Reversible fuel cells instead of electrolysers and batteries for large-scale renewable energy storage

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Reversible fuel cells instead of electrolysers and batteries for large-scale renewable energy storage

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20th November 2013
Sustainable Fuels from Renewable Energies workshop
IASS Potsdam Germany

Outline

- Background
- What is a reversible fuel cell
- vs Batteries
- vs Electrolysers

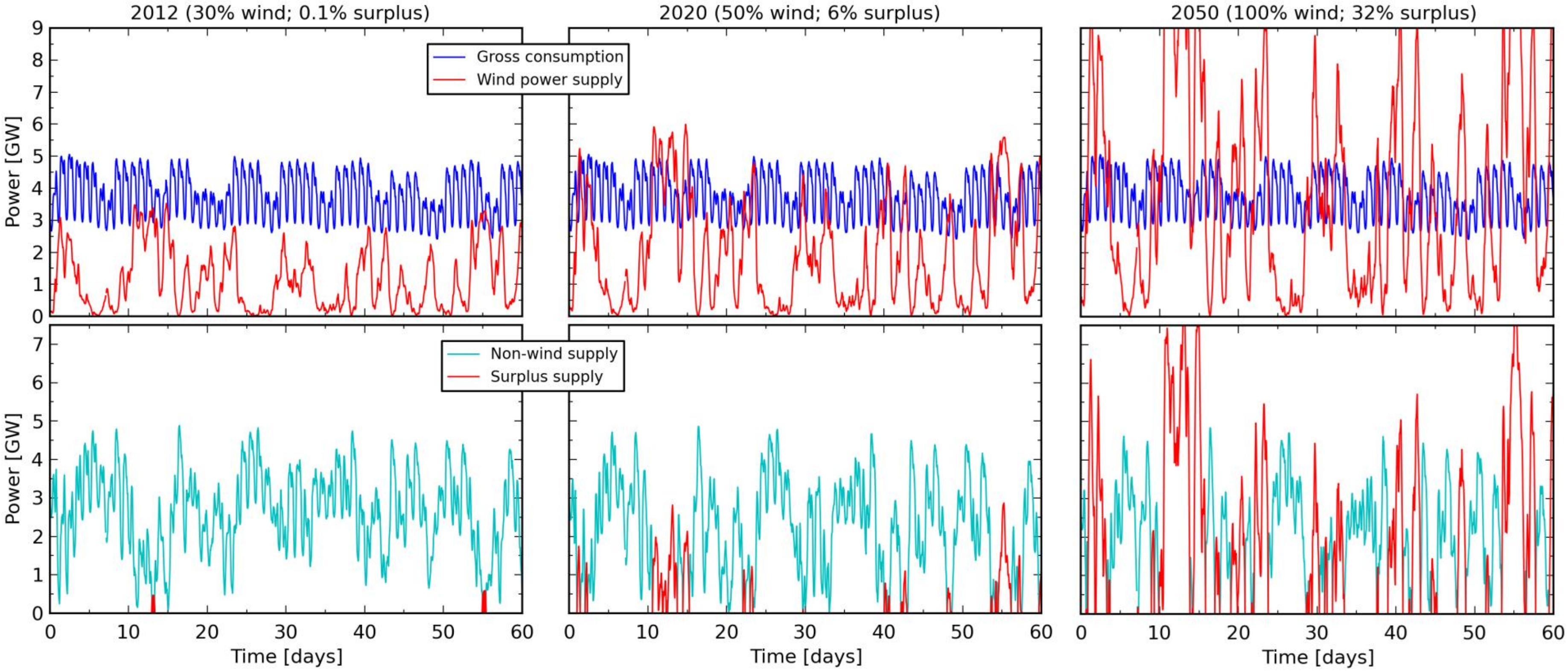
Efficiency

Resource use

Capital cost & lifetime

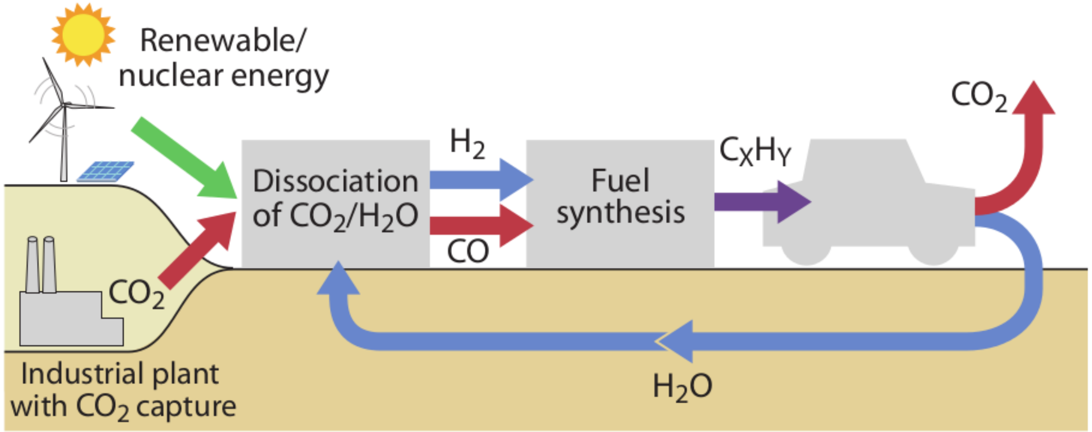
- Case study of 100% wind/solar using RFCs

Denmark’s need for energy storage

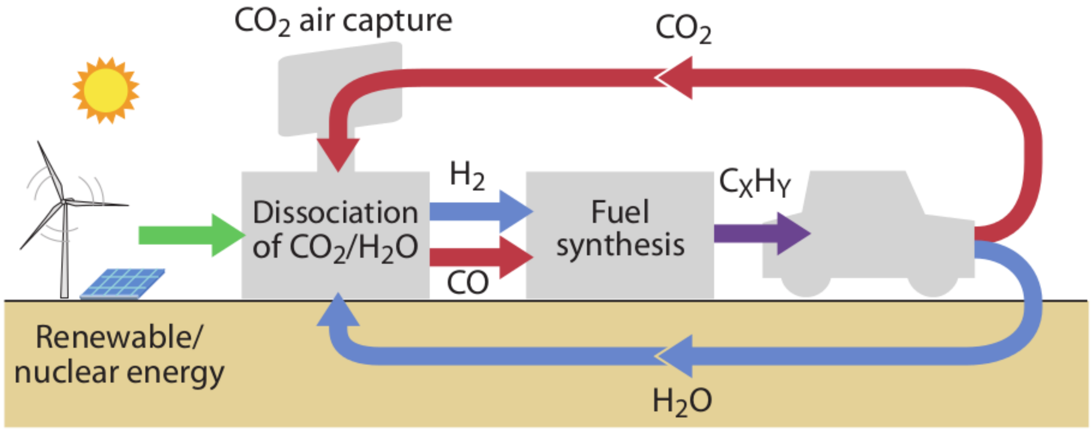


Data for 2012 from energinet.dk; future wind supply scaled up based on Danish roadmap.

Storing surplus wind power as hydrocarbon fuels



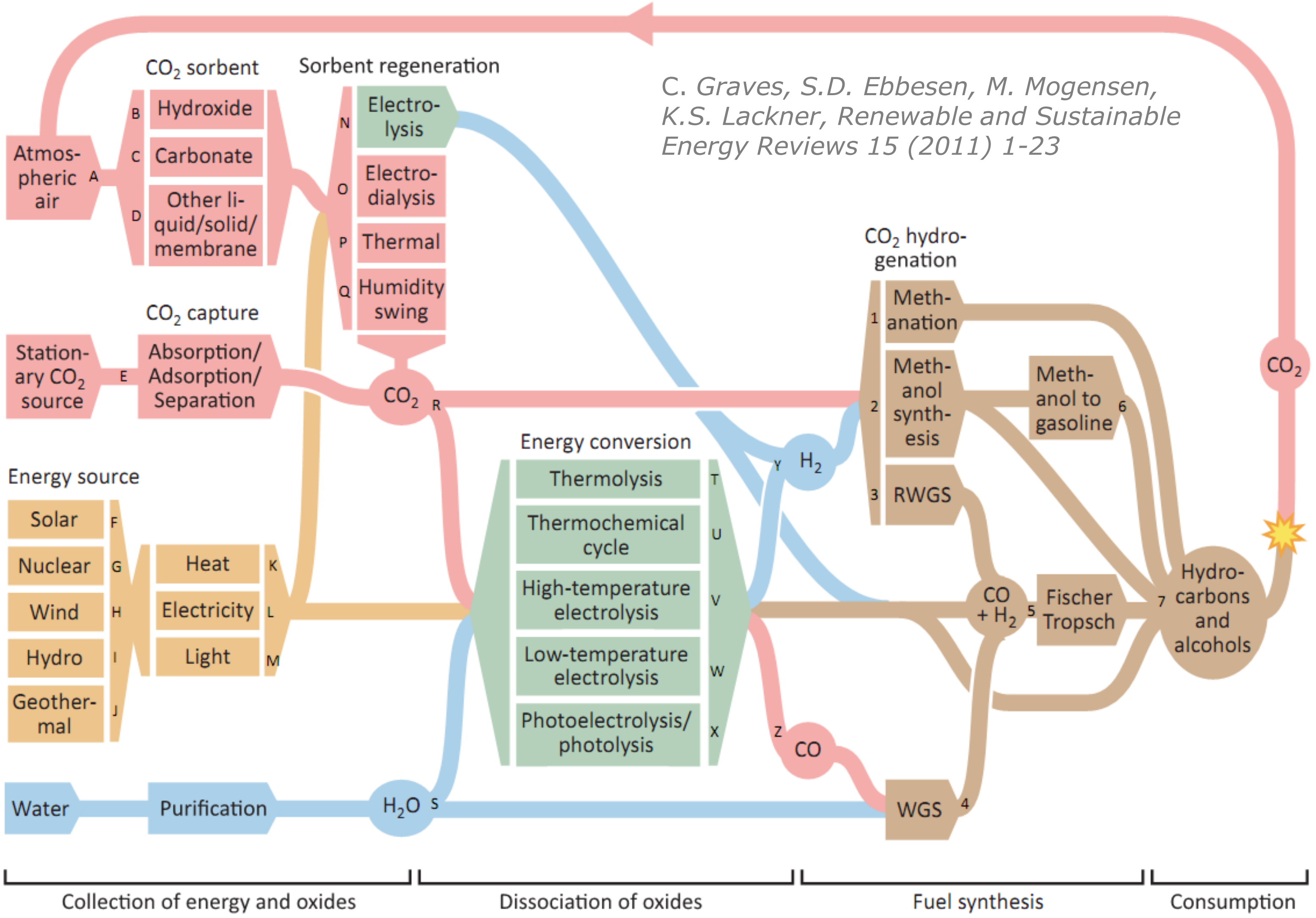
Reuse CO_2 once



Closed-loop cycle

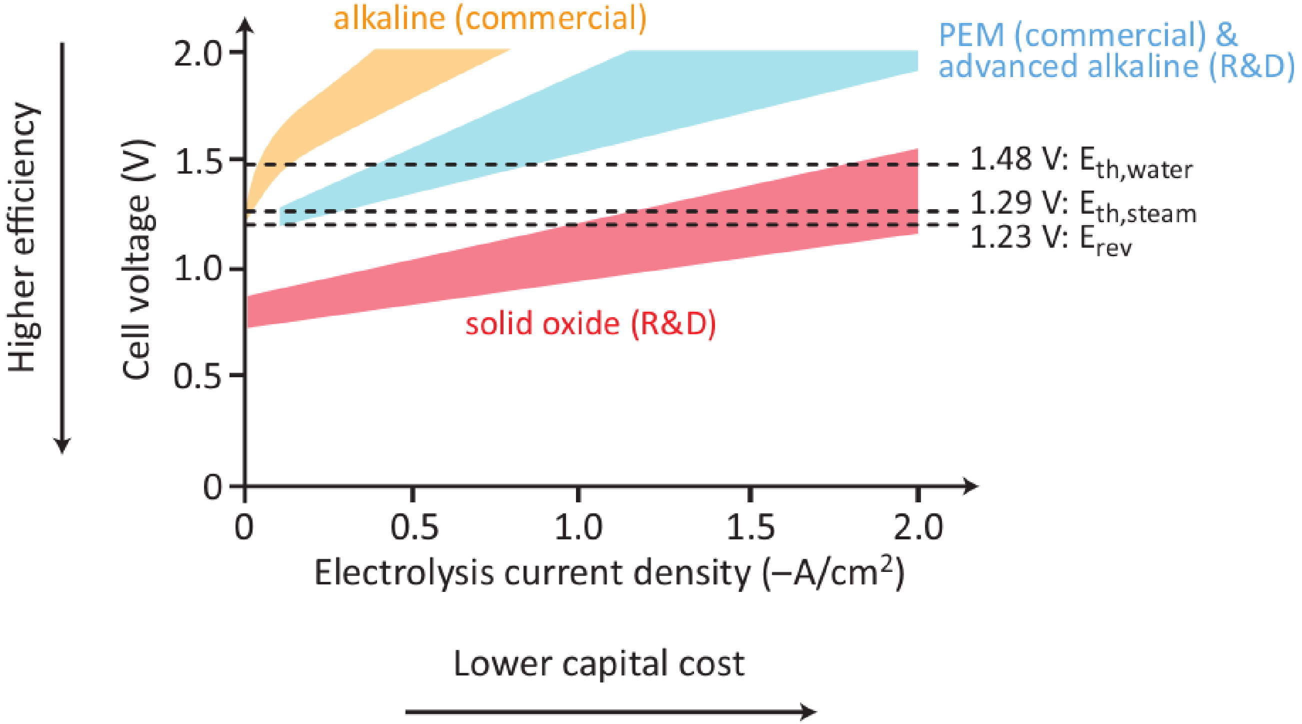
C. Graves, S.D. Ebbesen, M. Mogensen, K.S. Lackner, *Sustainable hydrocarbon fuels by recycling CO_2 and H_2O with renewable or nuclear energy*, Renewable and Sustainable Energy Reviews. 15 (2011) 1–23.

Possible methods to convert CO_2 to fuels



C. Graves, S.D. Ebbesen, M. Mogensen, K.S. Lackner, Renewable and Sustainable Energy Reviews 15 (2011) 1-23

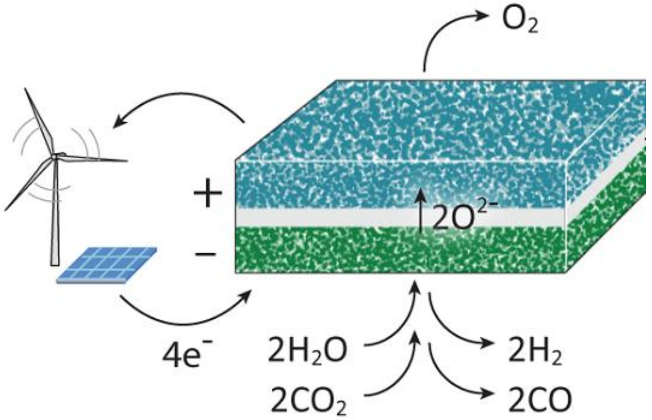
Electrolysis

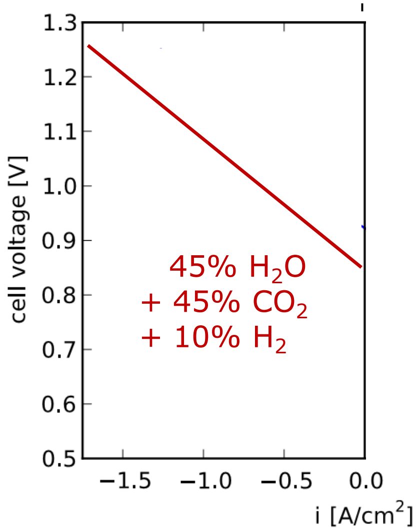


C. Graves, S.D. Ebbesen, M. Mogensen, K.S. Lackner, Renewable and Sustainable Energy Reviews 15 (2011) 1-23

Solid oxide electrochemical cells

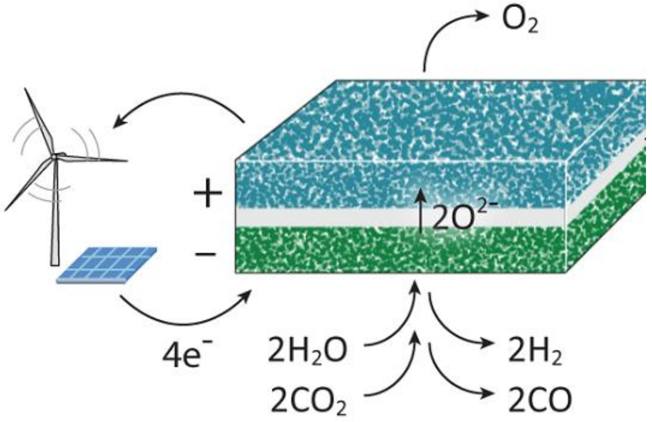
Electrolysis mode
electricity → fuels



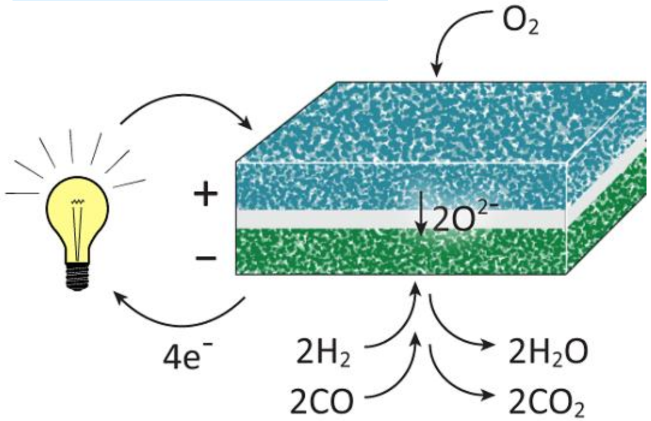


Solid oxide electrochemical cells

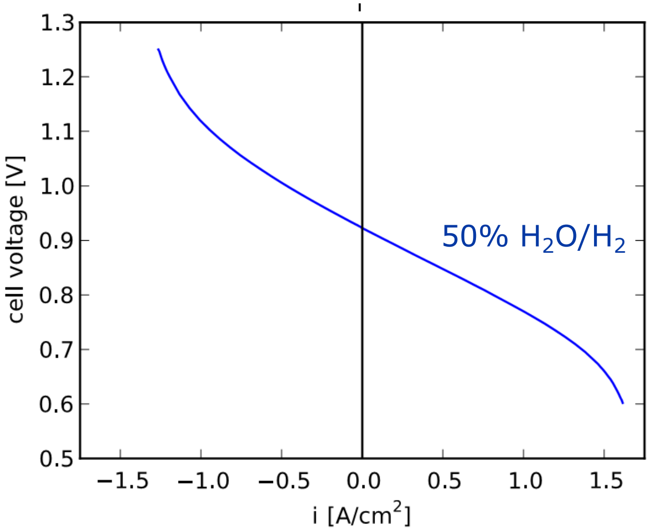
Electrolysis mode
electricity → fuels



Fuel cell mode
fuels → electricity



supply > demand



supply < demand

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Batteries, flow batteries, & reversible fuel cells

Battery

“A device consisting of one or more* electro-chemical cells that convert stored chemical energy into electrical energy” *– Merriam-Webster dictionary*

=

Galvanic/voltaic cell

“A simple device with which chemical energy is converted into electrical energy”

– Columbia Electronic Encyclopedia

*originally only >1

Rechargeable battery

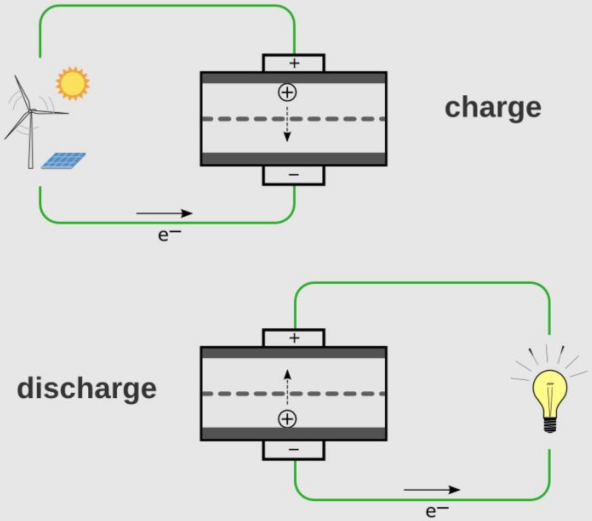
“acts as a galvanic cell when discharging (converting chemical energy to electrical energy), and an electrolytic cell when being charged (converting electrical energy to chemical energy).”

Flow batteries and reversible fuel cells

are special types of rechargeable batteries

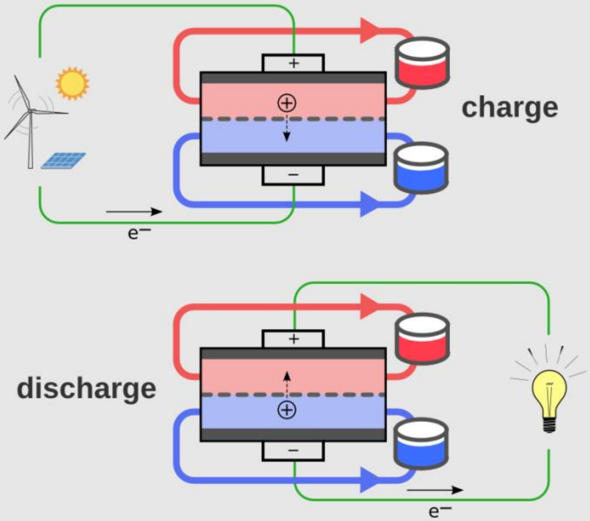
Batteries, flow batteries, & reversible fuel cells

Battery



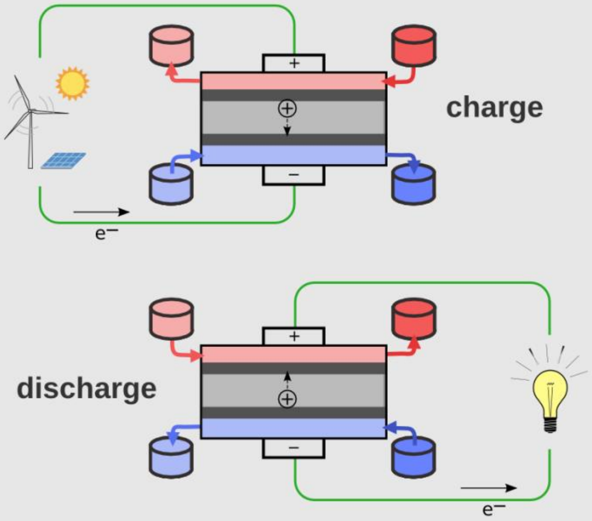
Energy stored in metal atoms on electrodes

Flow battery



Energy stored in metal atoms in reservoirs of electrolyte solutions, not on the electrodes
- **Separates energy and power density (capacity defined by size of reservoirs)**

Reversible fuel cell



Energy stored in hydrogen/carbon atoms in reservoirs, not in electrolyte or electrodes
- **Separates energy and power density (capacity defined by size of reservoirs)**
- **Less expensive material used to store energy**
- **Energy storage medium can be energy-dense liquid hydrocarbon fuels useable in existing infratructure**
- **Independent level of charging and discharging (e.g. can discharge more than, and before, charging)**

Examples:

Lithium-ion
Lead-acid
Sodium-sulfur
Nickel metal hydride
Nickel-cadmium
Metal-air (special case)

Examples:

Vanadium redox
Zinc-bromine
Iron-chromium
Bromine-polysulfide
Zinc-cerium
Lithium-ion

Examples:

H_2+O_2 / H_2O
H_2+Br_2 / HBr
NH_3+O_2 / N_2+H_2O
$CO+O_2$ / CO_2
CH_4+O_2 / CO_2+H_2O
CH_3OH+O_2 / CO_2+H_2O
$C+O_2$ / CO_2

Note: For each, the charge carrier in the electrolyte need not necessarily be a positive species. Examples: Li^+, Na^+, H^+, OH^-, O^{--}, CO_3^{--}

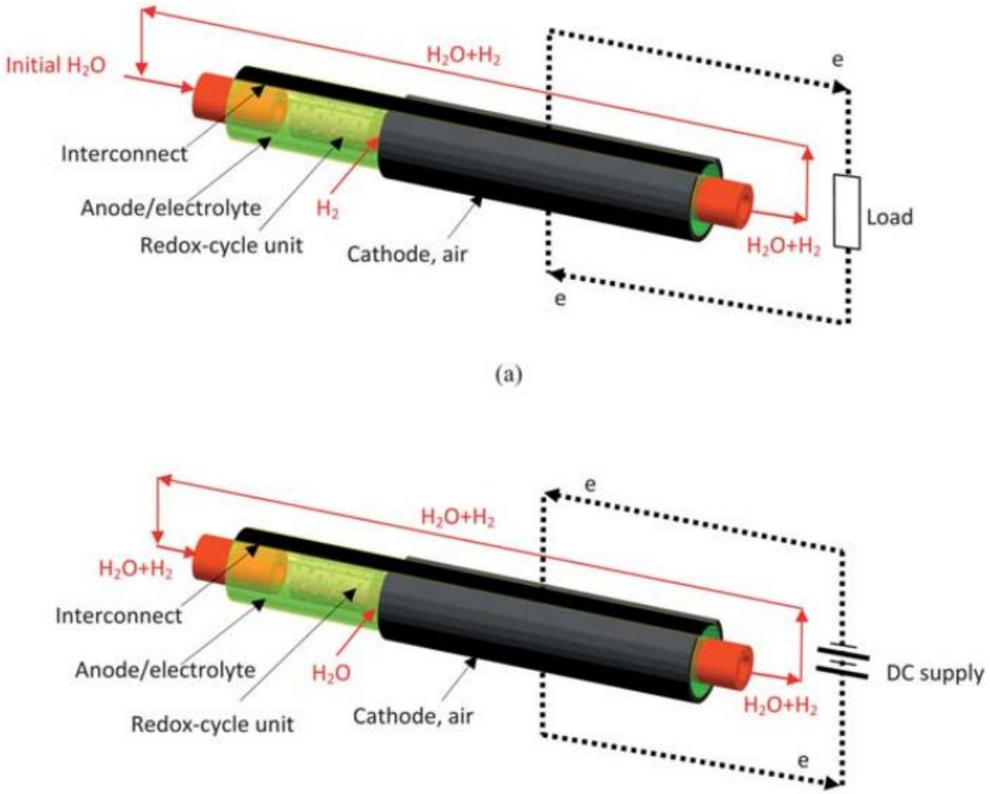
Batteries, flow batteries, & reversible fuel cells

- The main difference is **how the energy is stored**, which has important implications. Today, put numbers to those.
  - RFC stores electrical energy as fuels (such as H_2 and hydrocarbons) whereas a conventional battery stores energy in metal atoms (typically Pb, Ni, Li, V, etc.)
  - Certain types of RFCs such as solid oxide cells can produce/consume a wide variety of fuels including hydrocarbons which can be used in existing infrastructure – not only hydrogen, as in most low-T RFCs

- The **roundtrip electric-to-electric efficiency** of RFCs is typically perceived as too low, but there is no inherent reason. Today, numbers.
  - Redox chemistries besides $H_2O \rightarrow H_2 + O_2$ can match the near-100% maximum theoretical efficiency of some conventional batteries.
  - Also, inefficiency yields high-T (high-value) heat, which can be exported, or stored and re-utilized in the system

Batteries, flow batteries, & reversible fuel cells

Is this a reversible fuel cell or a battery?



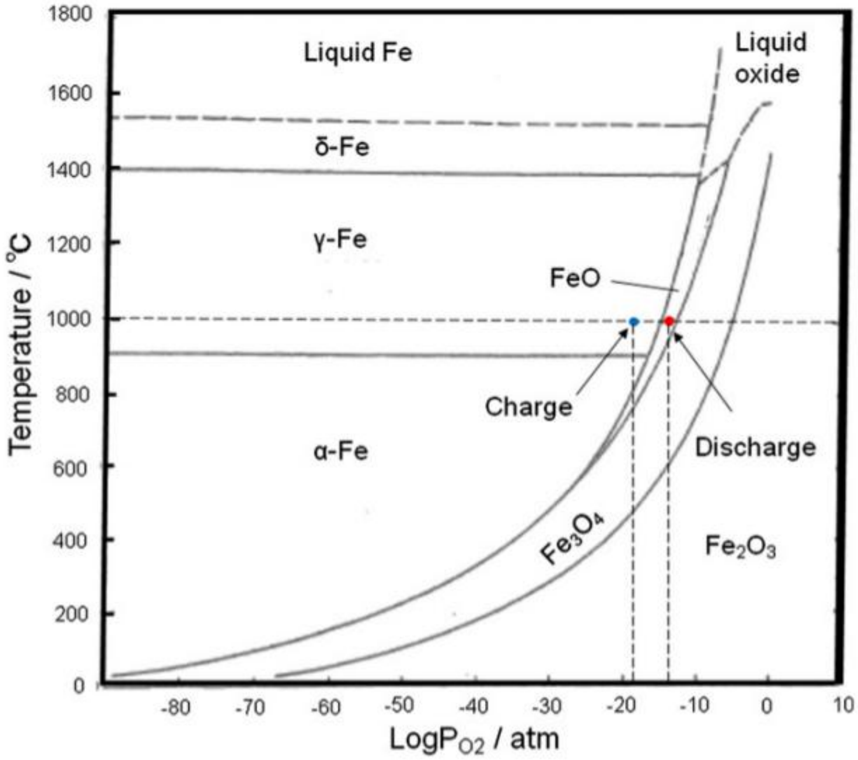


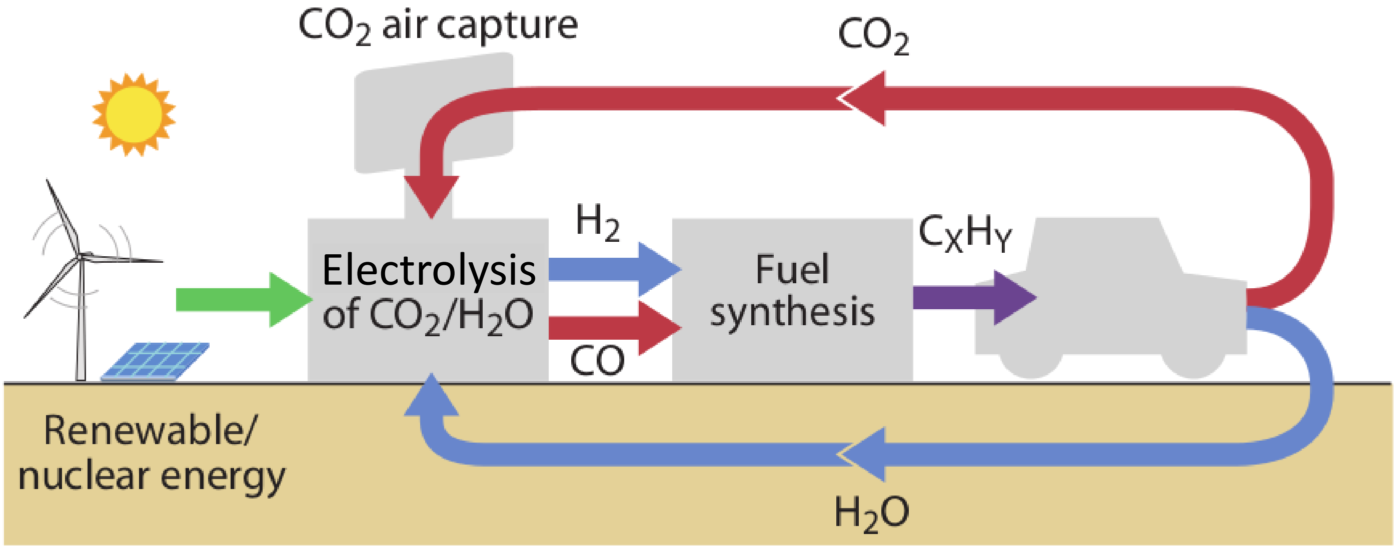
Fig. 4. Keringum diagram of Fe–O_2 and P_{O_2} in charge and discharge.

N. Xu, X. Li, X. Zhao, J.B. Goodenough, K. Huang, A novel solid oxide redox flow battery for grid energy storage, Energy Environ. Sci. 4 (2011) 4942–4946.

A. Inoishi, T. Ishihara, S. Ida, T. Okano, S. Uratani, High capacity of an Fe–Air rechargeable battery using LaGaO3-based oxide ion conductor as an electrolyte, Physical Chemistry Chemical Physics. (2012).

Batteries, flow batteries, & reversible fuel cells

- What about a battery-like system with the atmosphere/environment as a storage reservoir? And one device charges while another discharges?



charge discharge

To even further complicate it, we consider operating profiles for balancing the entire energy system where the first device charges+discharges with *net* charging (for transport fuel production)…

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Possible redox chemistries

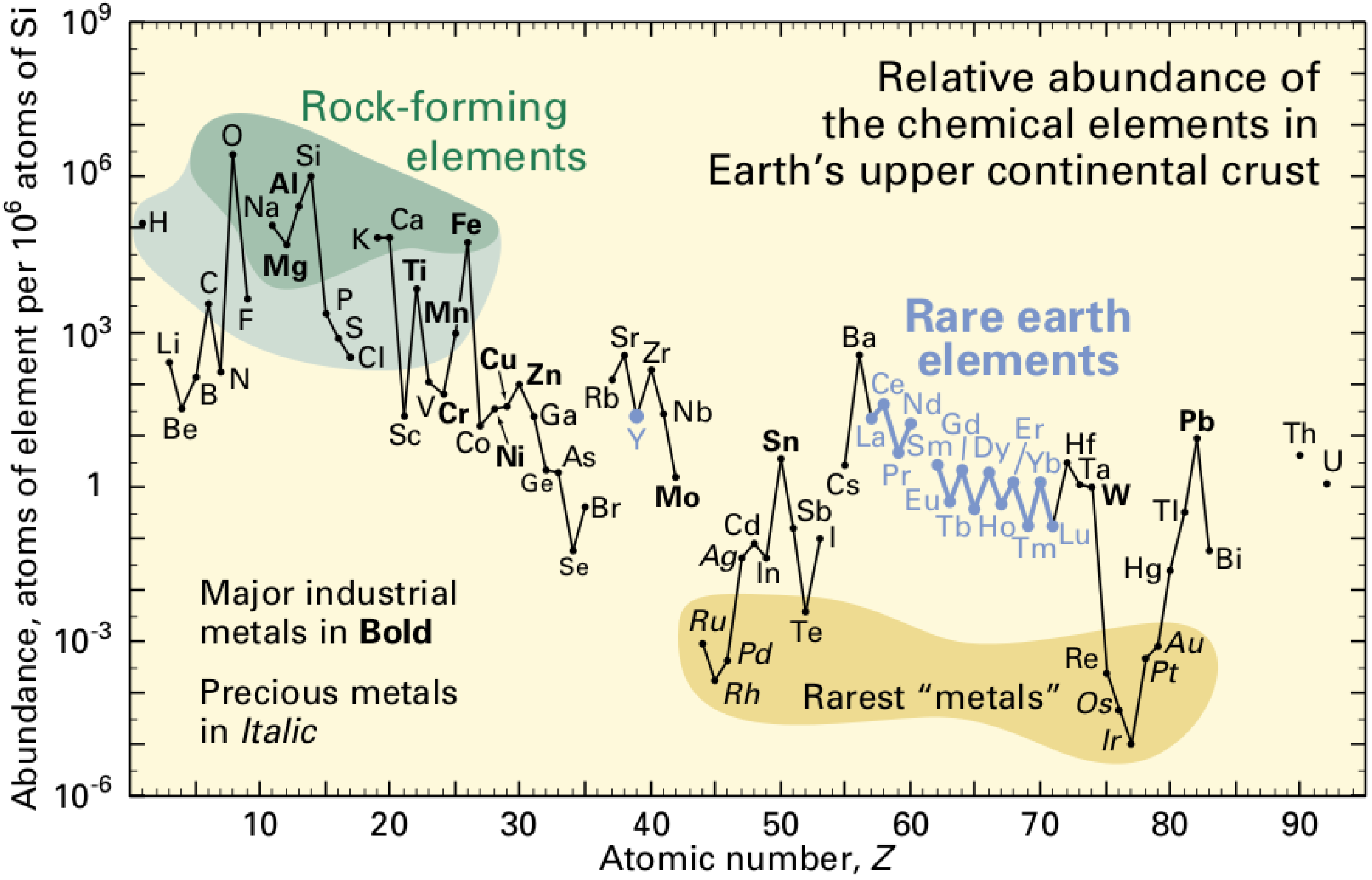
- Selecting from the entire periodic table is possible…
  - A recent study examined the theoretical energy density of 1172 possible redox chemistries for batteries.

Zu, C.X., Li, H., 2011. Thermodynamic analysis on energy density of batteries. Energy and Environmental Science 4, 2614–2624.

- The point of using RFCs as batteries is to use common fuels or elements; to avoid tying up expensive metals

http://pubs.usgs.gov/fs/2002/fs087-02/

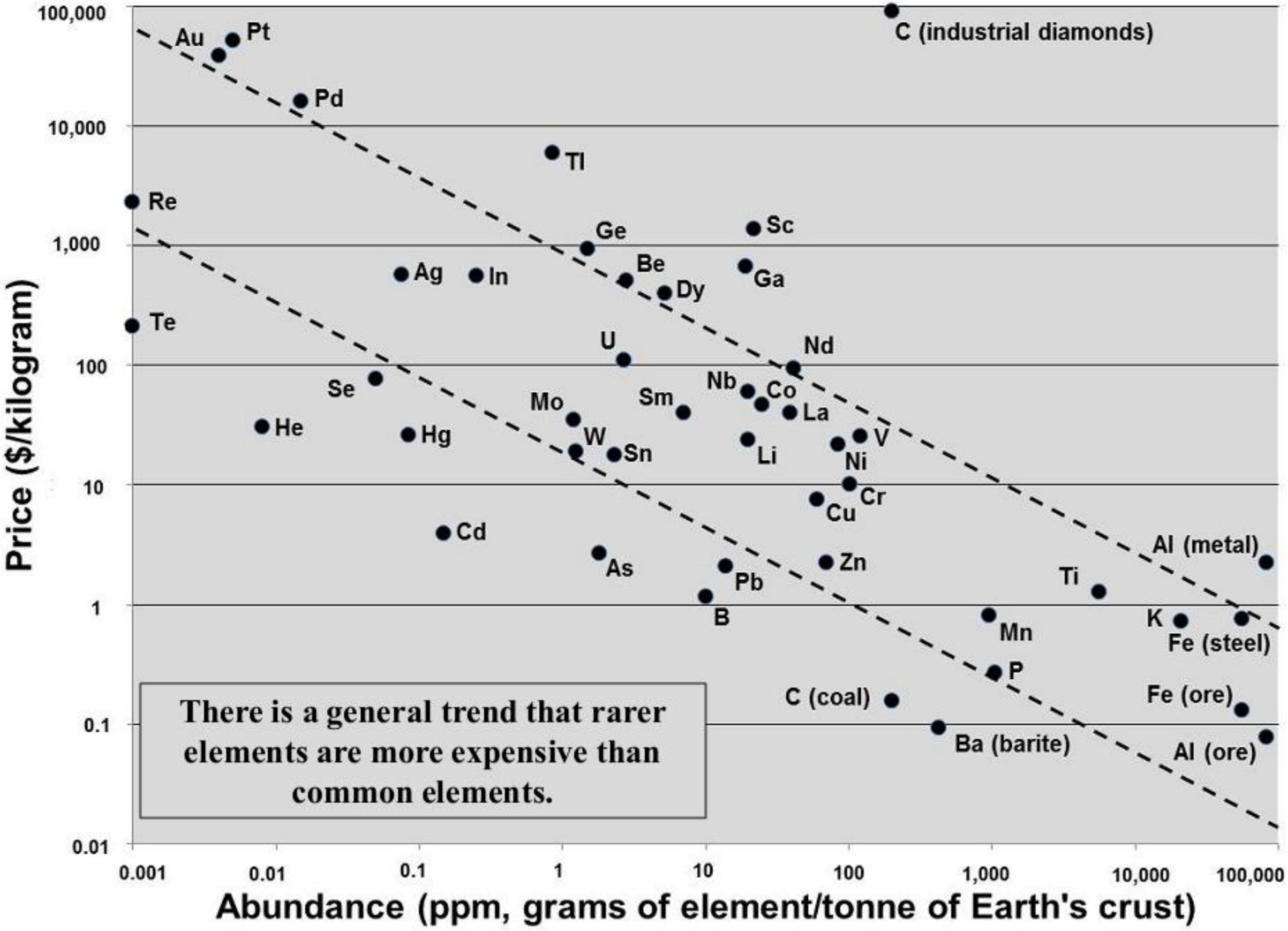
Possible redox chemistries – abundance



http://pubs.usgs.gov/fs/2002/fs087-02/

Possible redox chemistries – abundance & cost

Raw materials costs and abundance



There is a general trend that rarer elements are more expensive than common elements.

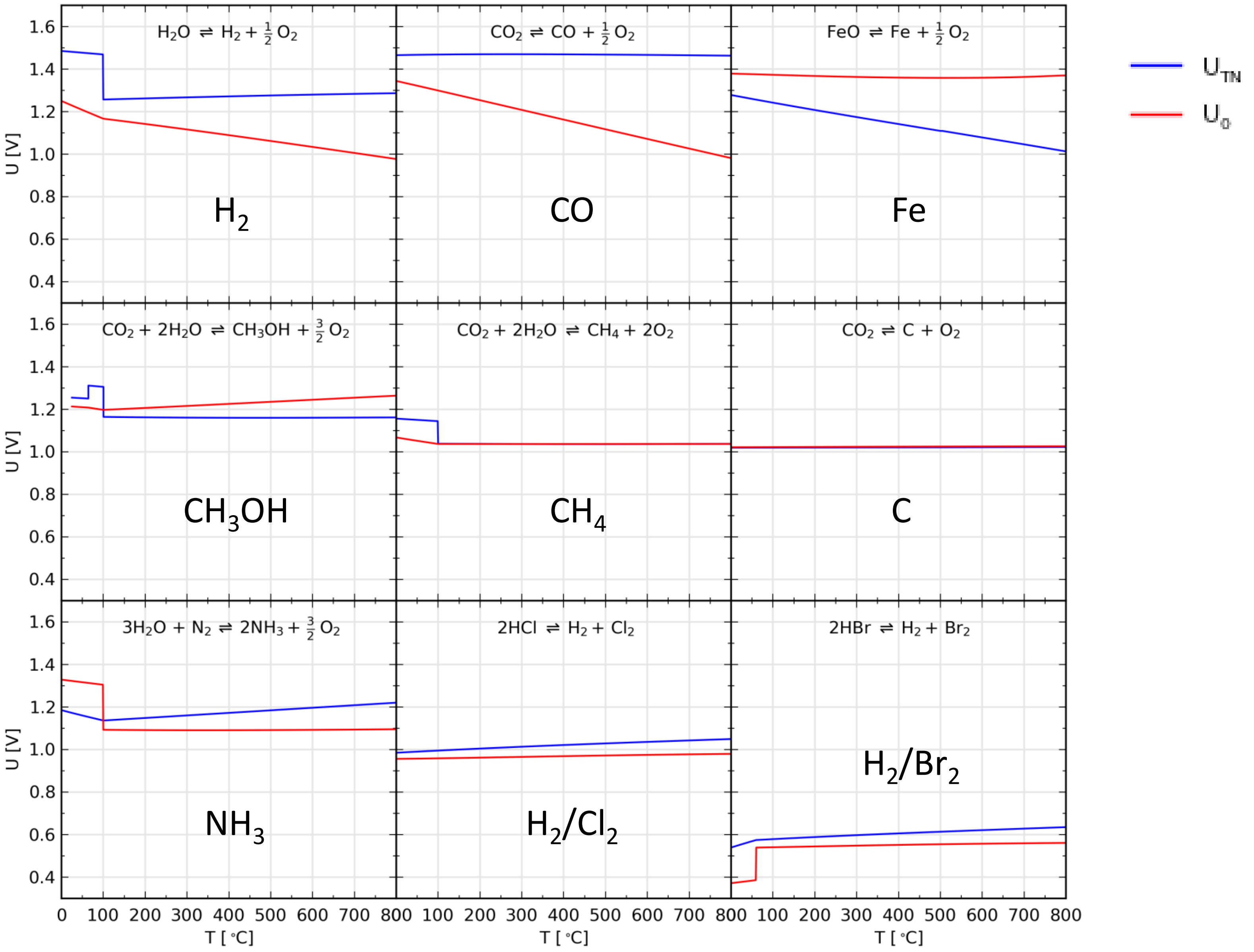
Source of figure: R Jaffe & J Price, 2011, APS reports on Energy Critical Elements
Their Source of data: USGS, EIA, CRC Handbook of Chemistry and Physics, others

Possible redox chemistries

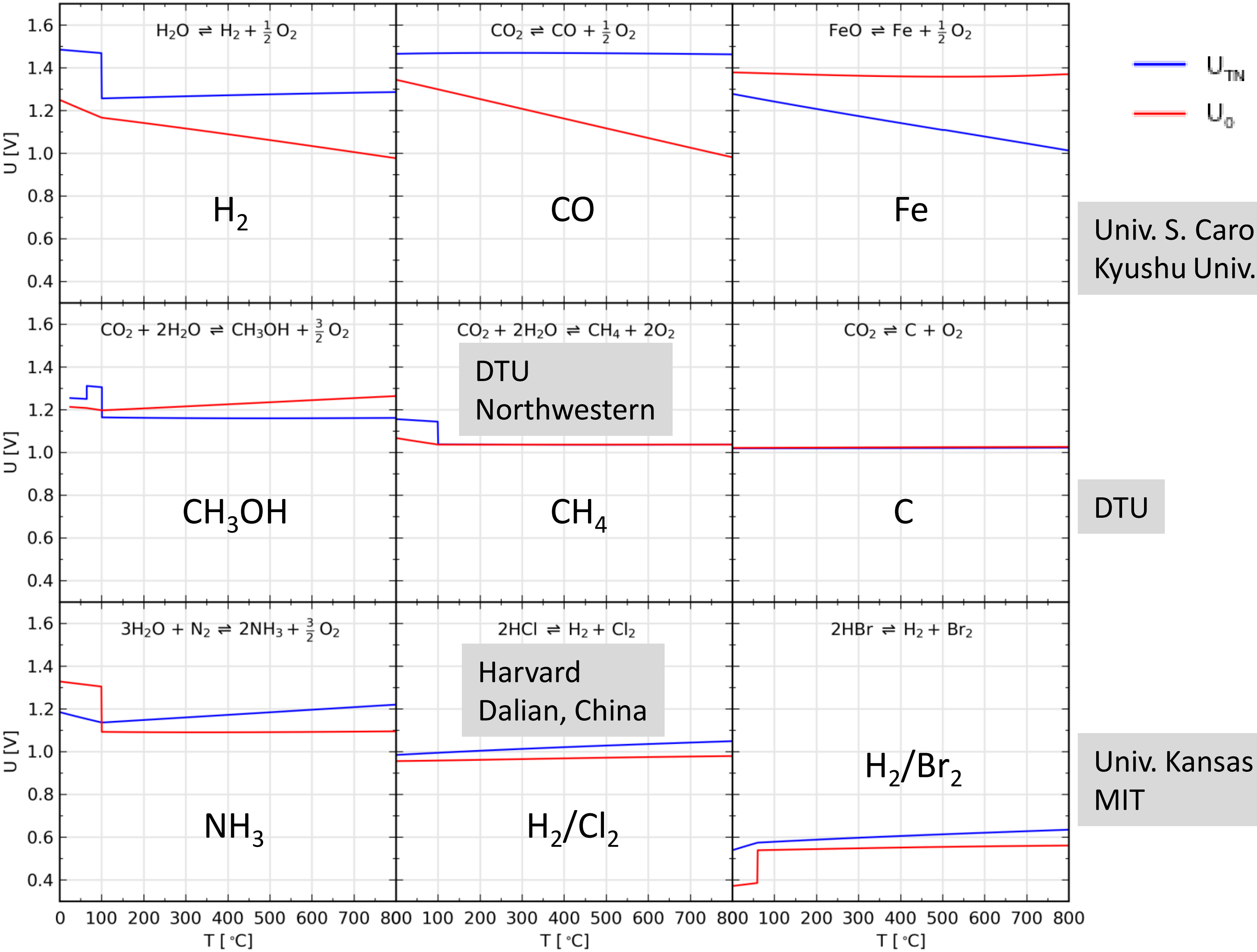
- Most abundant elements include H, C, Fe, Na, Si, Al, Ca
- Besides low cost, they are also the lightest → high energy density
- Focus first on H and C

H_2	CO
CH_4	C

Possible redox chemistries - thermodynamics



Possible redox chemistries - thermodynamics



DTU
Northwestern

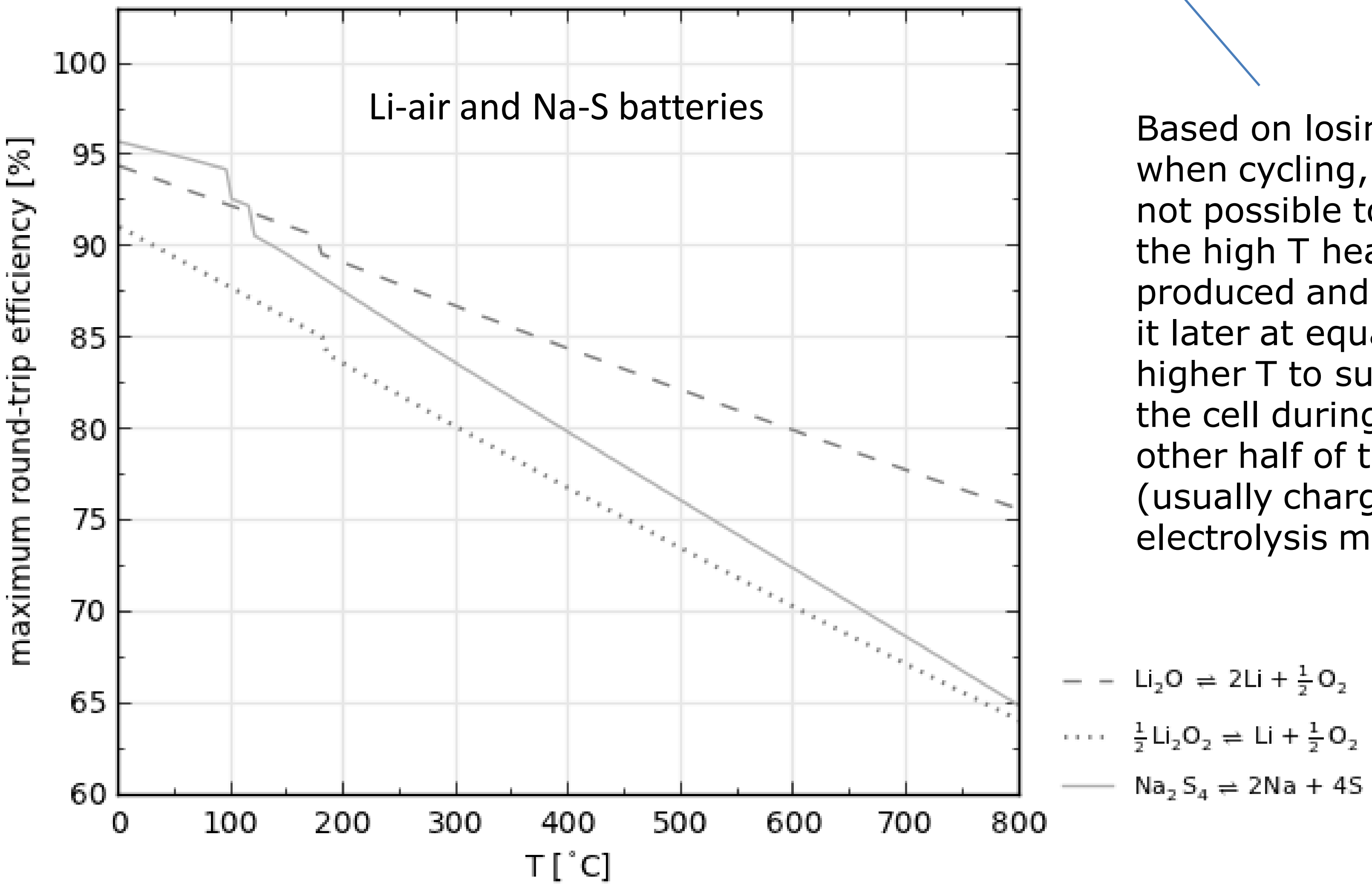
Harvard
Dalian, China

Univ. S. Carolina
Kyushu Univ.

DTU

Univ. Kansas
MIT

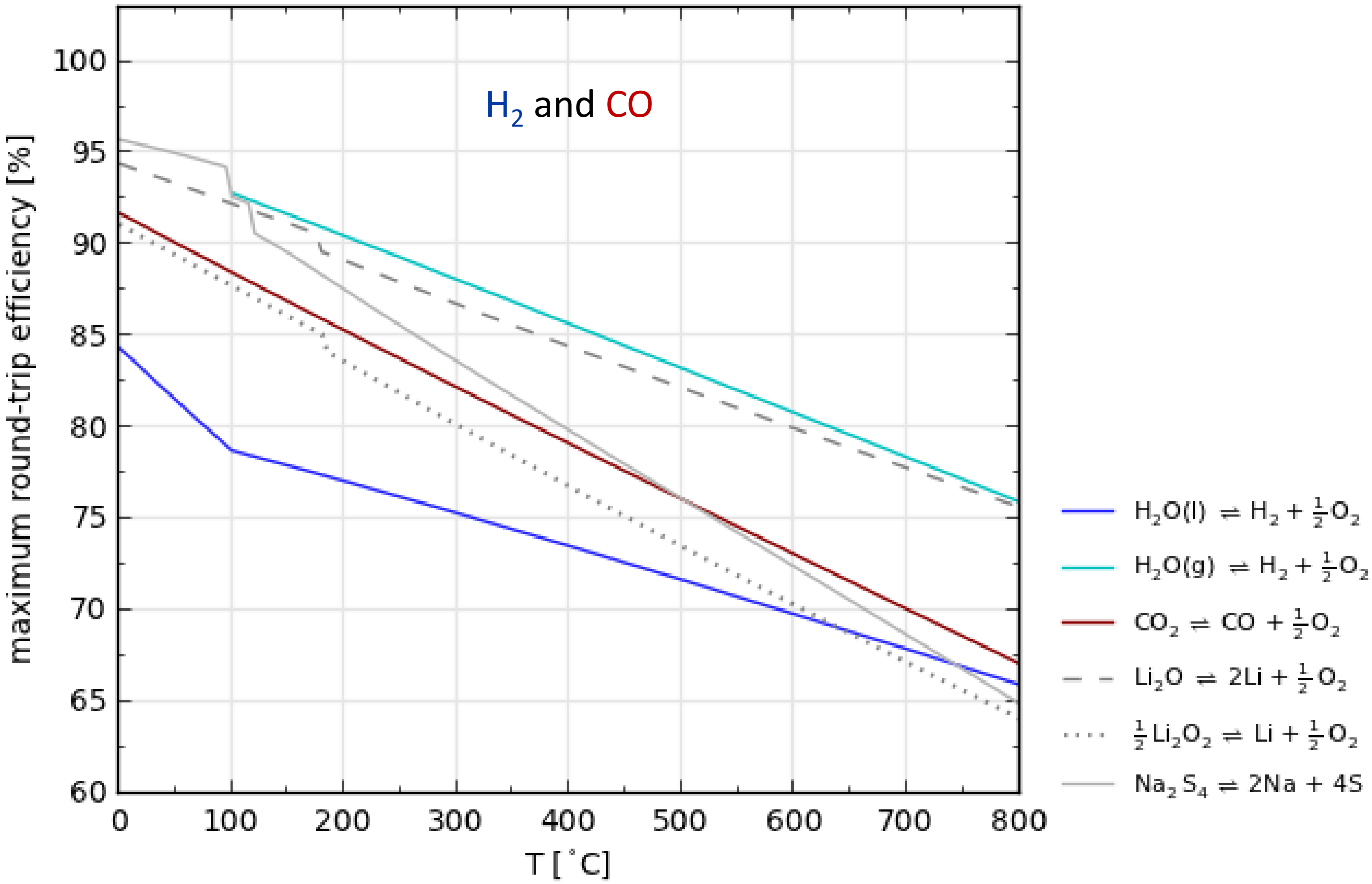
Possible redox chemistries – max. roundtrip efficiencies



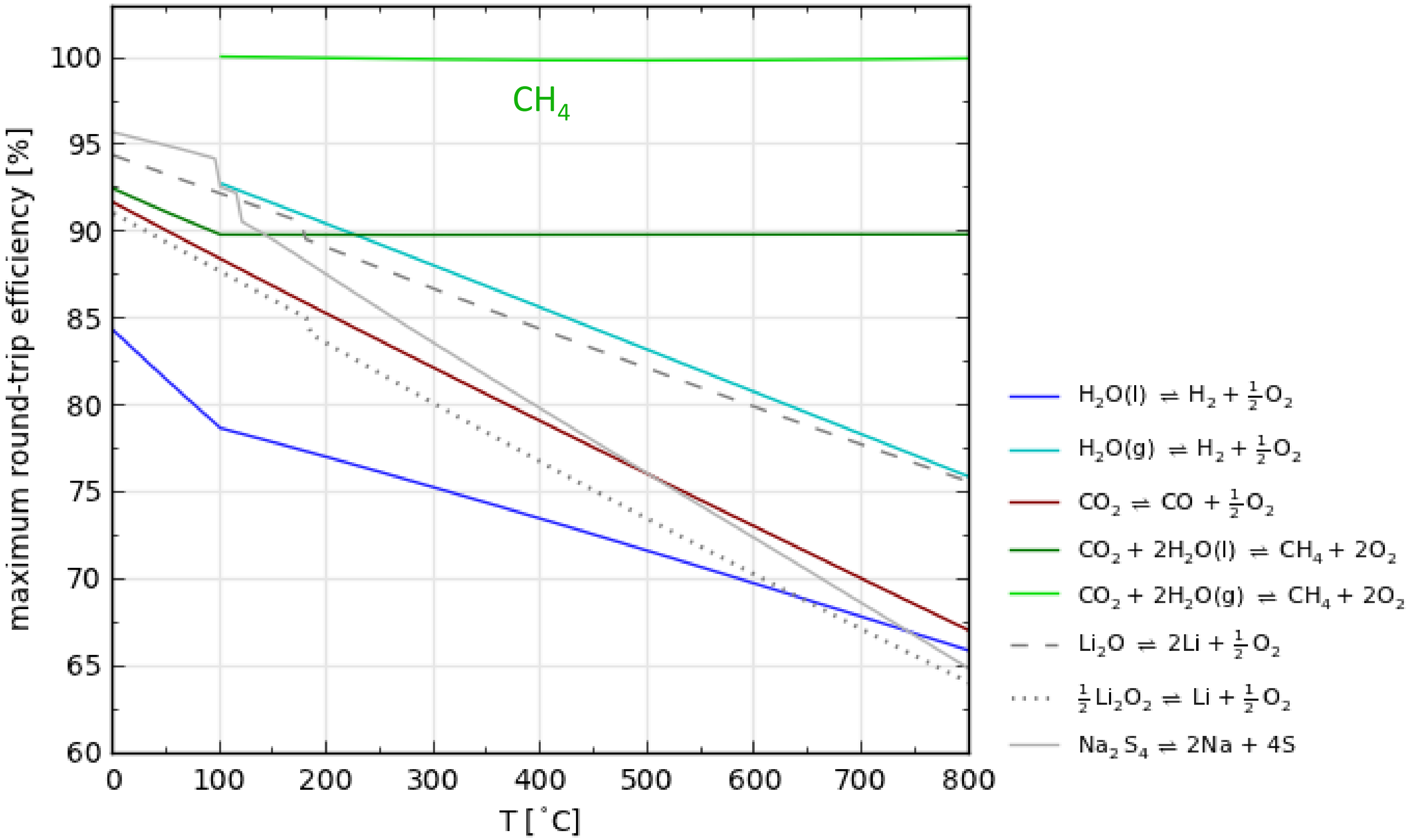
Li-air and Na-S batteries

Based on losing T∆S when cycling, e.g. it is not possible to store the high T heat that is produced and recover it later at equal or higher T to supply to the cell during the other half of the cycle (usually charge/ electrolysis mode).

Possible redox chemistries – max. roundtrip efficiencies



Possible redox chemistries – max. roundtrip efficiencies



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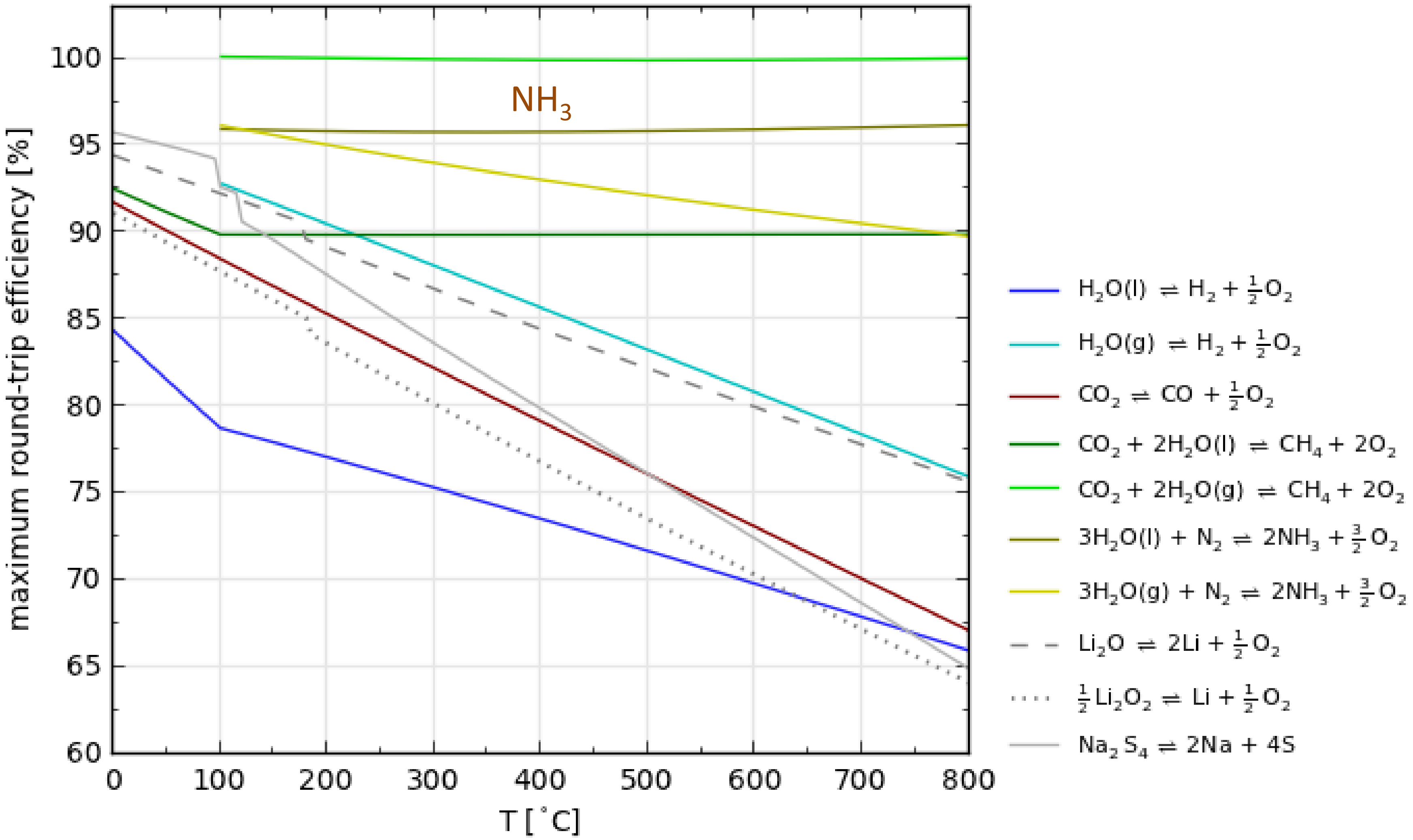
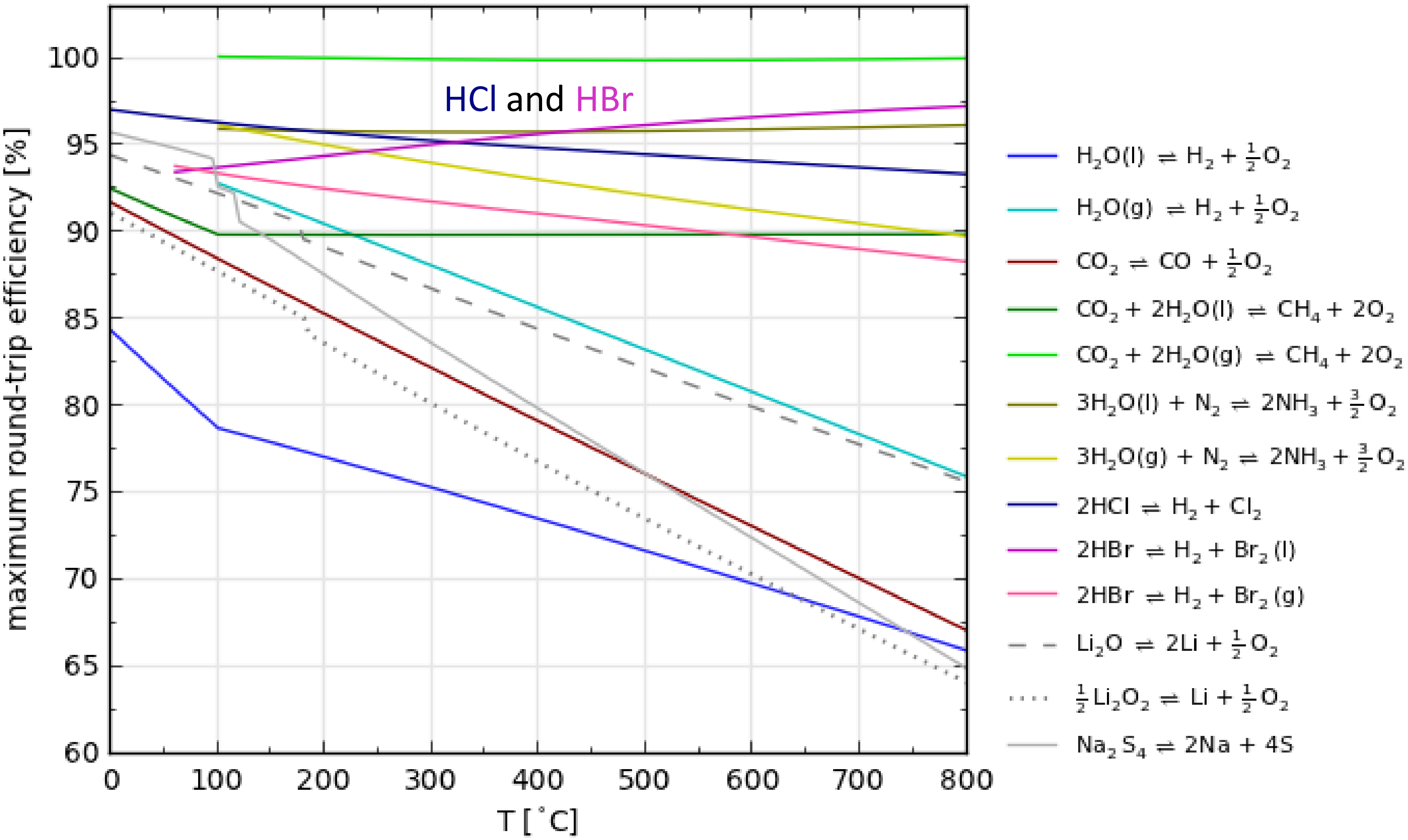
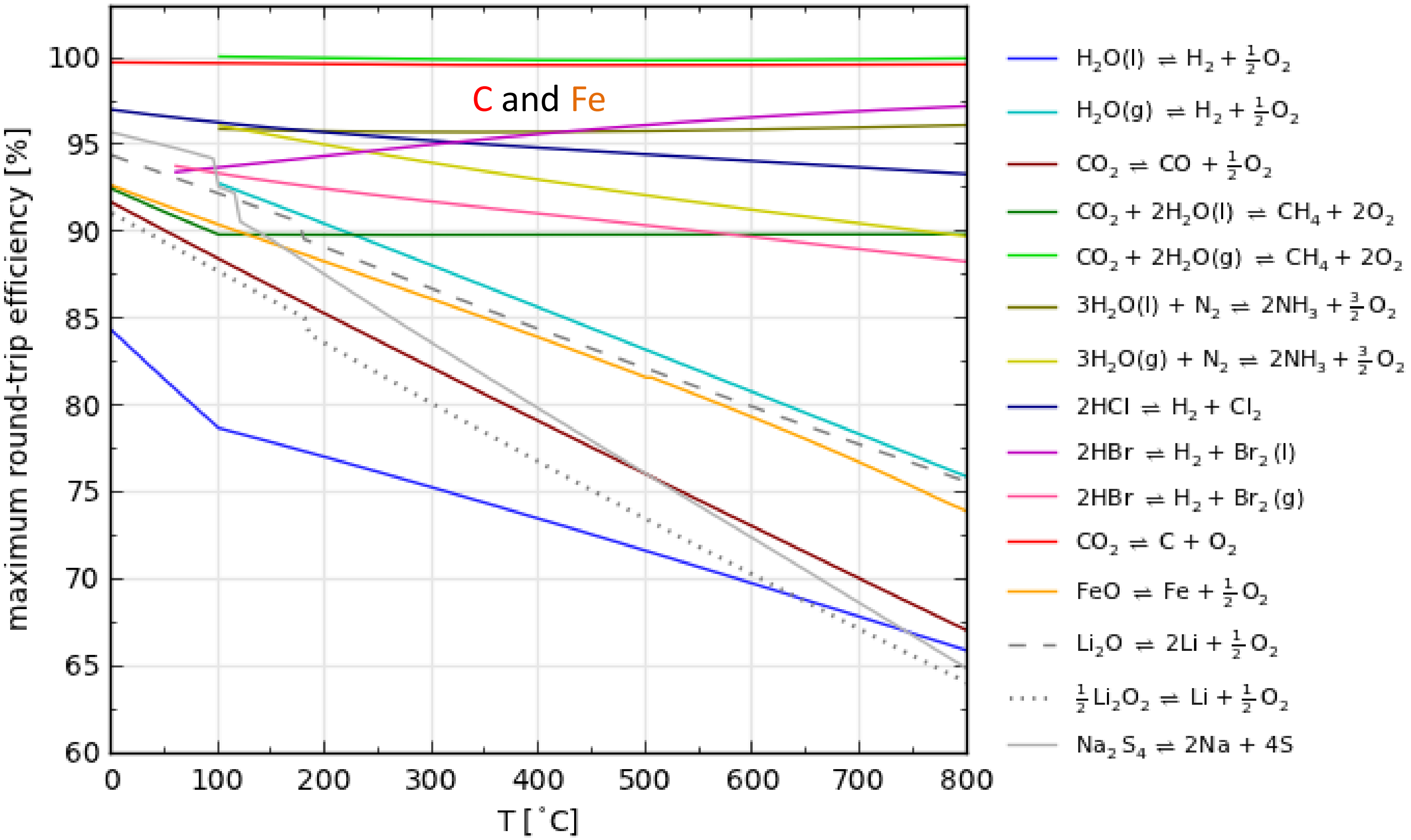


Possible redox chemistries – max. roundtrip efficiencies



HCl and HBr

Possible redox chemistries – max. roundtrip efficiencies



C and Fe

Efficiency

- Maximum theoretical efficiency $\rightarrow$ practical efficiency ε
  - Overpotentials η to actually produce current
  - Heat losses
  - Energy consumed by balance of system

Efficiency

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- Example: H_2 vs CH_4 at 600 °C
  - $\eta = 0.1$ V for all cells (e.g. 0.5 A/cm^2 x 0.2 Ω cm^2) plus voltage drop due to gas conversion, 90% reactant utilization for both charge (electrolysis) and discharge (fuel-cell mode) (ignoring possible C deposition),
    gives $\varepsilon(H_2) = 69\%$ and $\varepsilon(CH_4) = 86\%$. + Heat and system losses ~10-20%.

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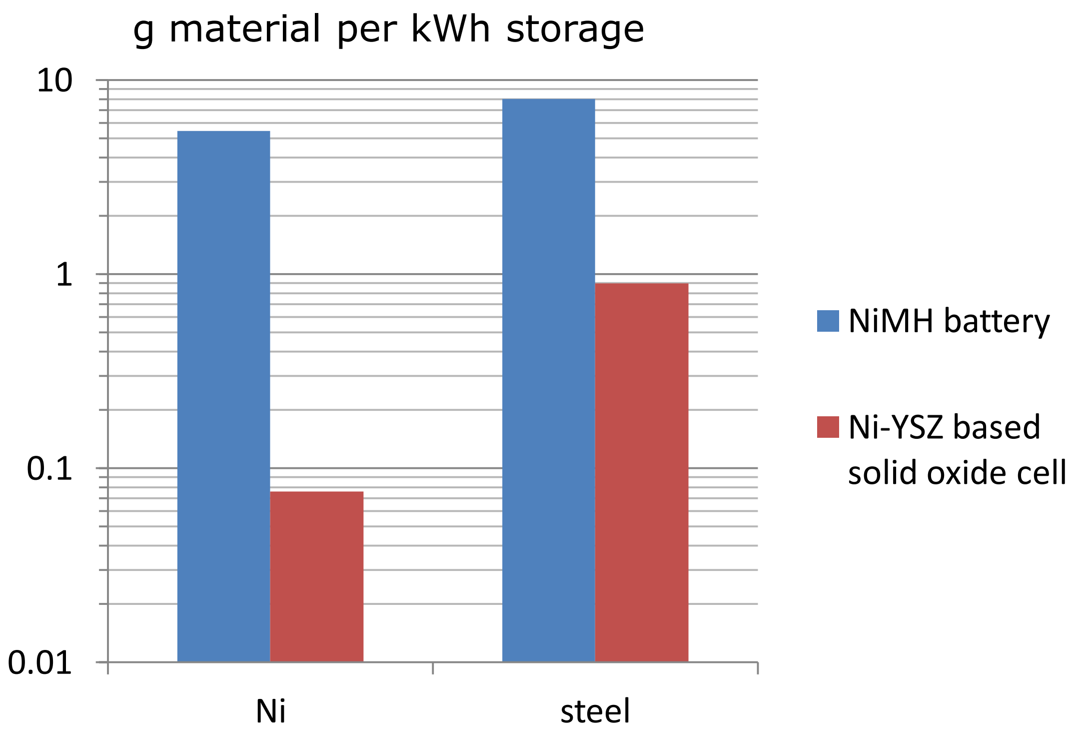
    gives $\varepsilon(H_2) = 69\%$ and $\varepsilon(CH_4) = 86\%$. + Heat and system losses ~10-20%.
  - However, the difference could become smaller or larger depending on the required operating profile:
    For example, energy balancing an intermittent renewable energy source which has a low 20-30% capacity factor requires operating at higher electrolysis current density for a shorter time than in fuel-cell mode, which can lower $\varepsilon(CH_4)$ because both modes are exothermic, but it does not affect $\varepsilon(H_2)$ until electrolysis operation rises above thermoneutral.

Resource Use

- Amount of material tied up in a kWh of stored electricity

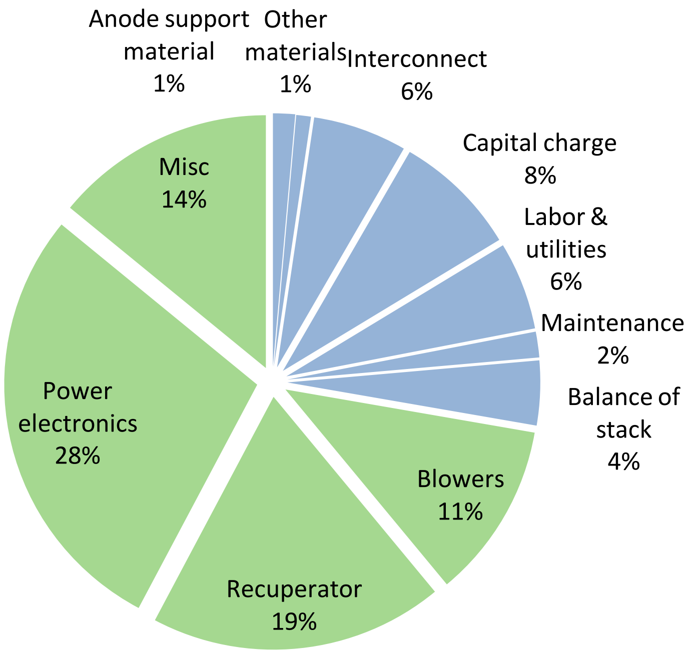
  → Cost, Sustainability, Ability to scale-up (and toxicity)



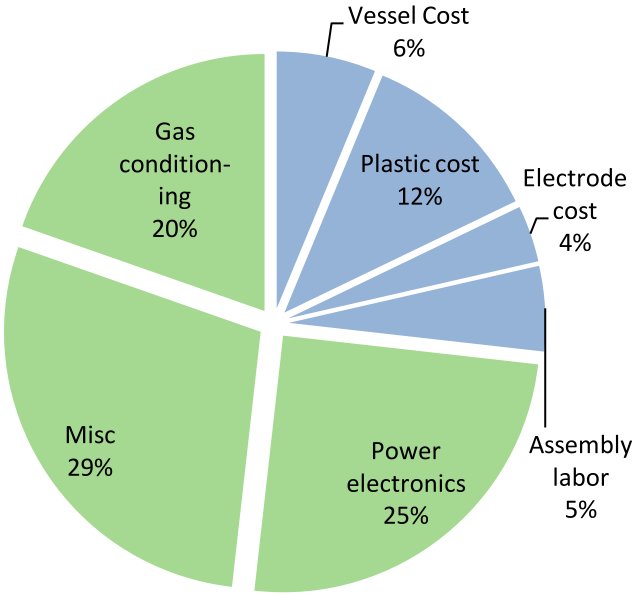
- Similar magnitudes of Li+Co for Li-ion and Pb for Pb-acid batteries
- Using life cycle analysis from literature and device lifetimes
  - NiMH battery 2000 cycles at 50% DOD; SOC 5-yr (1800 daily cycles)

Economics – capital cost breakdowns ($/kW)

Solid oxide cell



Alkaline fuel/electrolysis cell



Balance of system dominates!

An issue with flow systems? Compared with self-contained batteries…

Data collected from:

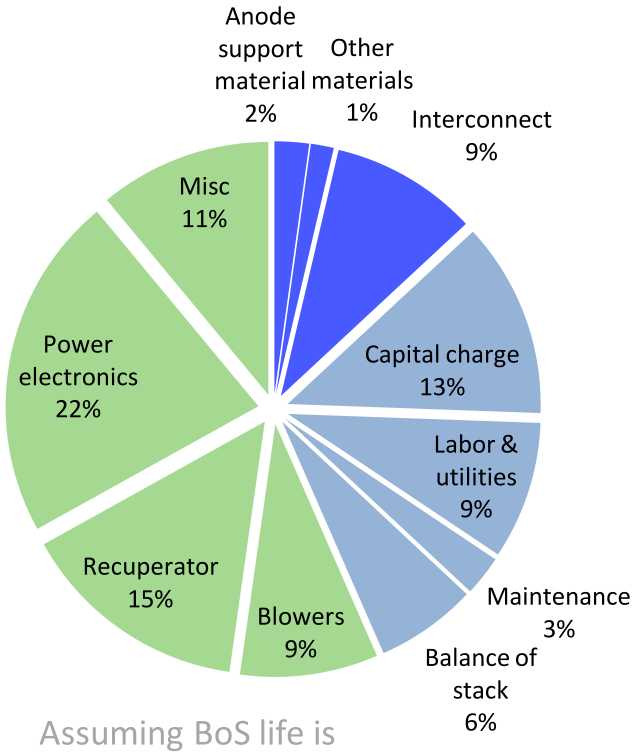
Saur (2008) NREL technical report - Wind-To-Hydrogen Project- Electrolyzer Capital Cost Study

Thijssen, Jan. The Impact of Scale-Up and Production Volume on SOFC Manufacturing Cost. J. Thijssen, LLC. Prepared for National Energy Technology Laboratory, U.S. DOE, A pril 2, 2007.

Thijssen, Jan, and W. A. Surdoval. “Stack Operating Strategies for Central Station SOFC” presented at the 2009 Fuel Cell Seminar, Palm Springs, California, November 16, 2009.

Economics – capital cost breakdowns ($/kWh)

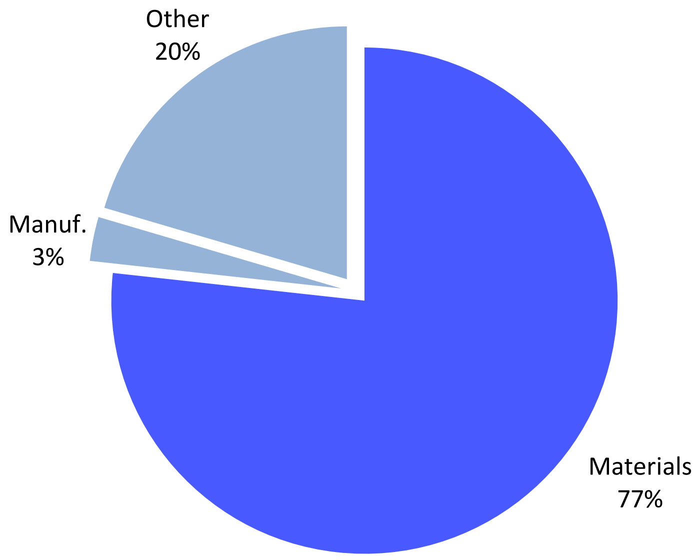
Solid oxide cell



Assuming BoS life is 2x that of stack.

Li-ion battery

D. Anderson, An Evaluation of Current and Future Costs for Lithium-Ion Batteries for Use in Electrified Vehicle Powertrains, (2009).



Opposite!

Li-ion mass production is optimized and cost reduction potential is relatively limited

Simple economics estimations

Battery	**CAPEX (U.S. cents/kWh elec)**	**Notes**
Pb-acid	15 – 40	# cycles (700-1800), DOD
Li-ion	5 – 17	# cycles (1000-8500), DOD
NiMH	15 – 20	# cycles (1000-3000), DOD
V redox	16	10 000 cycles
SOC	1.5 – 9	5-10 yr, $500-2000/kW

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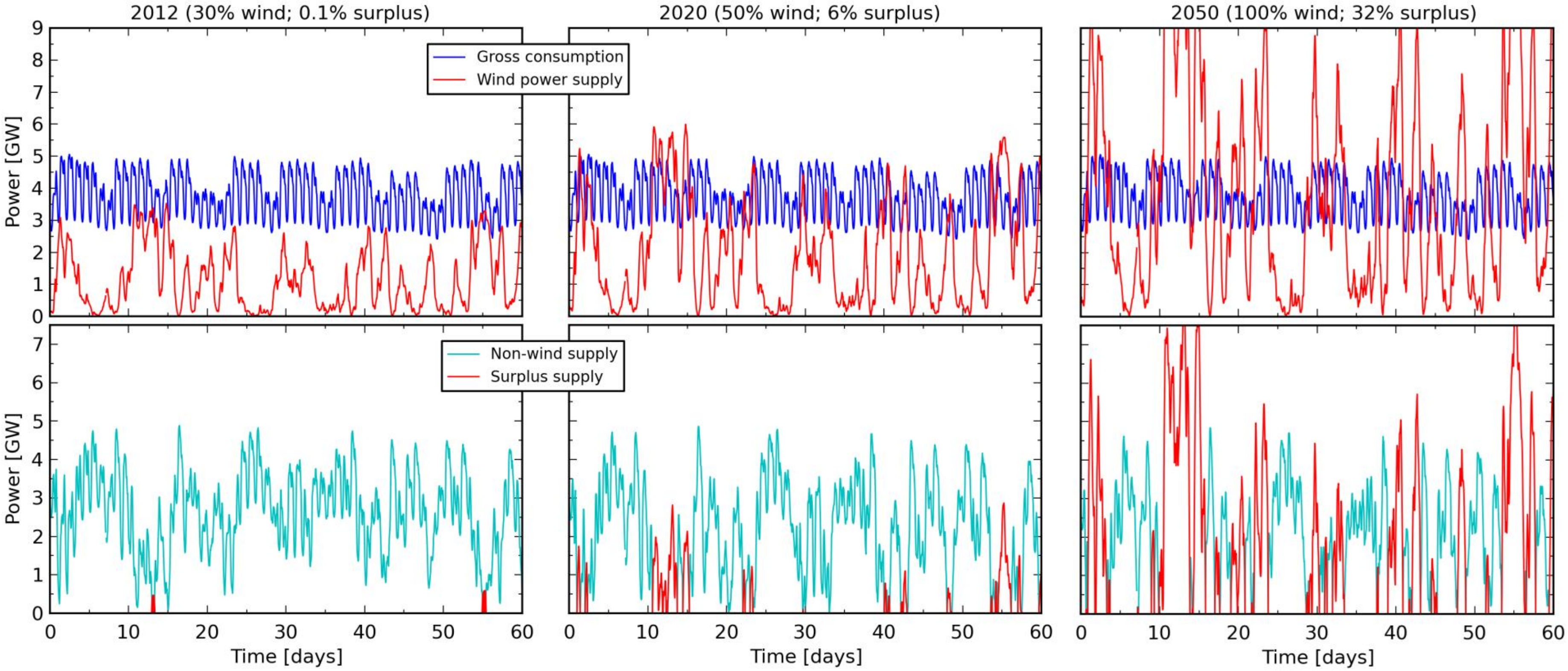
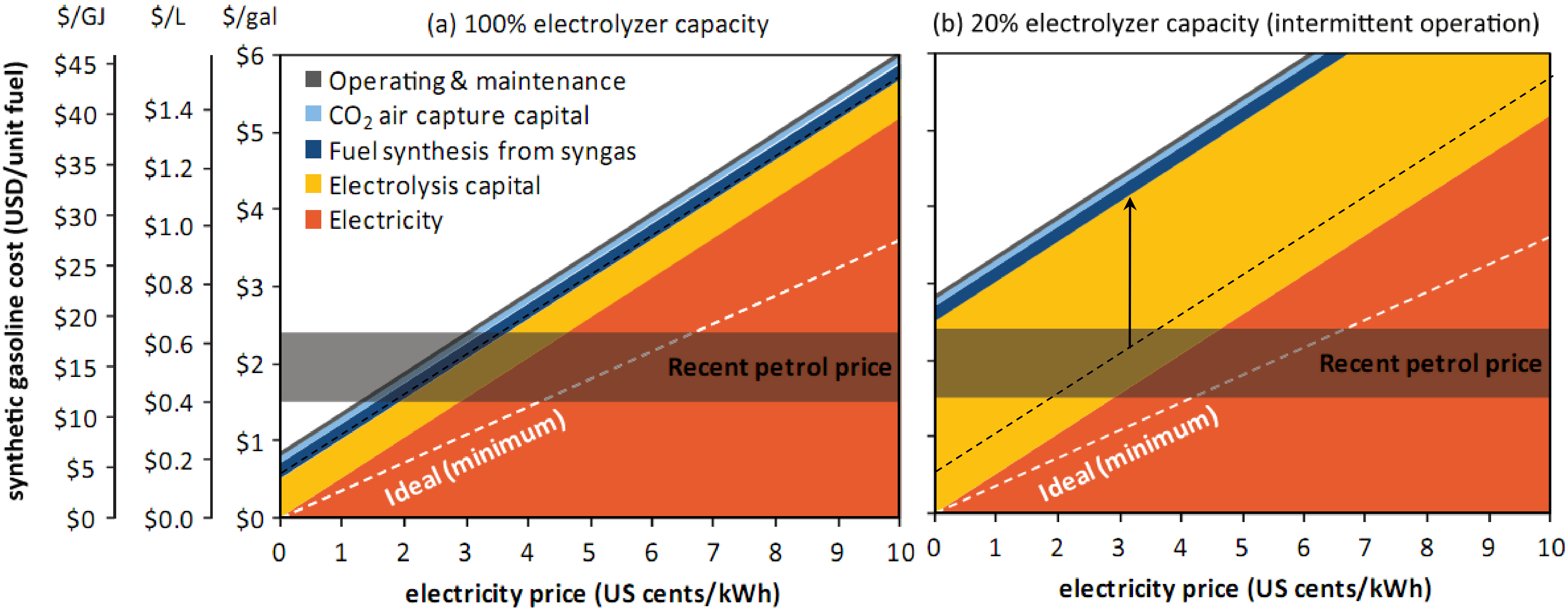


4% storage capacity factor

13% storage capacity factor

Electrolytic CO_2-to-fuels economics



C. Graves, S.D. Ebbesen, M. Mogensen, K.S. Lackner, *Sustainable hydrocarbon fuels by recycling CO_2 and H_2O with renewable or nuclear energy*, Renewable and Sustainable Energy Reviews. 15 (2011) 1–23.

Reversible fuel cell capacity factor

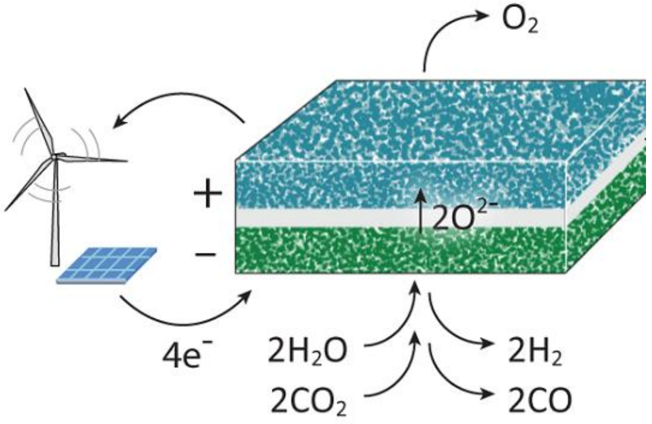
All 3 types of devices buy electricity when the price is low, and sell:

	Sell electricity (spot market arbitrage)	**Sell fuel (e.g. transportation)**
Battery	X	
Electrolyser		X
Reversible fuel cell	X	X

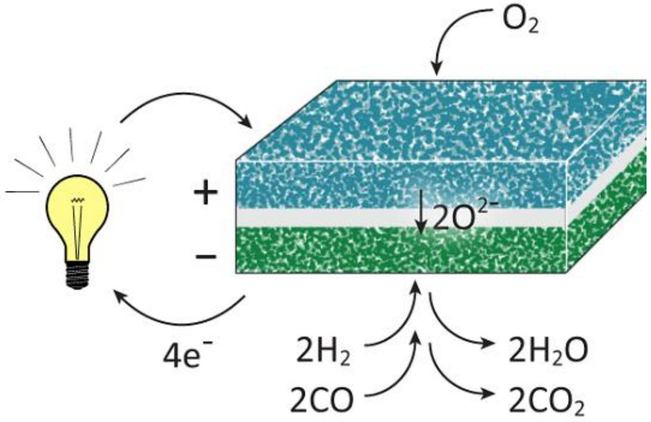
Also, in order to keep a high-temperature electrolyser hot,
one may run it in fuel-cell mode anyway during idle periods,
thereby having the ability to operate as RFC…

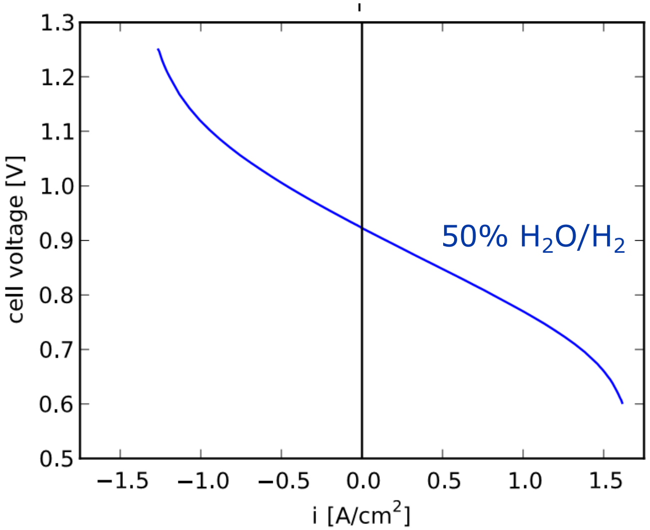
Lifetime of reversible solid oxide cells

Electrolysis mode
electricity → fuels



Fuel cell mode
fuels → electricity





Cell type: most common Ni–YSZ | YSZ | LSM–YSZ

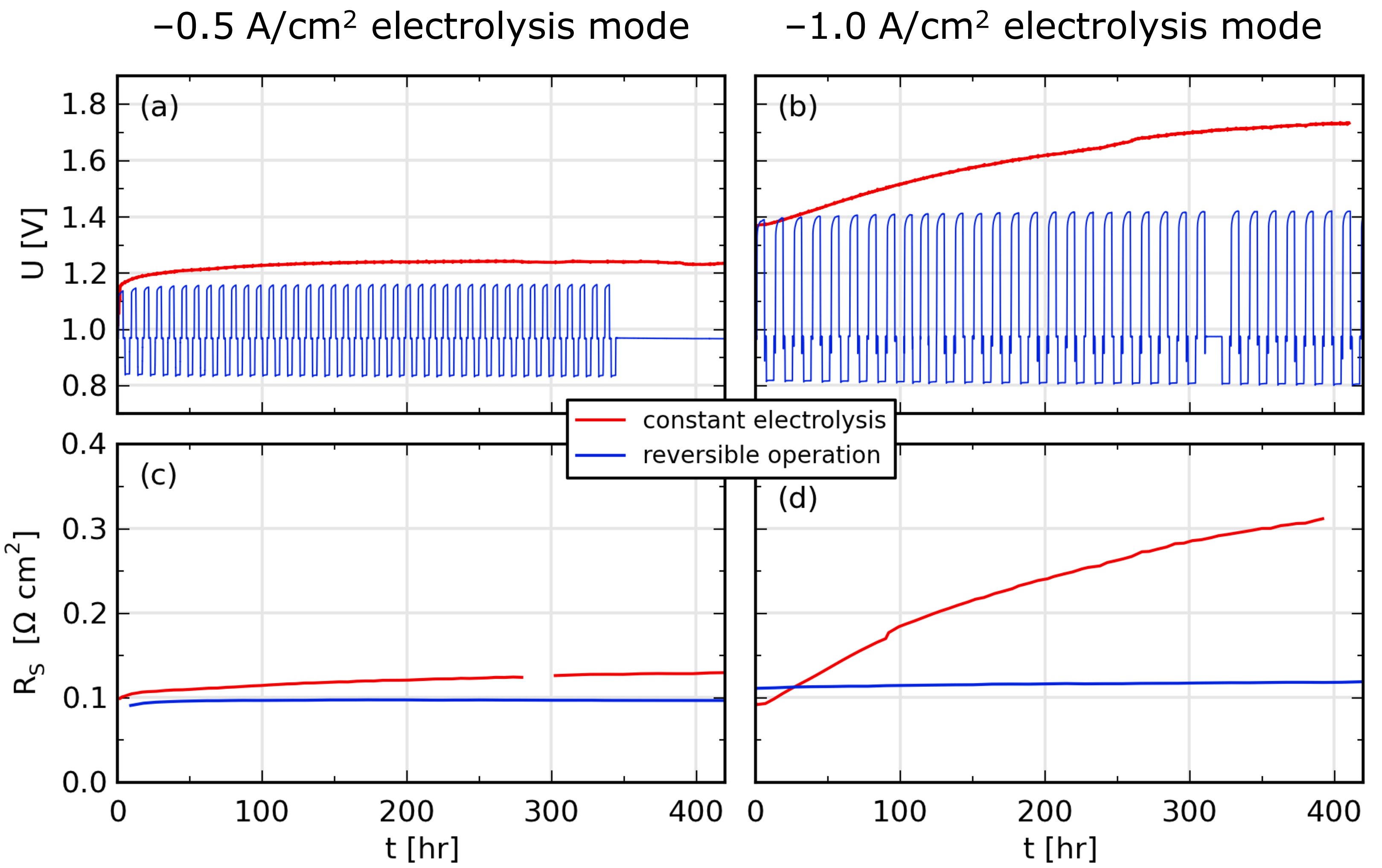
Redox chemistry: most common $H_2O \leftrightarrow H_2 + O_2$

To facilitate interpretation and comparison with prior work

Lifetime of reversible solid oxide cells

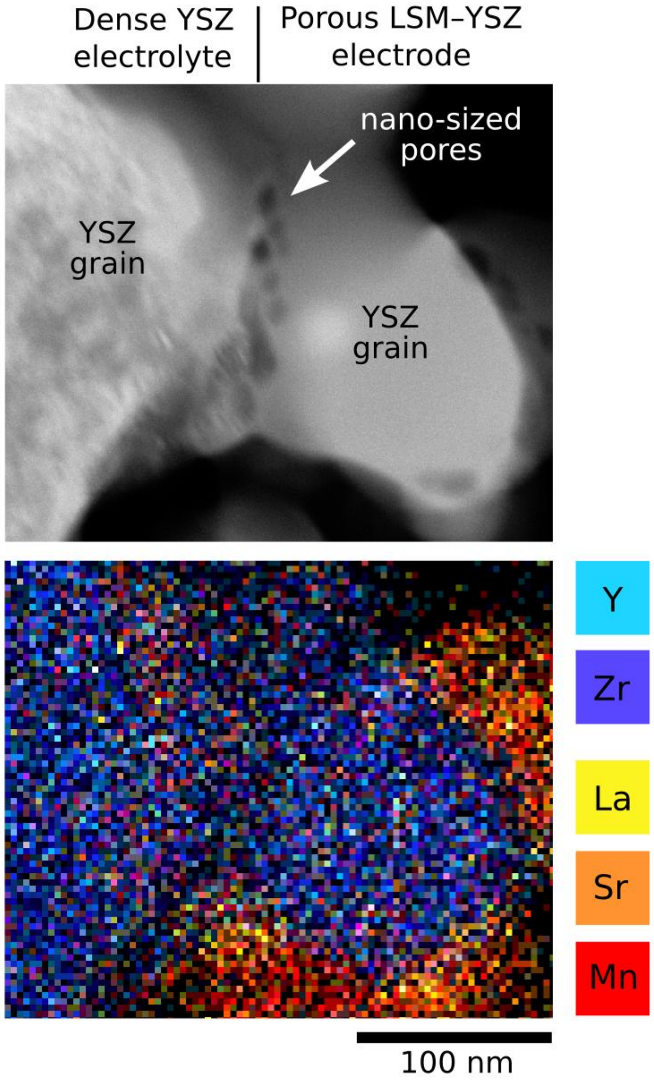
- During continuous electrolysis operation at high current densities, severe microstructural damage occurs in the YSZ electrolyte near the oxygen-electrode/electrolyte interface
  - caused by a buildup of high internal oxygen pressure
- We investigated whether this electrolysis-induced degradation might be decreased by operating the cell reversibly
  - periodically cycling between fuel-cell and electrolysis modes (charge-discharge)

Constant electrolysis vs charge-discharge cycles



Electrolysis degradation could be completely eliminated by reversible operation

Lifetime of reversible solid oxide cells



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Case study of a Danish island powered by 100% wind

Ærø island in Denmark, already supplies 50% of its power by wind and wishes to be a 100% renewable island

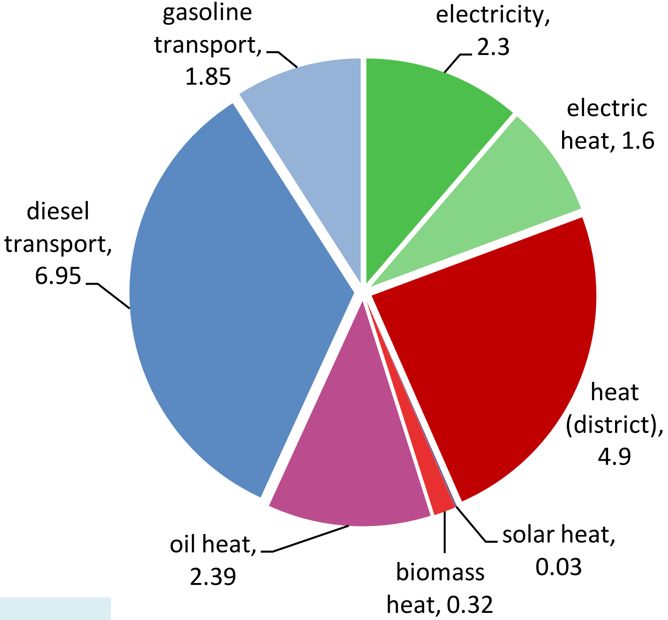
Energy consumption of Ærø island for 2010

(all expressed in MW average based on annual MWh)

Since Ærø already wants energy self-sufficiency, so we can make the assumption of isolation, that it will not interact in the Danish/European/world energy market.

- 3.9 MW electricity consumption
  - 1.6 MW is used for electric heating
- 11.5 MW fuels consumption
  - 2.7 MW is used for heating
  - 8.5 MW is used for transportation
    - Diesel: 3.8 MW for ferries + 3.2 MW for road vehicles
    - Gasoline: 1.85 MW for road vehicles
- 20.4 MW in total (above plus district heat)

and small amount of biomass and solar heat

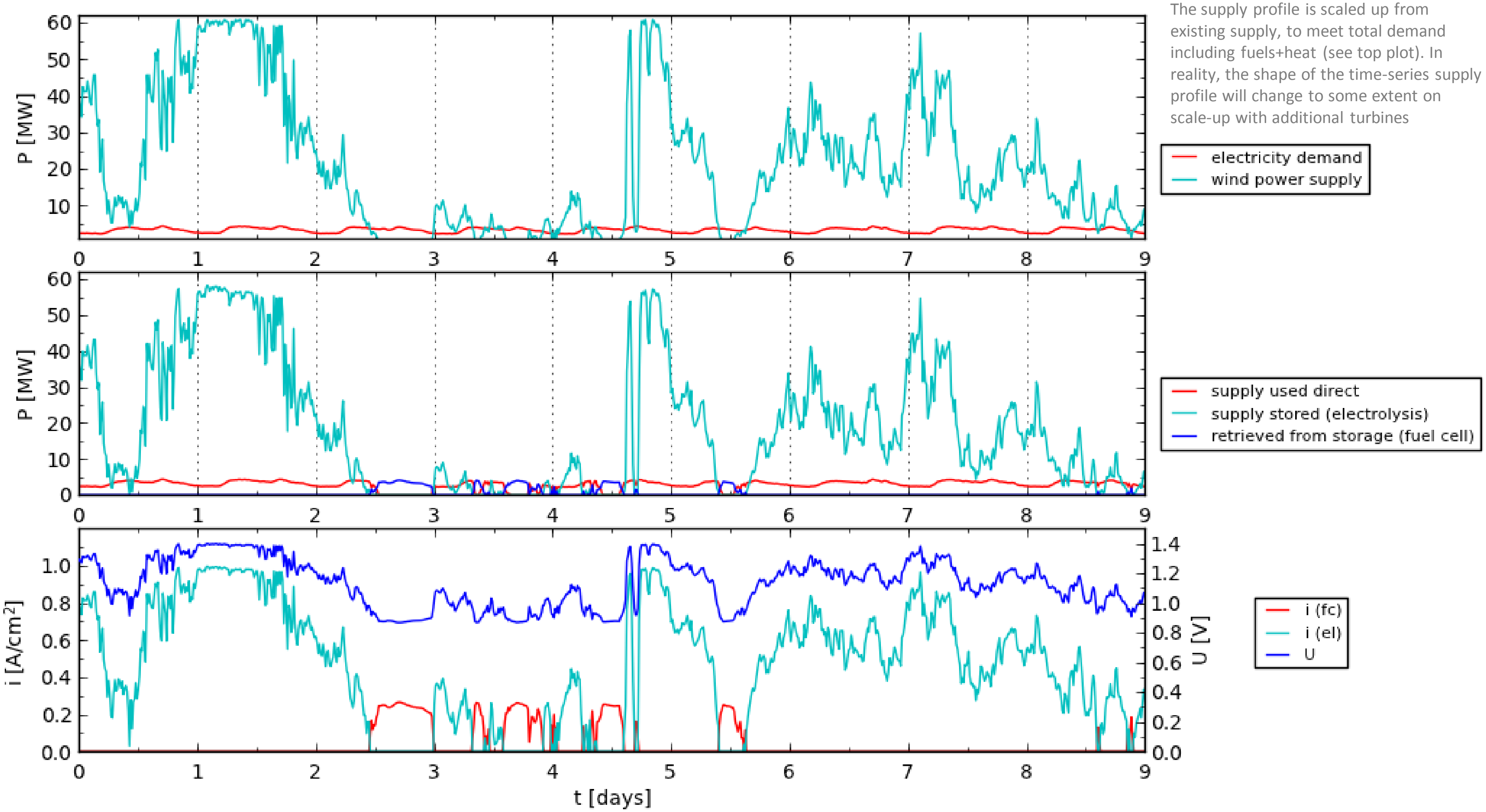


- To supply the above entirely with wind:

  (using time-series supply and demand data, but "rough" estimate before optimization)
  - Electricity @ 100% effic. direct and @ 50% for roundtrip storage = 3.9*(80%/100%+20%/50%) = 4.7 MW wind power*
  - Fuels @ 65% effic. = 11.5/65% = 17.7 MW wind power
  - The inefficiencies give 7.0 MW high-grade heat, which meets the district heating.

Since Ærø has no natural gas storage already, we can use methanol as reversible storage medium and convert it to DME as needed for transportation.

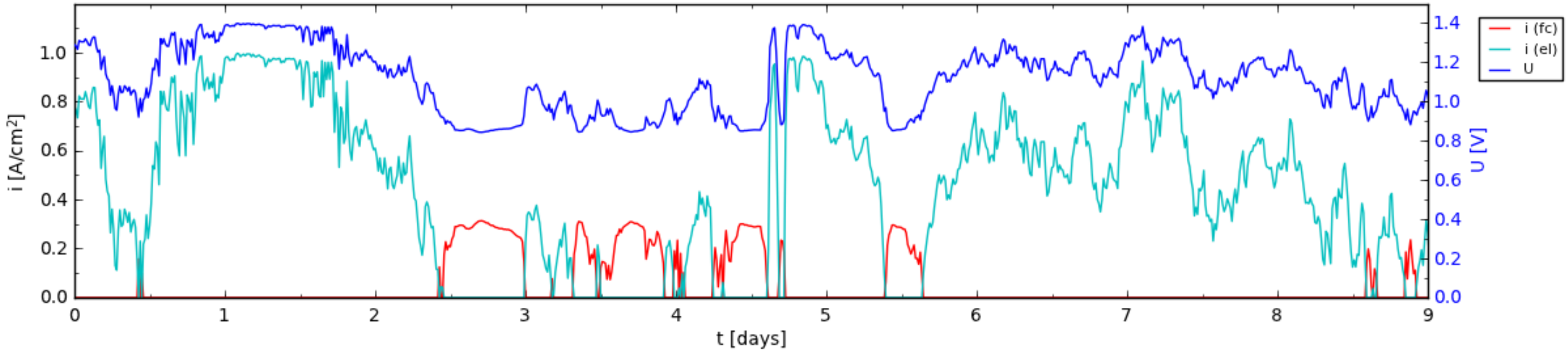
Case study of a Danish island powered by 100% wind



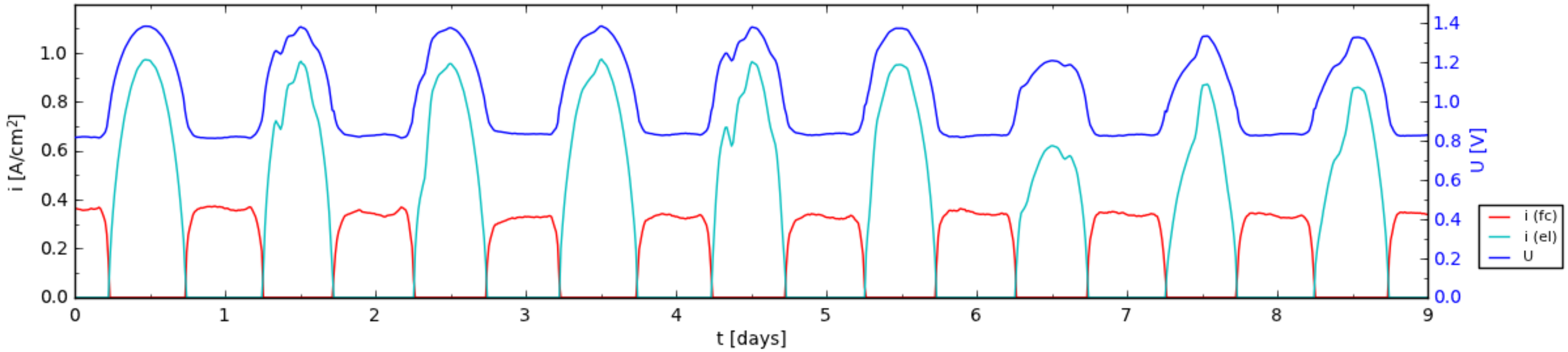
The supply profile is scaled up from existing supply, to meet total demand including fuels+heat (see top plot). In reality, the shape of the time-series supply profile will change to some extent on scale-up with additional turbines

Case study of 100% wind/solar using RFCs

Besides wind power balancing in Denmark,



we are also looking at solar power balancing in California, USA.



Conclusions

- RFCs vs Batteries
  - Match **efficiency** of conventional batteries, using chemistries besides $H_2O \leftrightarrow H_2 + O_2$
  - Lower **resource use** and **cost** per kWh of energy stored
- RFCs vs Electrolysers
  - Lower **cost** due to higher utilization factor (lower idle time)
  - Reversible battery-like operation of solid oxide cells can enhance cell stability, providing **longer lifetime** compared with steady-state electrolysis operation
- It is possible to put together an energy balancing system which supplies **both on-demand electricity & green fuels** with low energy losses with only 3 devices (RFCs, catalytic reactors, and air capture or biomass capture of CO_2)
- Since RFCs can use common fuels, one can install RFC systems today and operate only in FC mode until the renewable supply increases, then operate reversibly (**no need to install a dedicated energy storage system** if it is initially designed for reversible operation). & Perfect capacity sizing is less important since charge mode need not always precede discharge mode (fuels can be imported to the system).

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