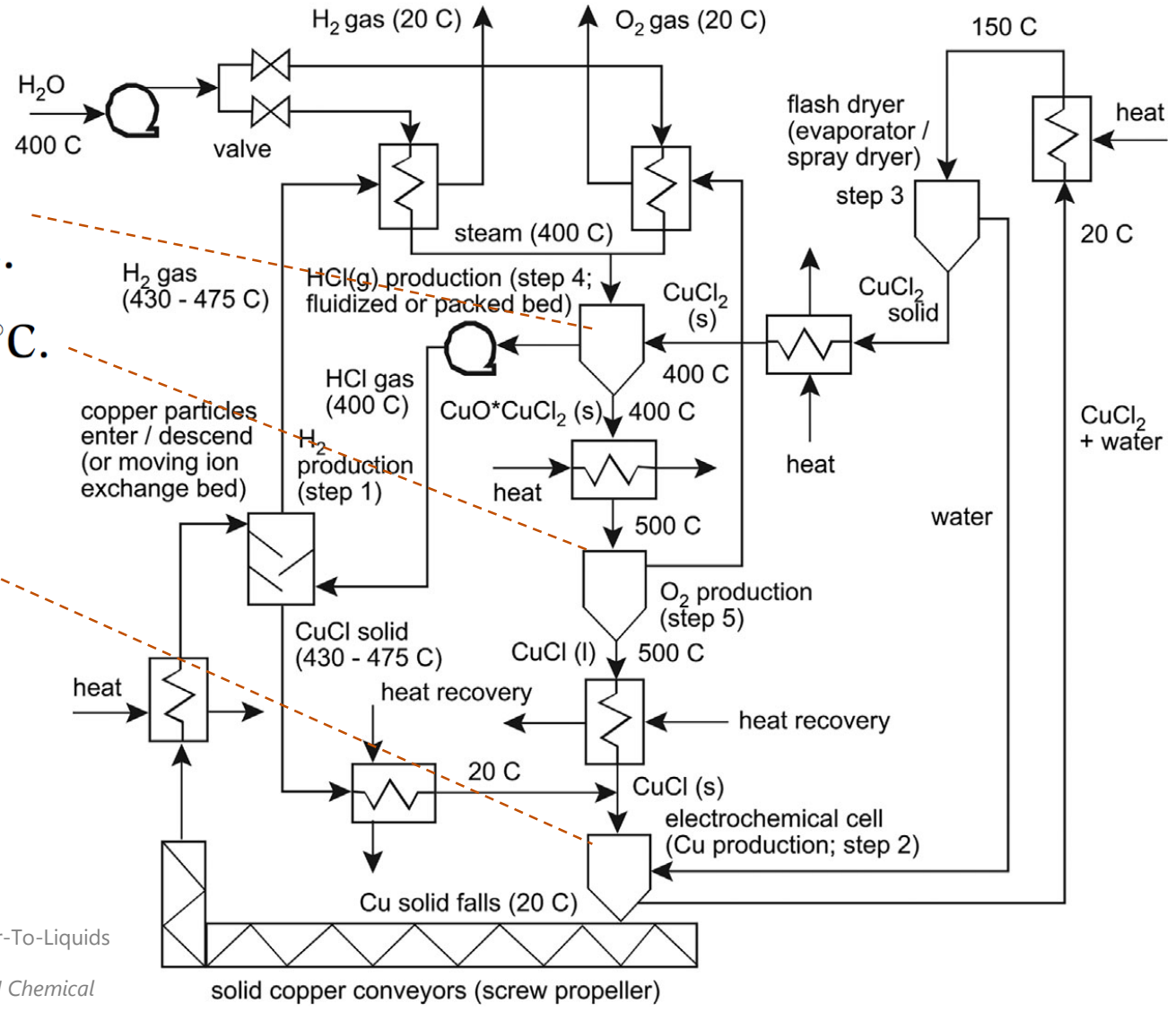
$$2CuCl(s) \rightarrow Cu(s) + Cu\text{-}Cl_2(aq)$$

(Consumes Electricity)

Gets the copper back

$$2Cu(s) + 2HCl(g) \rightarrow 2CuCl\,(l) + H_2(g) \text{ at } 430\text{–}475\ ^\circ\text{C}.$$

Releases the H



Sources: M. A. Rosen, Energy 2010, 35, 1068.
Scott JA, Adams TA II. Biomass-Gas-and-Nuclear-To-Liquids (BGNTL) Processes Part I:
Model Development and Simulation. *Canadian J Chemical Engineering* 96:1853-1871 (2018)

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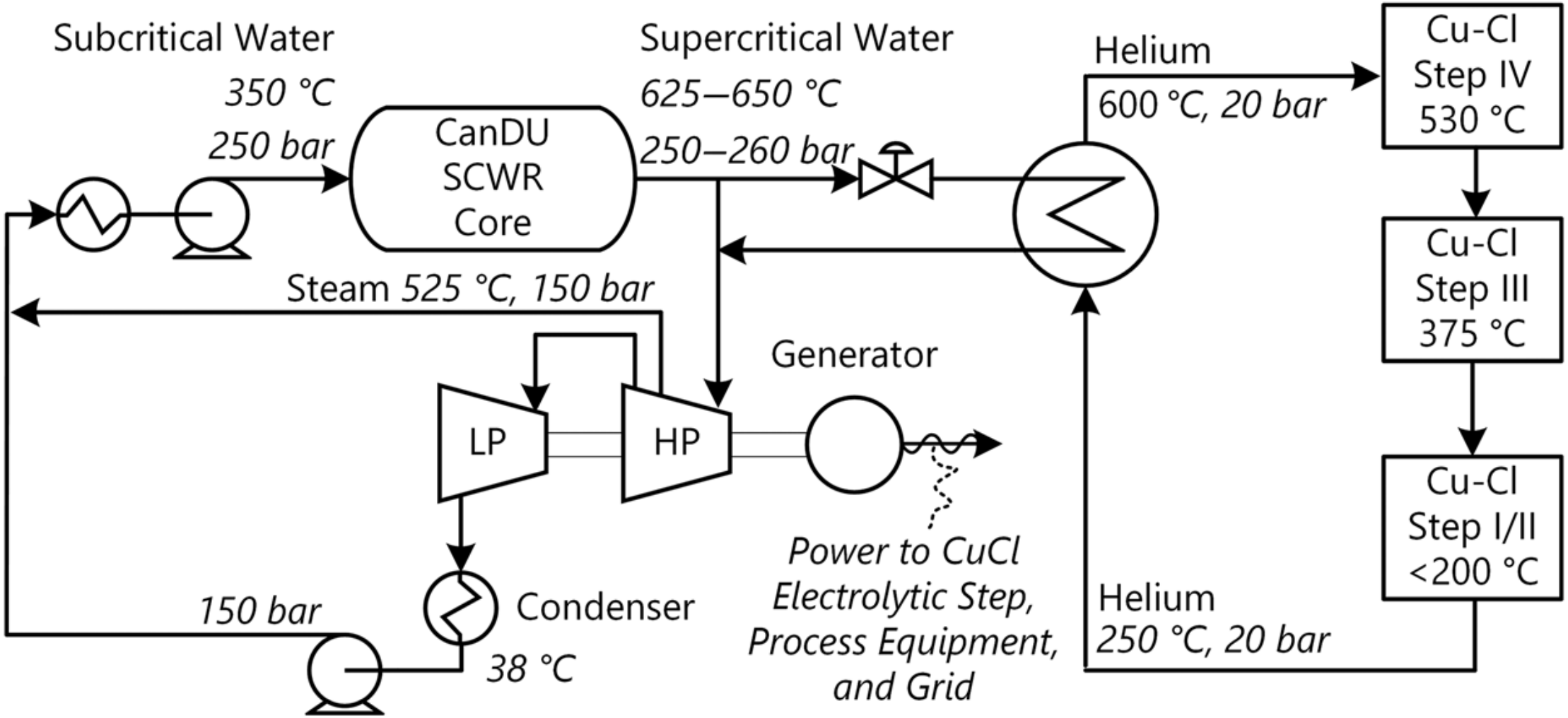
Integrated with Nuclear (carbonless)



Sources: Scott JA, Adams TA II. Biomass-Gas-and-Nuclear-To-Liquids (BGNTL) Processes Part I: Model Development and Simulation. *Canadian J Chemical Engineering* 96:1853-1871 (2018)

Carbonaceous H_2 Production

Steam Reforming

$CH_4 + H_2O \rightarrow CO + H_2$

Water Gas Shift

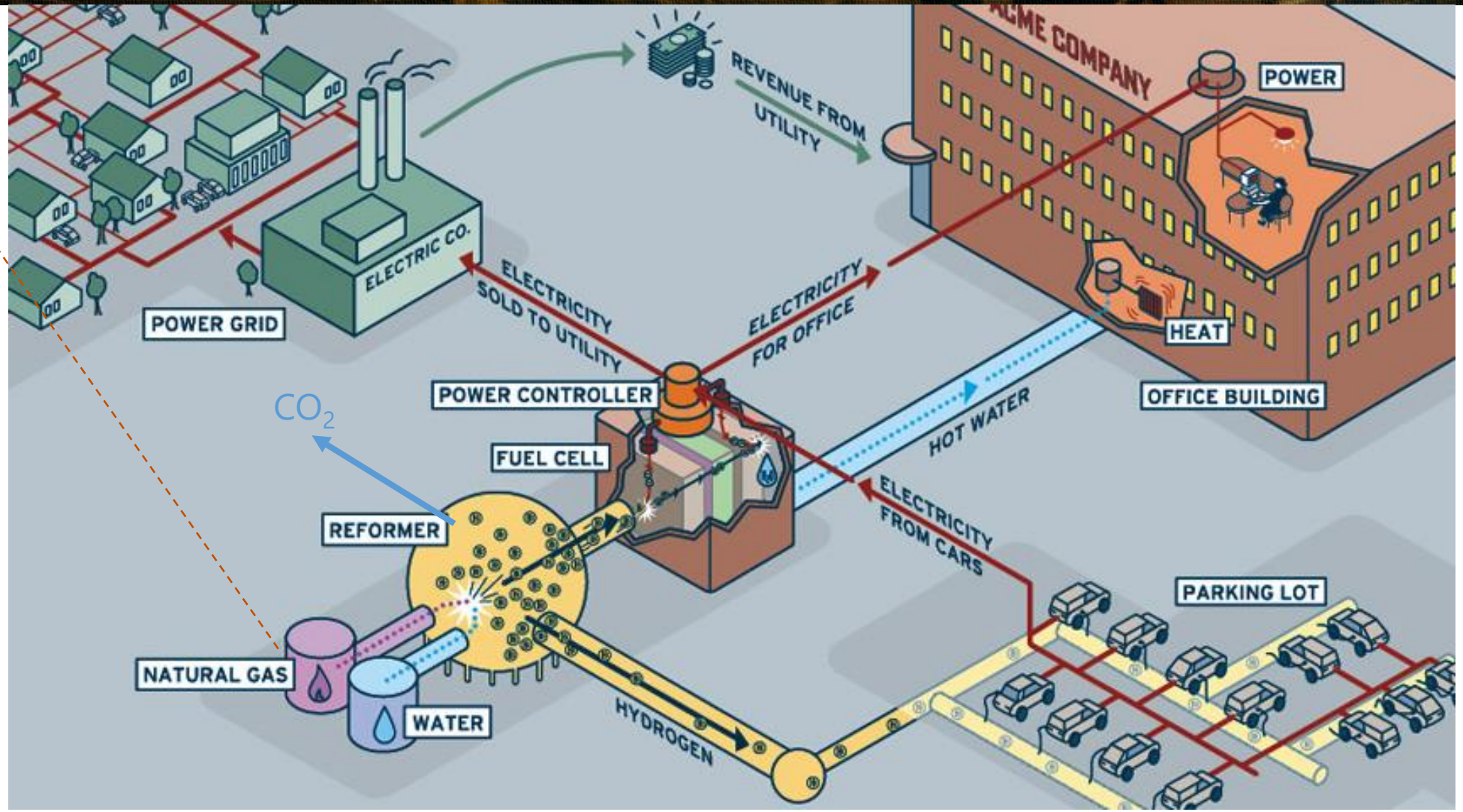
$CO + H_2O \rightarrow CO_2 + H_2$

Not shown:

Lots of CO_2 Emissions (or Expensive, Energy Intensive CO_2 capture and sequestration)

Shown:

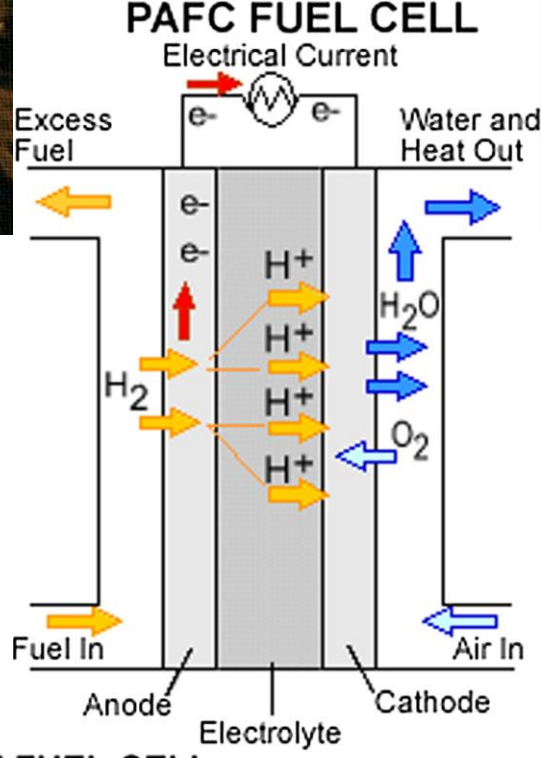
Waste hot water sold as product. (Heat + power co-generated)

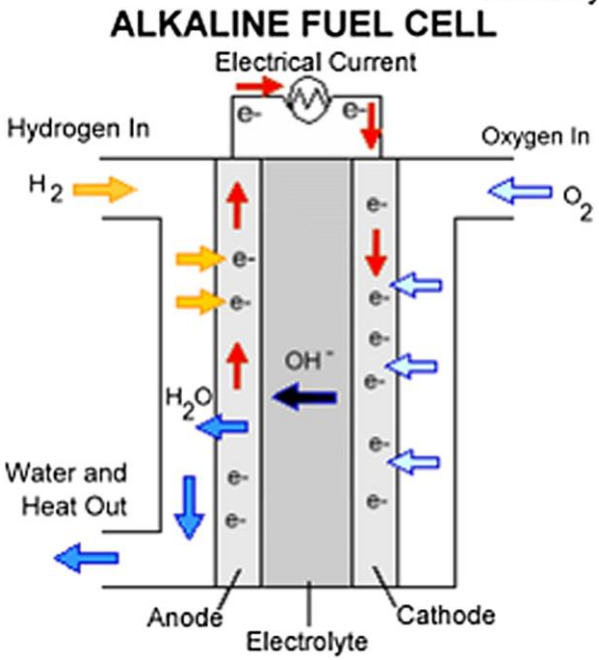


Sources: Funnel incorporated. Hydrogen Economy Infographic.

Other H_2-Based Cells

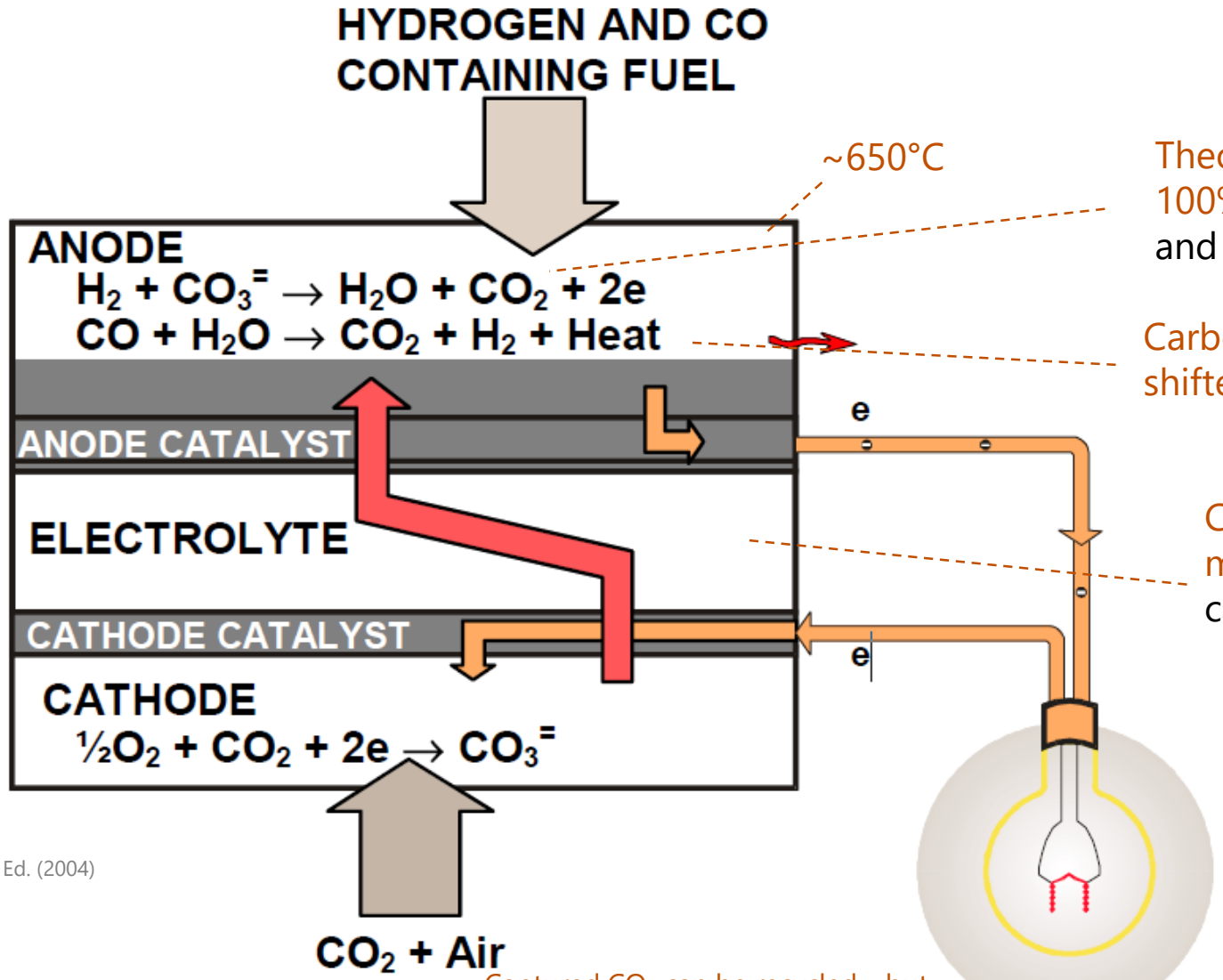
- Phosphoric Acid Fuel Cells (PAFC)
  - H_3PO_4 is the electrolyte and proton (H^+) carrier.
    - Have to replenish as it is gradually lost.
  - 200°C, up to 8 bar.
  - Uses platinum electrodes (Expensive!!)
  - CO and sulfurs are poison. High purity H_2-only.
  - Not expected to be economic within next two decades
- Alkaline Fuel Cells (AFC)
  - KOH used as electrolyte.
  - OH^- is oxygen carrier from cathode (air) to anode (fuel).
    - Need to mix O_2 and H_2O on cathode side.
  - K gets mixed into water, has to get recirculated.
  - CO_2 is an impurity! Have to scrub it from the air first (expensive)





Sources: EG&G. Fuel Cell Handbook, 7th Ed. (2004)
Vaghari et al. Sustainable Chemical Processes 2013, 1:16

Molten Carbonate Fuel Cells (MCFC)



~650°C

Theoretically can capture 100% CO_2. Just complex and lots of it.

Carbonaceous fuels must be shifted. Can happen on-board.

$CO_3^{=}$ is transported through molten carbonate as the oxygen carrier.

Has been successfully commercialized by one US company (Fuel Cell Energy) but they are transitioning to SOFCs. (high costs)

Captured CO_2 can be recycled… but complex. Suitable for large-scale only.

Sources: EG&G. Fuel Cell Handbook, 7th Ed. (2004)

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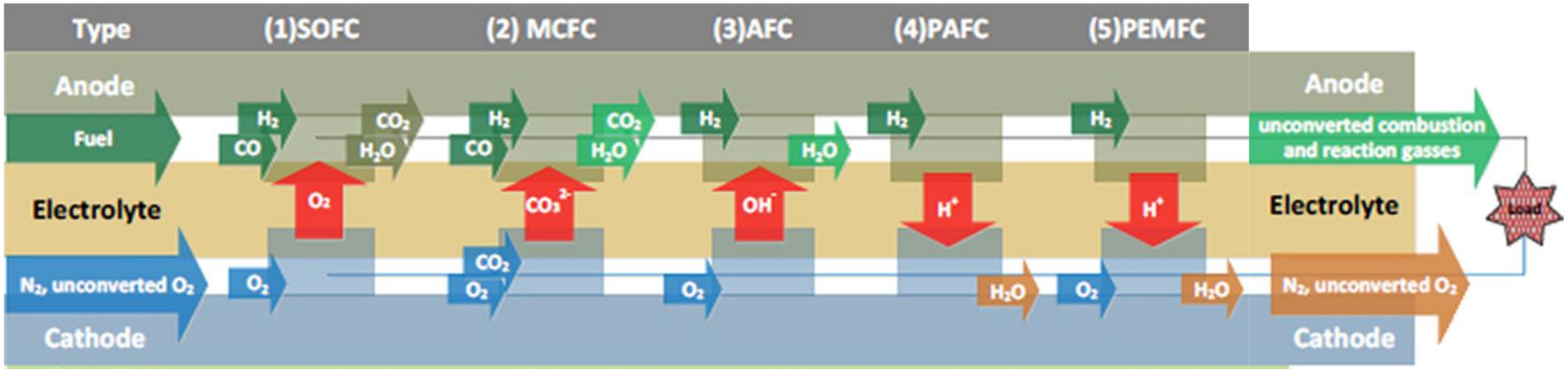
Fuel Cell Overview



Type	(1)SOFC	(2) MCFC	(3)AFC	(4)PAFC	(5)PEMFC
Operating Temperature	700-1000 °C	630-650 °C	50-200 °C	190-210 °C	50-200 °C
Electrolyte	Ceramic solid oxide zirconia	Ceramic solid oxide ceragadolinia	Molten lithium carbonate	Potassium hydroxide	Sulphonic acid Incorporated into a solid membrane

Sources: EG&G. Fuel Cell Handbook, 7th Ed. (2004)
Vaghari et al. Sustainable Chemical Processes 2013, 1:16

Comments

- PEMS are key driver of the "hydrogen economy"
  - (major GW Bush initiative)
- Require high purity H_2 to avoid failure.
- H_2 creation, storage, transport, and infrastructure problems very challenging
- "Government gave up" on H_2 / PEM economy. US Dropped down fuel cell funding significantly as a result.
- Changes with administration.
- For eco-purposes: Since you need renewable power to make the hydrogen in the first place, they are really an ingredient in an energy storage system rather than the main driver for a bulk power system

Some Example Impact Factors

Production of chemicals and others (in millipoints per kg) Tabulated cradle-to-gate production values

	Indicator	Description
Ammonia	160	NH_3
Argon	7.8	Inert gas, used in light bulbs, welding of reactive metals like aluminium
Bentonite	13	Used in cat litter, porcelain etc.
Carbon black	180	Used for colouring and as filler
Chemicals inorganic	53	Average value for production of inorganic chemicals
Chemicals organic	99	Average value for production of organic chemicals
Chlorine	38	Cl_2. Produced with diaphragm production process (modern technology)
Dimethyl p-phthalate	190	Used as plasticizer for softening PVC
Ethylene oxide/glycol	330	Used as industrial solvent and cleaning agent
Fuel oil	180	Production of fuel only. Combustion excluded!
Fuel petrol unleaded	210	Production of fuel only. Combustion excluded!
Fuel diesel	180	Production of fuel only. Combustion excluded!
H_2	830	Hydrogen gas. Used for reduction processes
H_2SO_4	22	Sulphuric acid. Used for cleaning and staining

Sources: EcoIndicator99 User manual

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Some Example Impact Factors

Tabulated cradle-to-gate production values
Note: These are for EcoIndicator99, an older but still commonly used method. ReCiPe 2008 is meant to replace it.

Production of non ferro metals (in millipoints per kg)

	Indicator	Description
Aluminium 100% Rec.	60	Block containing only secondary material
Aluminium 0% Rec.	780	Block containing only primary material
Chromium	970	Block, containing only primary material
Copper	1400	Block, containing only primary material
Lead	640	Block, containing 50% secondary lead
Nickel enriched	5200	Block, containing only primary material
Palladium enriched	4600000	Block, containing only primary material
Platinum	7000000	Block, containing only primary material
Rhodium enriched	12000000	Block, containing only primary material
Zinc	3200	Block, containing only primary material (plating quality)

Sources: EcoIndicator99 User manual

Solid Oxide Fuel Cells

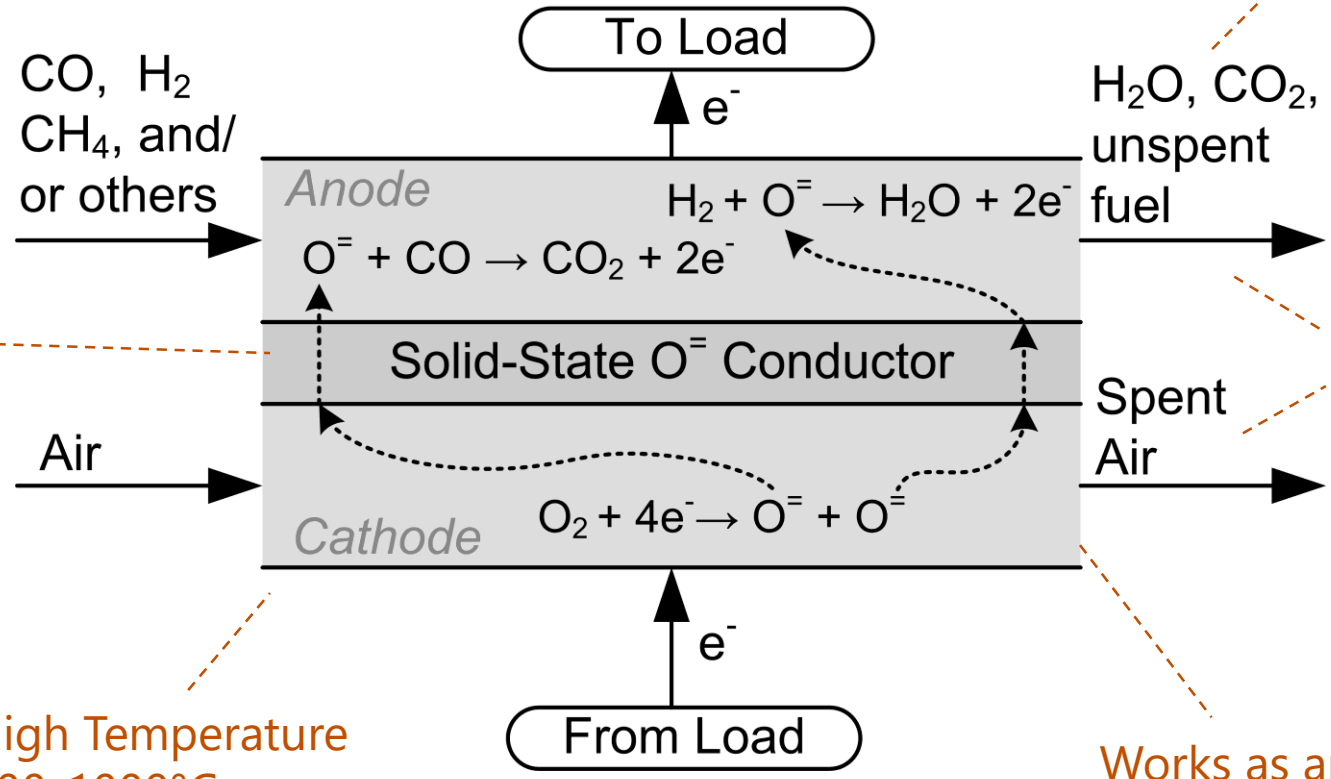
My personal suggestion for the world

Tech Overview

Fuel Flexible
Syngas, Nat. Gas, Coal-bed methane, diesel, gasoline, methanol, ammonia, jet fuel, methanol…

Most other FC's can't do this.

Fuel utilization 50-80% in practice today



No diffusion!

Outlets can be kept unmixed (2nd Generation)

High Temperature
700-1000°C

Works as an O_2 separator

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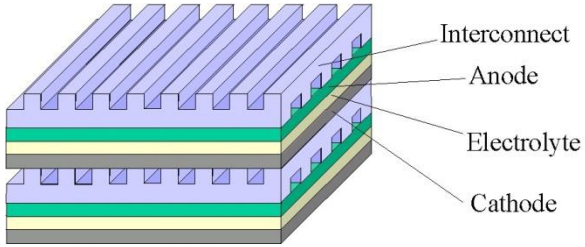
Sources: Adams TA II, Nease J, Tucker D, & Barton PI. *Ind Eng Chem Res* 52:3089–3111 (2013)

50-60% electrical efficiency at the cell level.
Very quiet! No spinning parts (here at least)

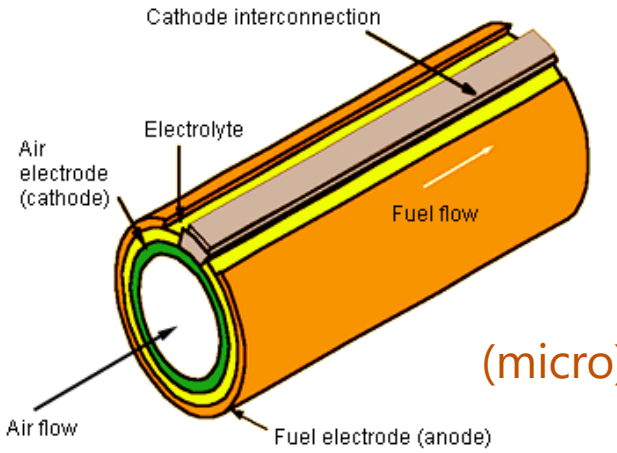
Planar vs. Tubular

Planar Cells
~10W – 1kW
Roughly 1ft^2



Bundle Planar Cells into Stacks
~10kW

Stacks into Modules
~200kW
8m wide, 2m tall, 2m deep



(micro) Tubular

Bundle the tubes
~300W. 36 cm x 20 cm

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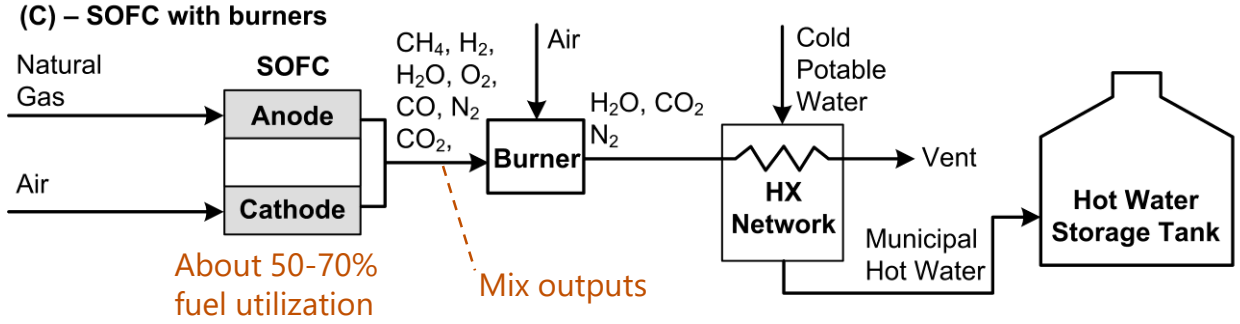
Sources: Materials Systems Research, Inc.. Also: BloomEnergy, "ES-5700 Energy Server". Also: Ultra Electronics, ROAMIO, D245XR
Adams TA II, Nease J, Tucker D, & Barton PI. *Ind Eng Chem Res* 52:3089–3111 (2013)

Current Uses – Distributed Power

- It's still way too costly and too small-scale for bulk power
- Appropriate for distributed production
  - Off-grid power production where battery lifetimes insufficient, rugged, low-vibration, or orientation-free service is needed.
    - Battery Chargers
    - Unmanned drones, subs
    - Space shuttle
    - Remote server farms

Military Rugged Power Supply (300W)

  - In-home power & hot water co-producer (Japan/Australia)



~1kW, about as big as furnace, not including water tank

Sources: Adams TA II, Nease J, Tucker D, & Barton PI. *Ind Eng Chem Res* 52:3089–3111 (2013)

Key Challenges to Mass Acceptance

- Manufacturing
  - Difficult make seals, manifolds, & interconnects properly
  - Limited pool of materials since it is high temperature
    - Ex: Anode must have just the right catalytic activity, porosity, thermal capabilities, porosity, resistance to carbon deposition and sulfur poisoning.
    - Lots of constraints to satisfy!
- Markets
  - Natural gas price crash:
    - Less incentive to invest in higher capital costs for higher fuel efficiency
  - Still little CO_2 regulation incentives

Sources: Adams TA II, Nease J, Tucker D, & Barton PI. *Ind Eng Chem Res* 52:3089–3111 (2013)

SOFC Lifetimes

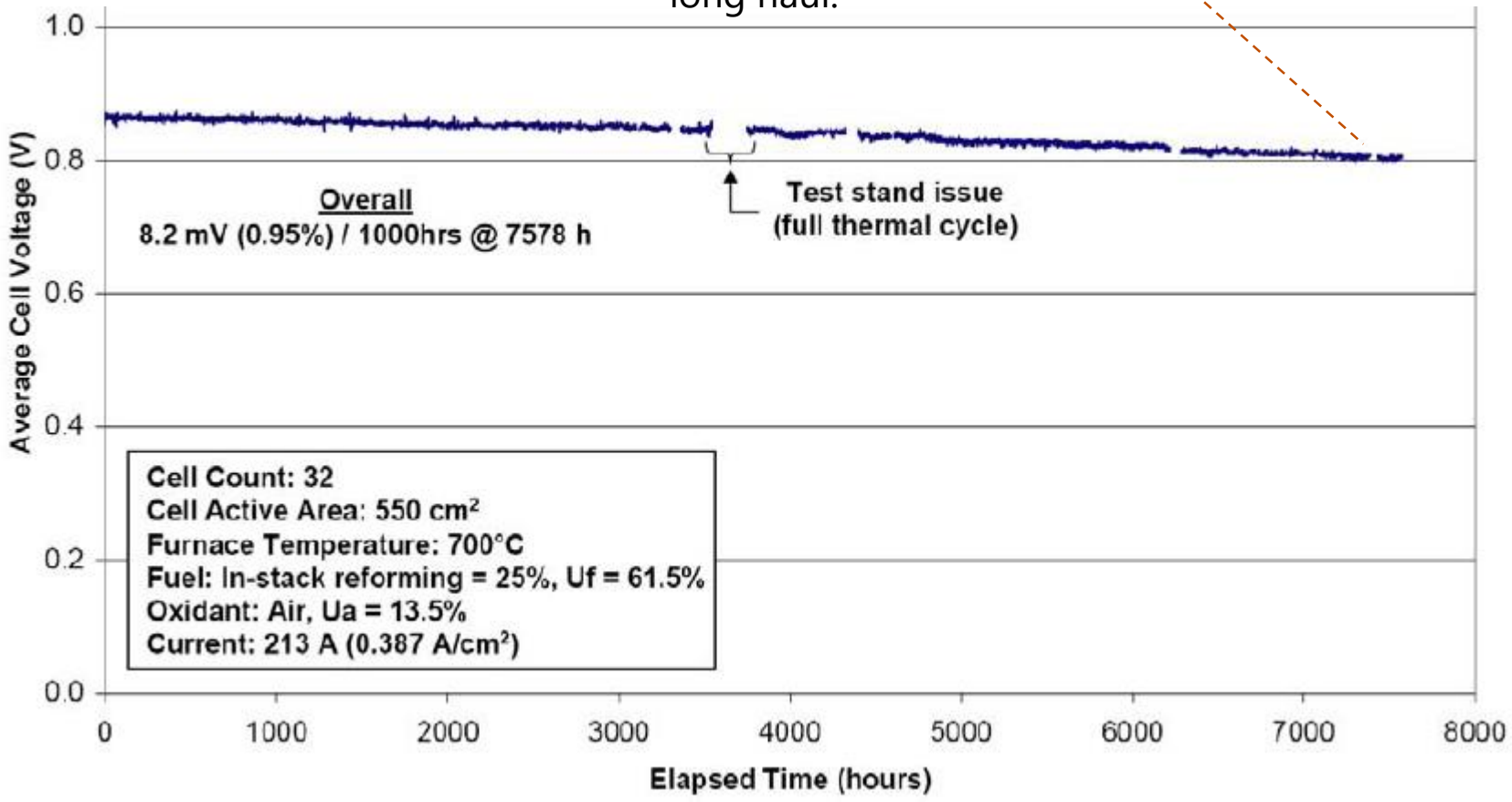
Power = Voltage * Current

Power plants supply a constant current

Loses about 1% of its power per 1000 hours

So roughly 5 year lifetime for 60% power capacity

So you need to be able to account for this in the long haul.



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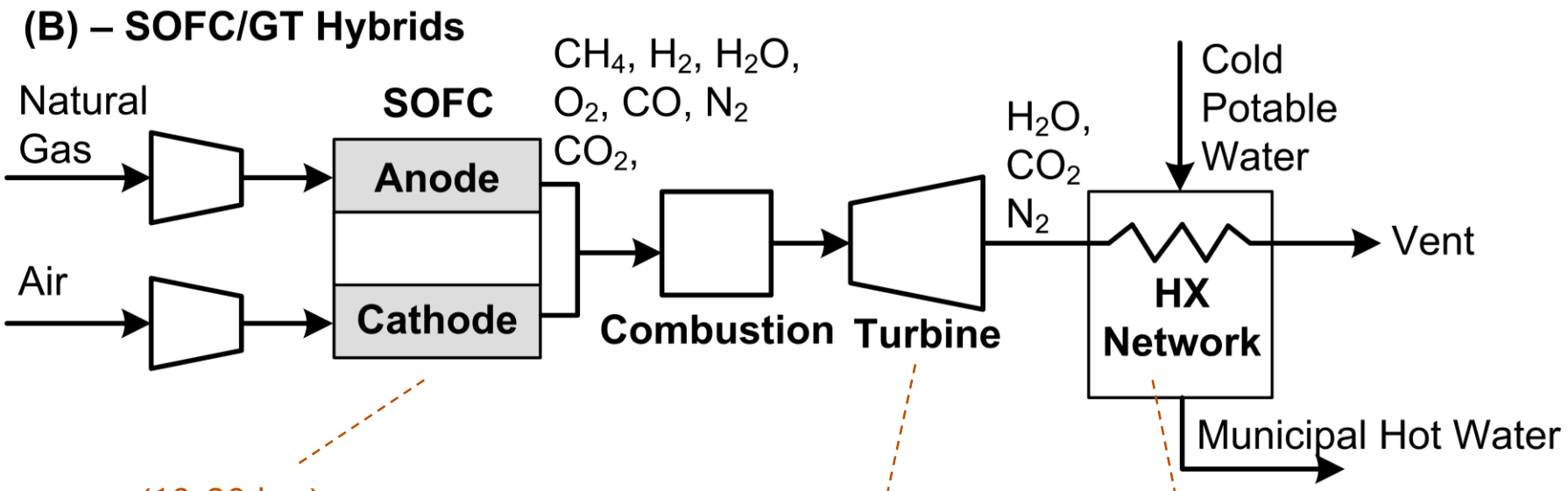
Sources: Borglum B., Tang E., Patsula M. Development of solid oxide fuel cells at Versa Power Systems. ECS Trans. 2011, 35, 63-69.

Medium Term Bulk Power



Operate at pressure (10-20 bar)
50-80% Fuel Utilization

Intermediate difficulty: Operate at higher pressure but don't need to worry so much about the high-temperature seal separating cathode & anode exhausts.

Combust unspent fuel in turbine.
Use normal air.

Advantage: as the SOFCs decay, the fuel utilization goes down, so the turbine can make up for the loss since more fuel is burnt there.

Can use the waste heat for hot water, or steam for power

For large bulk plants, a steam power cycle is more likely.
Three places to get power.
High efficiency.

Sources: Adams TA II, Nease J, Tucker D, & Barton PI. *Ind Eng Chem Res* 52:3089–3111 (2013)

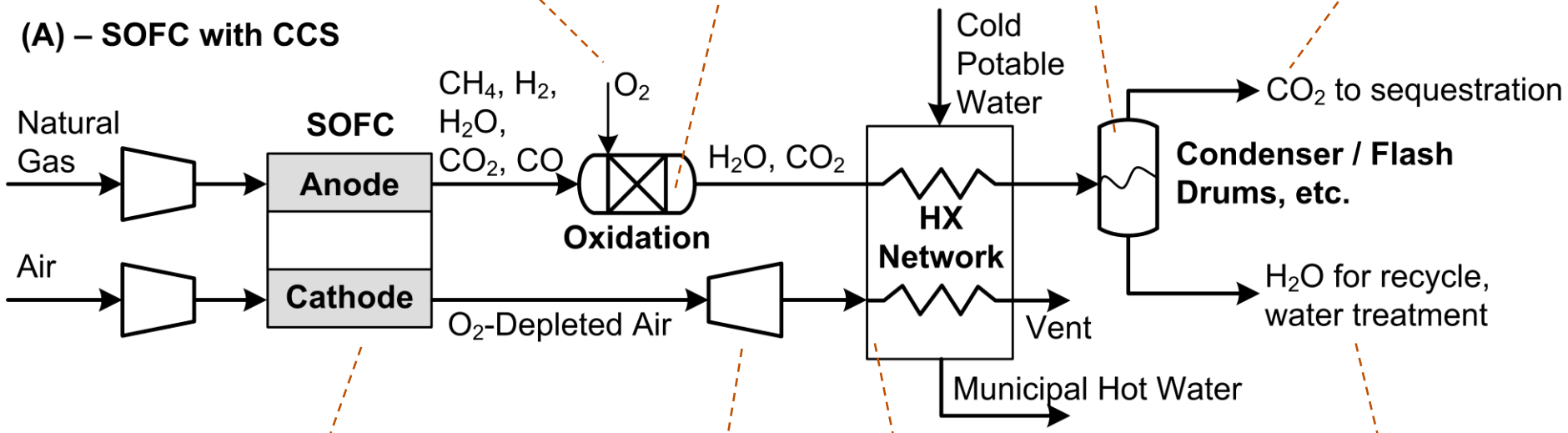
Long Term Bulk Power (NGFC)

Need high purity O_2 from air separation unit

Catalytically oxidize.

Very little energy penalty here

Pipeline purity CO_2
~100% capture
Still at 10-20 bar!



Operate at pressure (10-20 bar)
>80% Fuel Utilization

Higher difficulty: High pressure plus effective seals.

Extra power here from Brayton Cycle turbine

Can use the waste heat for hot water, or steam for power

Water is actually drinkable!

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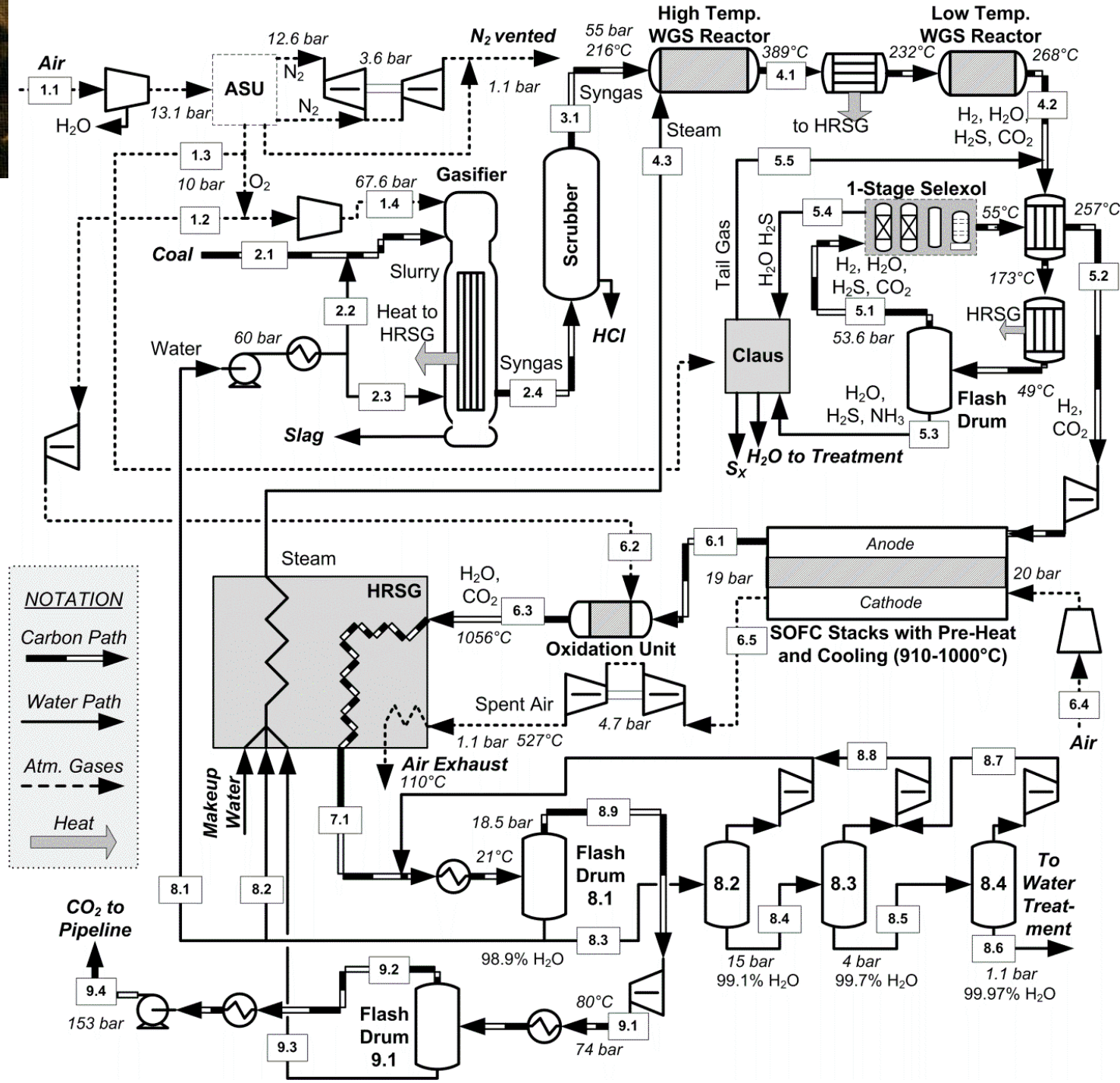
Sources: Adams TA II, Nease J, Tucker D, & Barton PI. *Ind Eng Chem Res* 52:3089–3111 (2013)

Coal Variants Too (IGFC)



Upper bound on pressure is limited by SOFC construction.

Sources: Adams & Barton. AIChE J (2010). See also NETL, Current and Future Technologies for Gasification-Based Power Generation, Vol 2, Rev 1 (2010).

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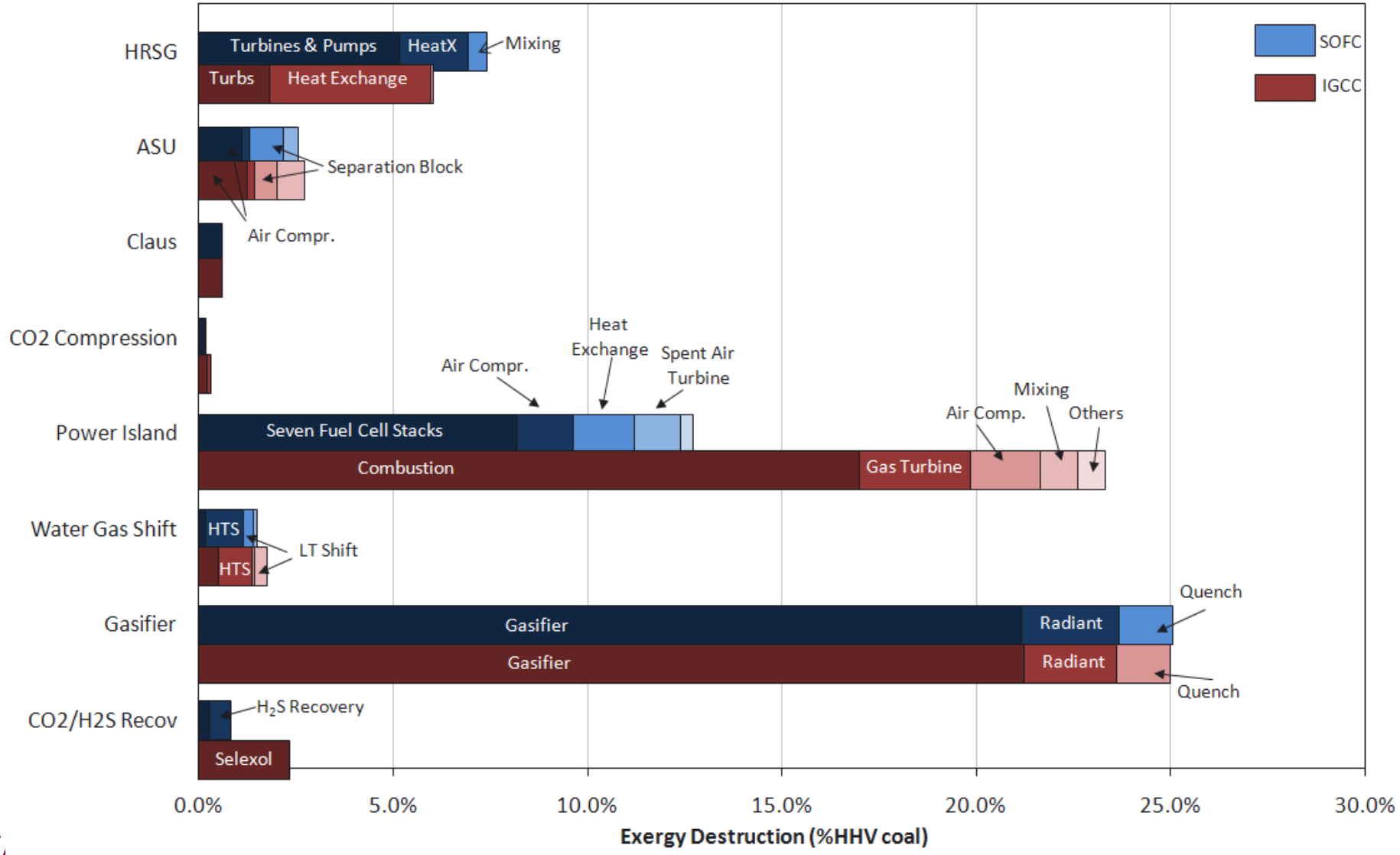
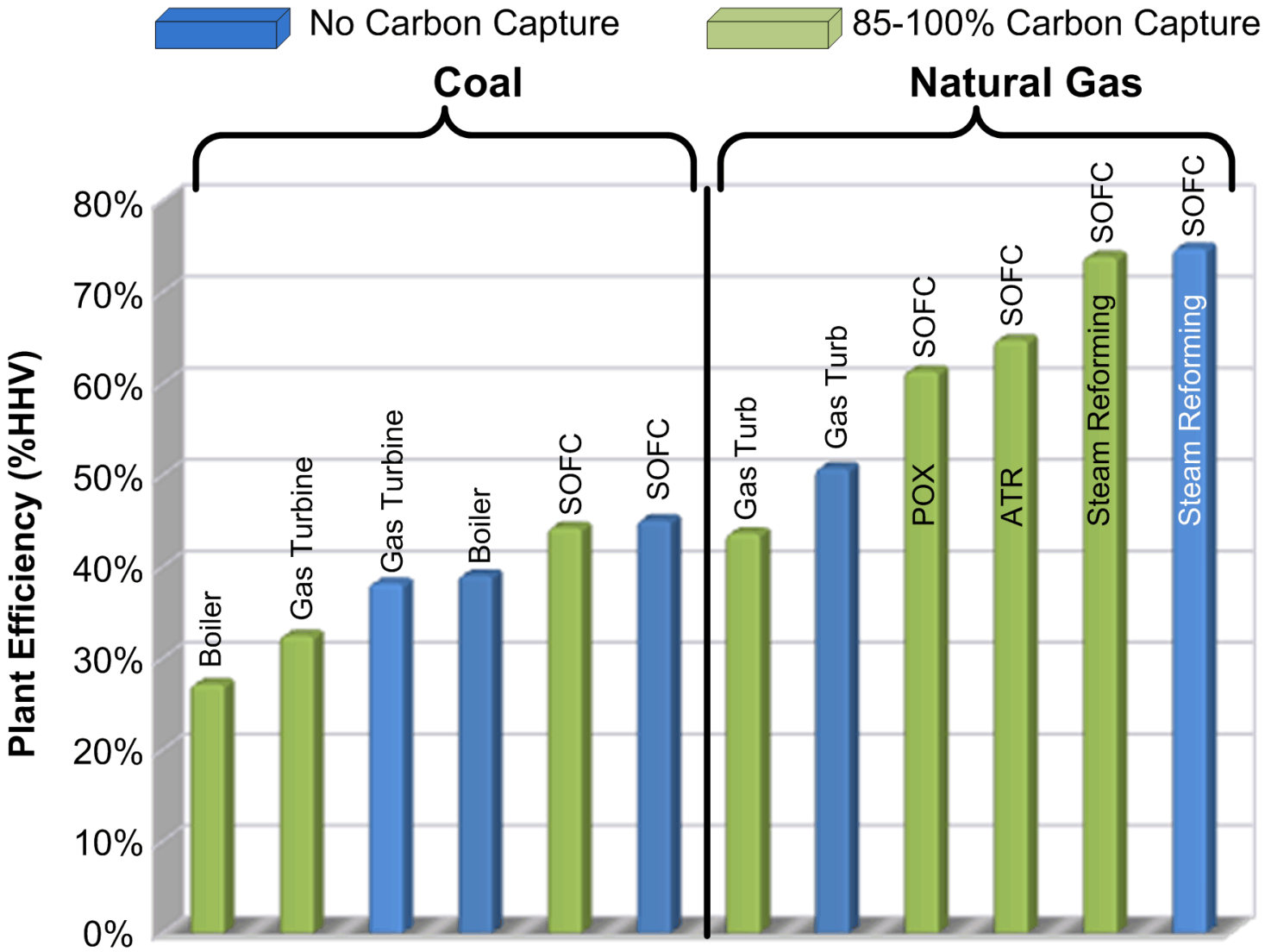
Exergy Analysis



Exergy numbers for IGCC thanks to Barbara Botros (MIT)

Efficiencies



Adams & Barton, AIChE J (2010)

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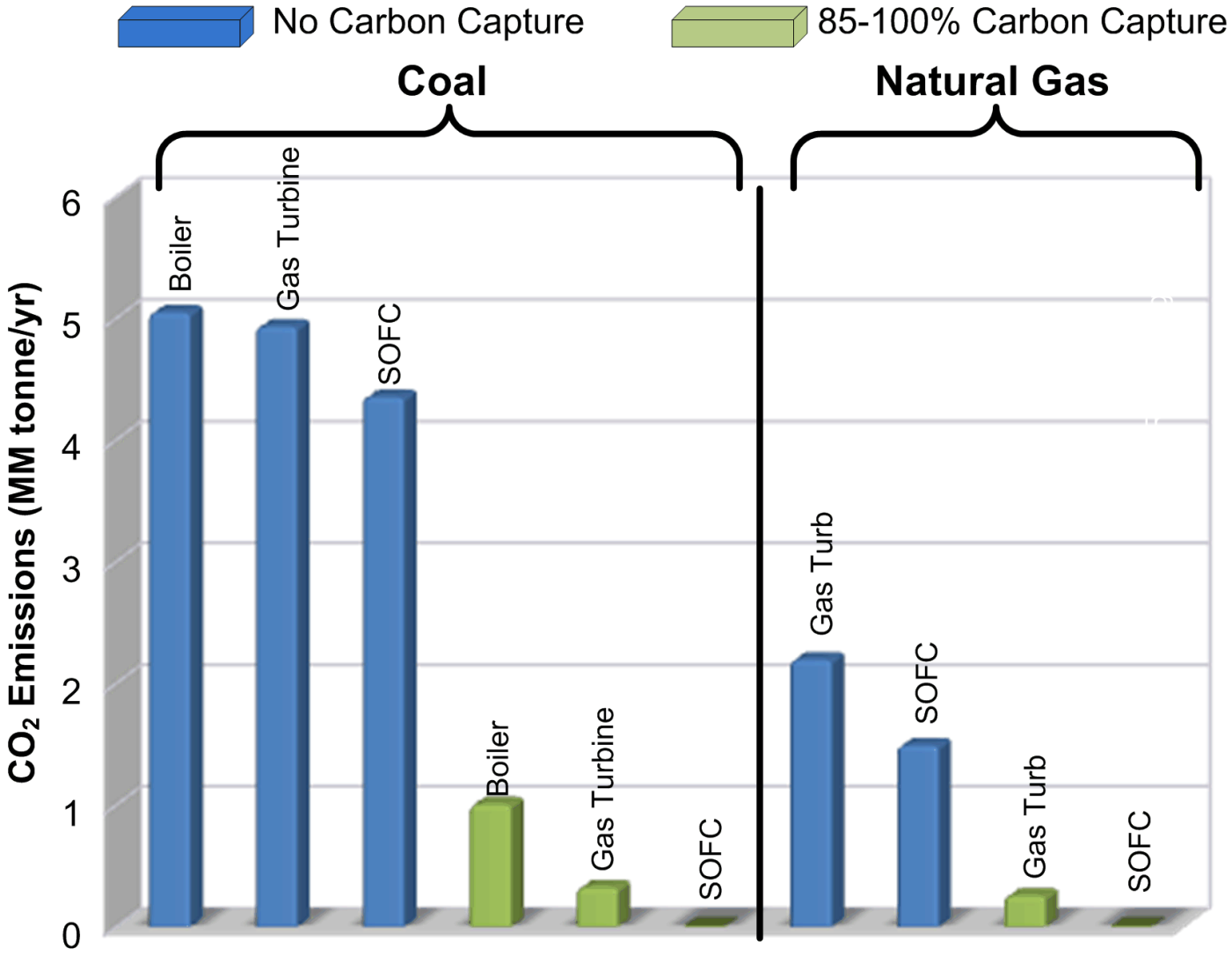
CO_2 Emissions



700MW Net Output

All NG-SOFC plants use steam reforming

Sources: Adams & Barton. J Power Sources (2010).
Adams & Barton, AIChE J (2010)

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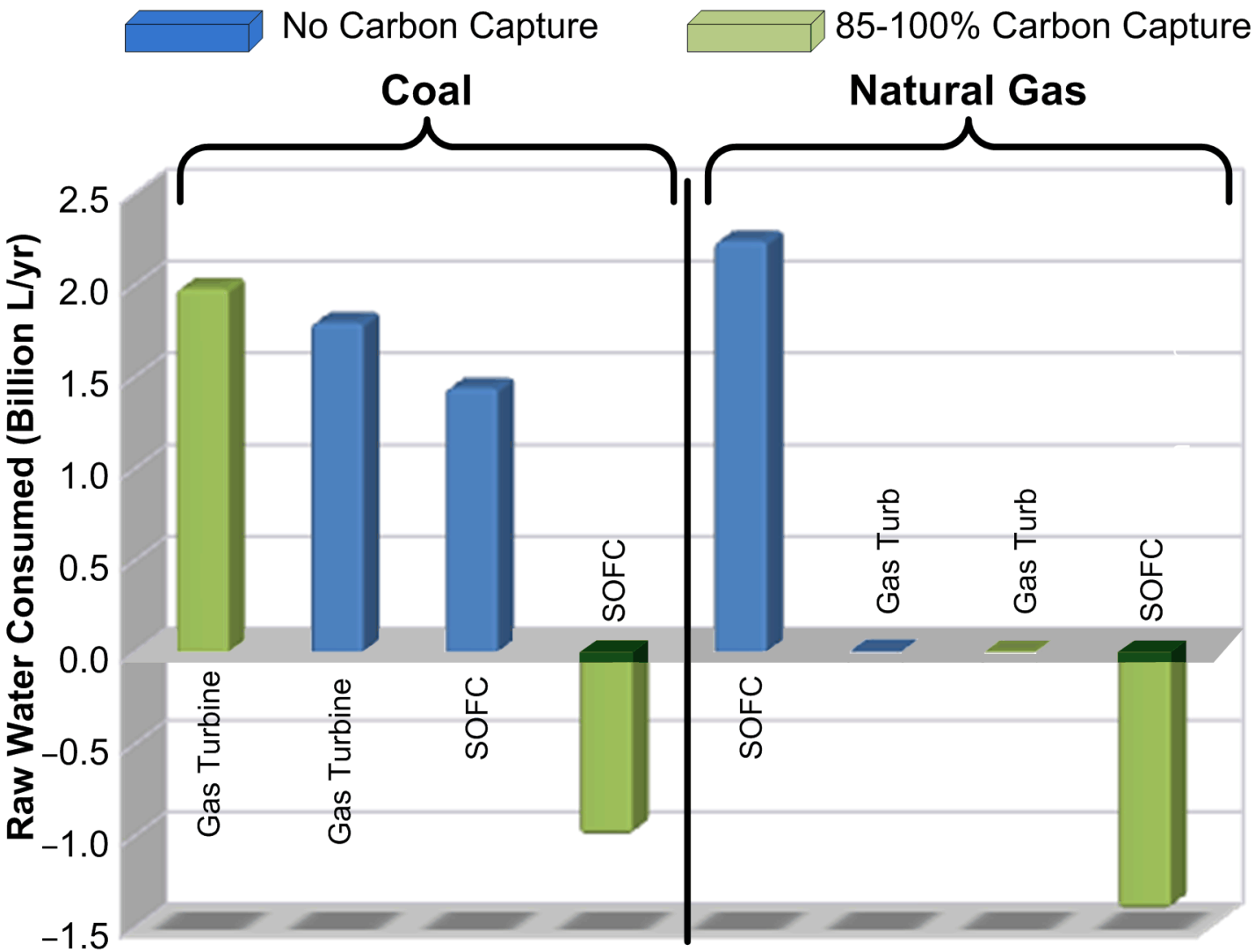
Water Consumption



700MW Net Output

All NG-SOFC plants use steam reforming

Dry cooling used (no water losses from cooling)

Sources: Adams & Barton. J Power Sources (2010).
Adams & Barton, AIChE J (2010)

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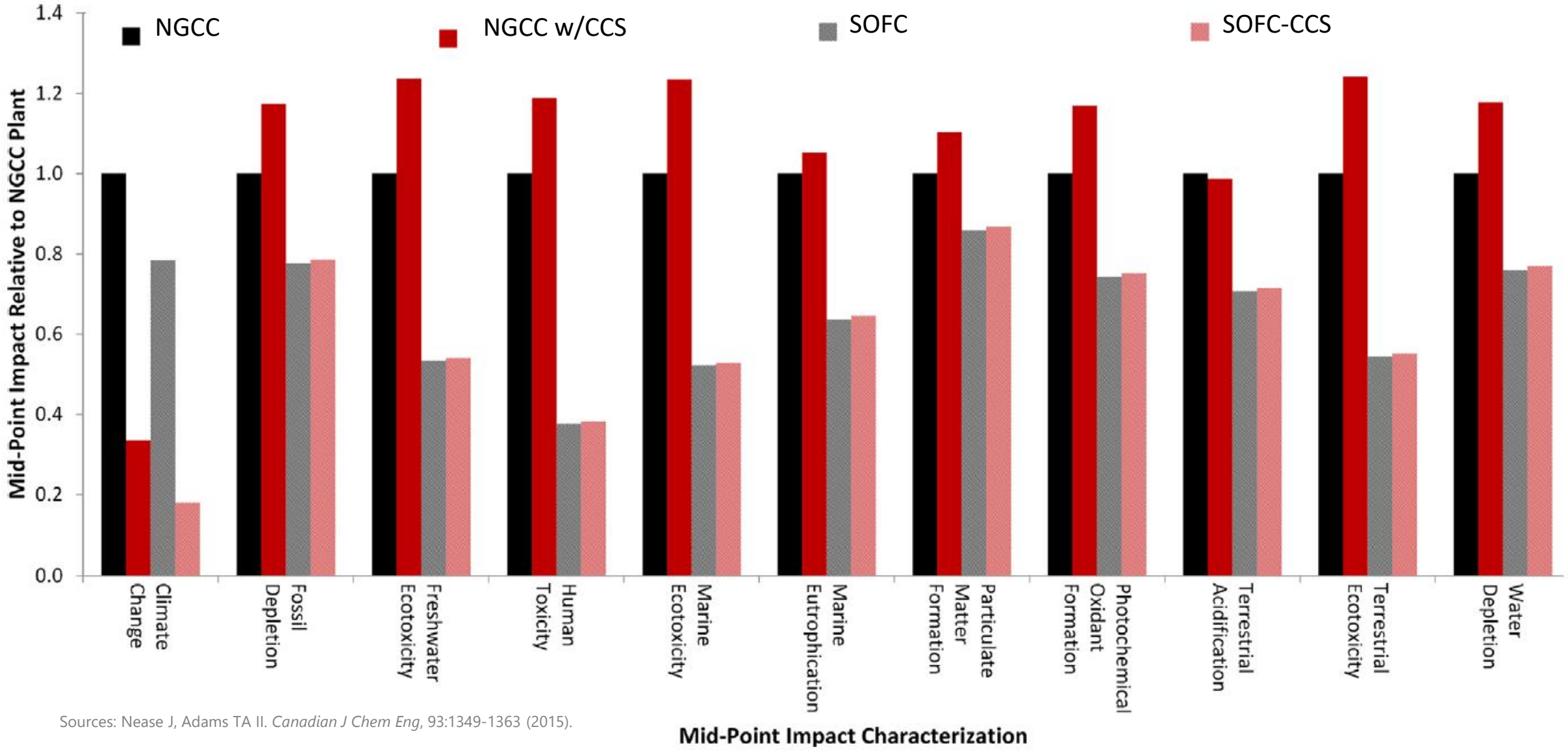
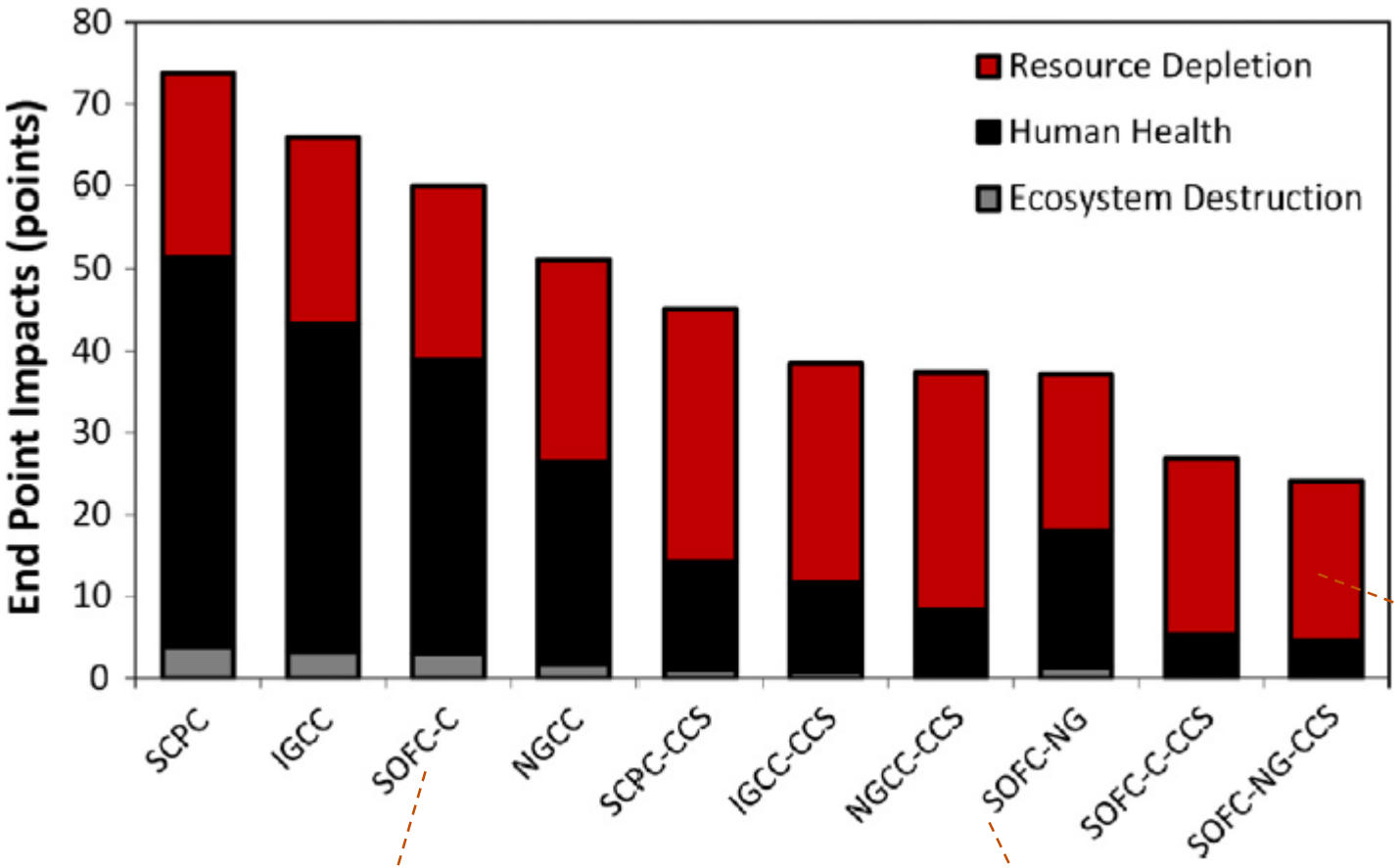
CTG Life Cycle Analyses (Nat Gas)



Sources: Nease J, Adams TA II. *Canadian J Chem Eng*, 93:1349-1363 (2015).

CTG LCA across fuels



With SOFCs and CCS, coal and gas have essentially the same impact.

Coal-based SOFCs cannot save coal. Still better to switch to NGCC.

Nat Gas SOFCs without CCS are just as good as NGCC with CCS

Sources: Nease J, Adams TA II. *Applied Energy*, 150:161-175 (2015)

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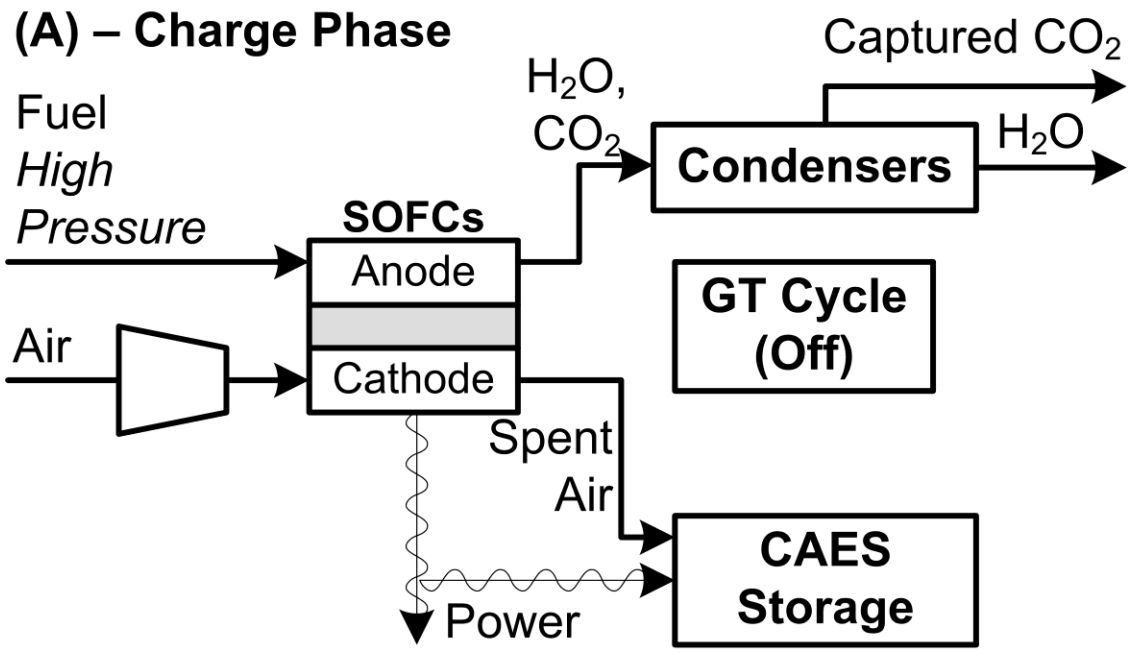
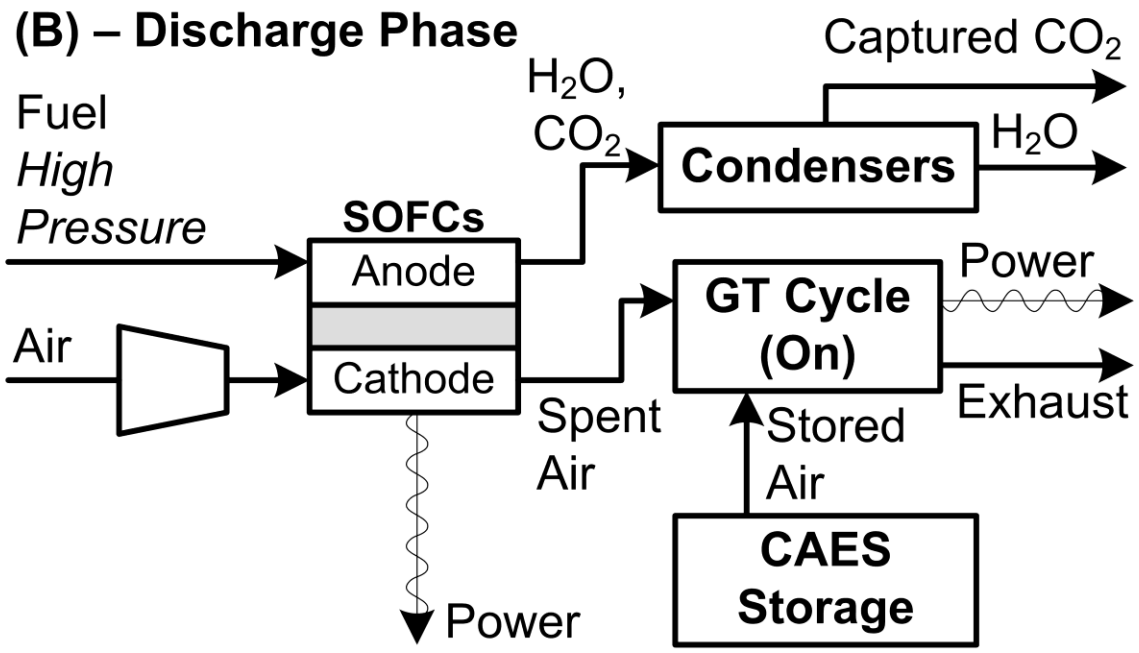
SOFCs with Compressed Air Energy Storage (CAES)



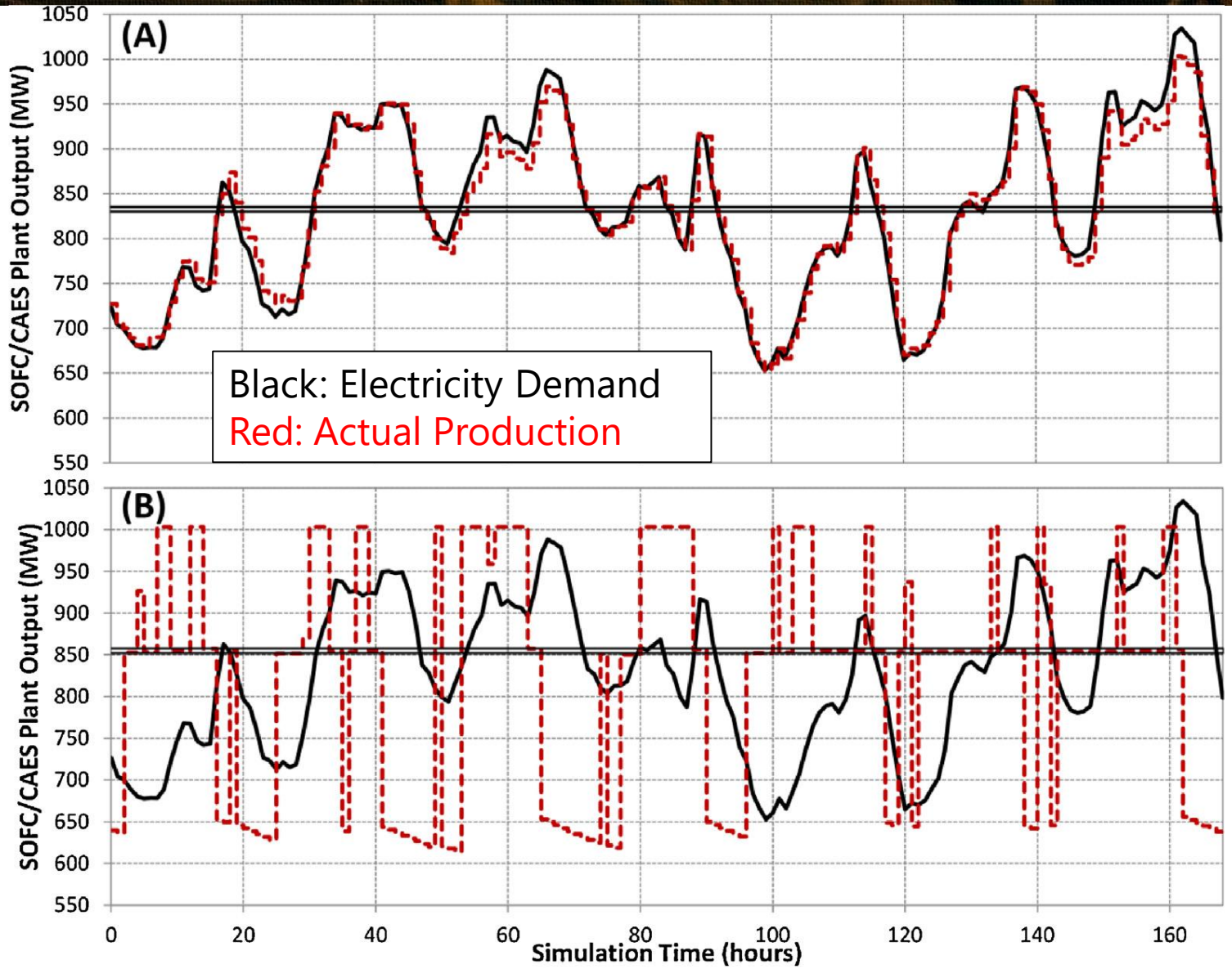


Sources: Nease, Adams, Real-Time Optimization of Integrated Solid-Oxide Fuel Cell and Compressed Air Energy Storage Plant for Zero-Emissions Peaking Power, submitted (2013)

Use Storage for Money or for Performance?

Baseload SOFC + CAES
Can optimize for load-following performance

Baseload SOFC + CAES
Can optimize for profit



Sources: J. Nease, Moneiro N, Adams TA II. / *Computers and Chemical Engineering* 94 (2016) 235–249

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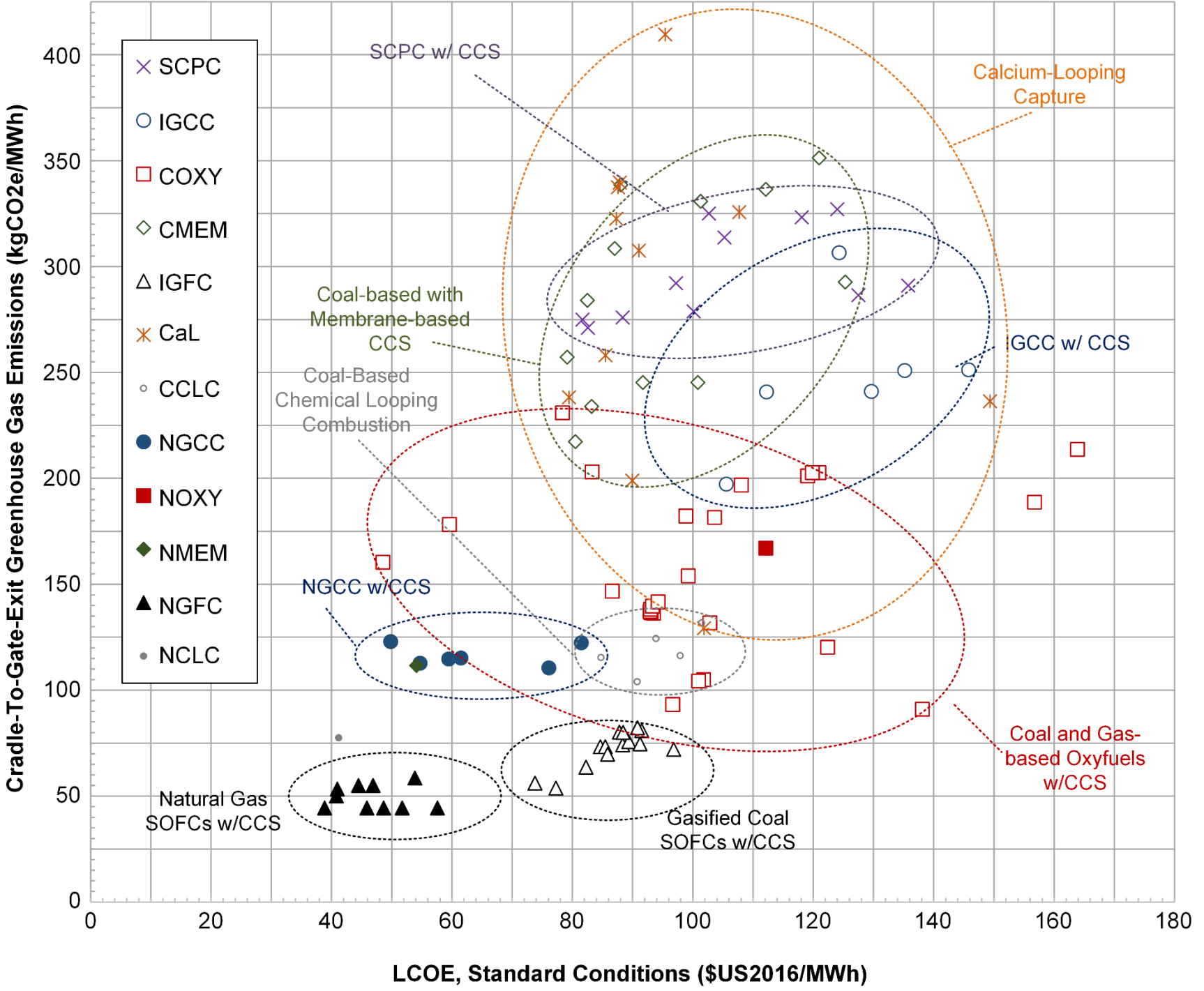
Big Picture



Sources: Adams, T. A. II, Hoseinzade, L., Madabhushi, P. B., Okeke, I. Comparison of CO2 Capture Approaches for Fossil-Based Power Generation: Review and Meta-Study, Processes,, 5 (3) 44 (2017)

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