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# Are reversible fuel cells better batteries for large-scale renewable energy storage?

**Graves, Christopher R.**

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# Are reversible fuel cells better batteries for large-scale renewable energy storage?

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Technical University of Denmark

6th September 2013
ISACS12: Challenges in Chemical Renewable Energy
Cambridge, UK

**DTU Energy Conversion**
Department of Energy Conversion and Storage

# Outline

1. Background

2. Batteries, flow batteries, & reversible fuel cells

3. Possible redox chemistries, thermodynamics & efficiencies

4. Resource use

5. Economics

6. Recent experimental results

# Denmark's need for energy storage
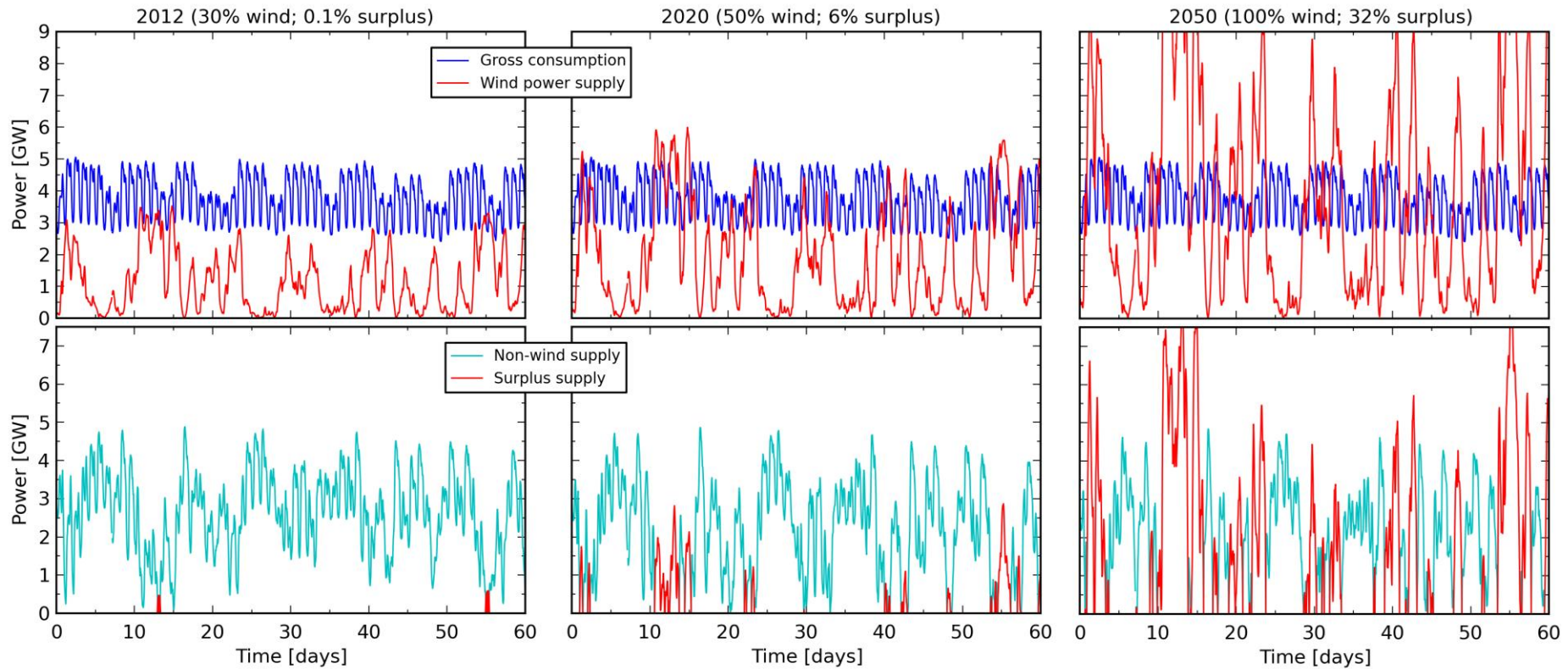


Data for 2012 from energinet.dk; future wind supply scaled up based on Danish roadmap.

# Storing surplus wind power as hydrocarbon fuels



Reuse $CO_2$ once

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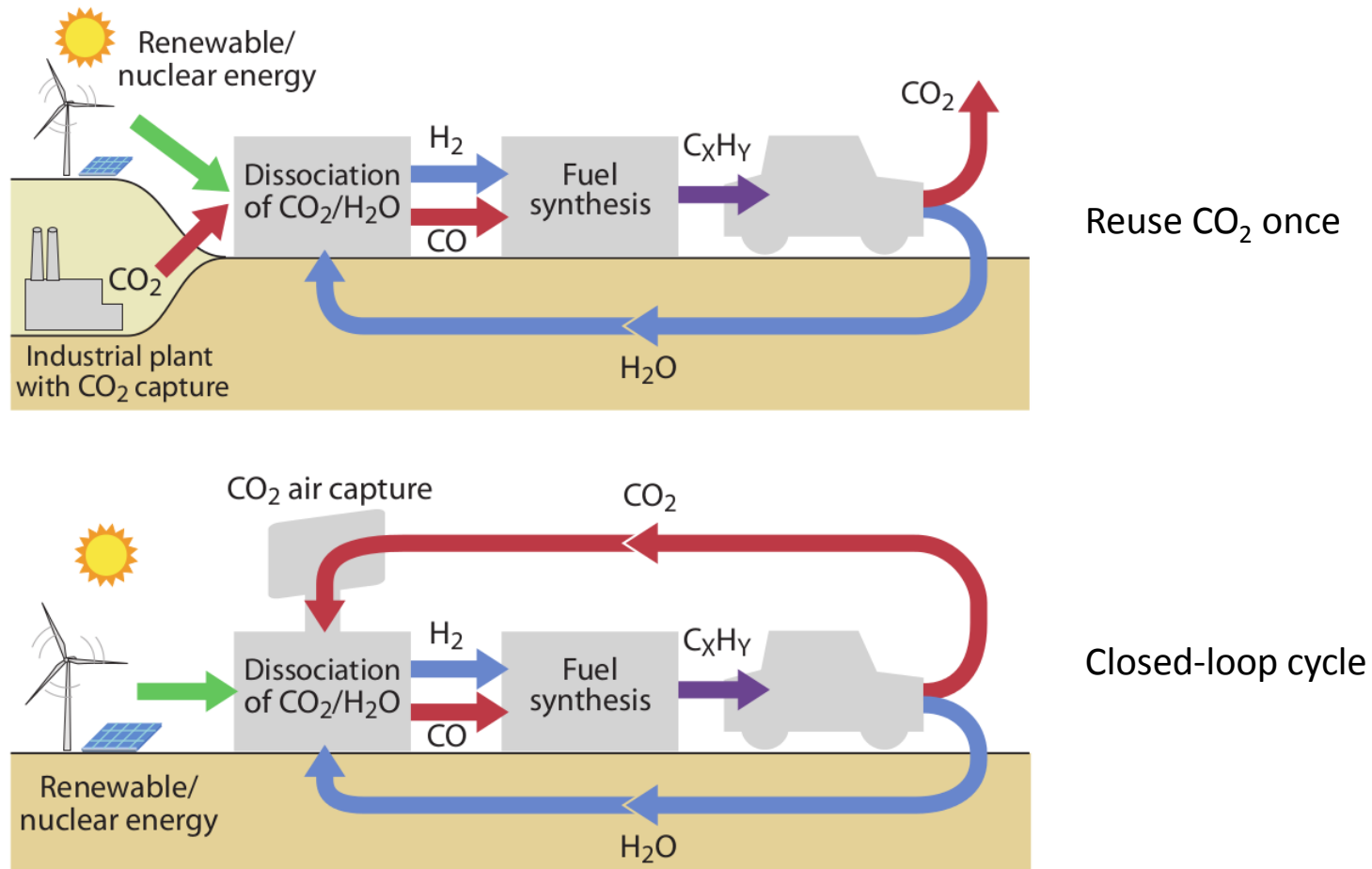
C. Graves, S.D. Ebbesen, M. Mogensen, K.S. Lackner, *Sustainable hydrocarbon fuels by recycling $CO_2$ and $H_2O$ with renewable or nuclear energy*, Renewable and Sustainable Energy Reviews. 15 (2011) 1–23.

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*

Electrolysis mode
electricity → fuels

$O_2$

$+$

$-$

$2O^{2-}$

$4e^-$   $2H_2O$ → $2H_2$
         $2CO_2$ → $2CO$

45% $H_2O$
+ 45% $CO_2$
+ 10% $H_2$

cell voltage [V]

i [A/cm$^2$]
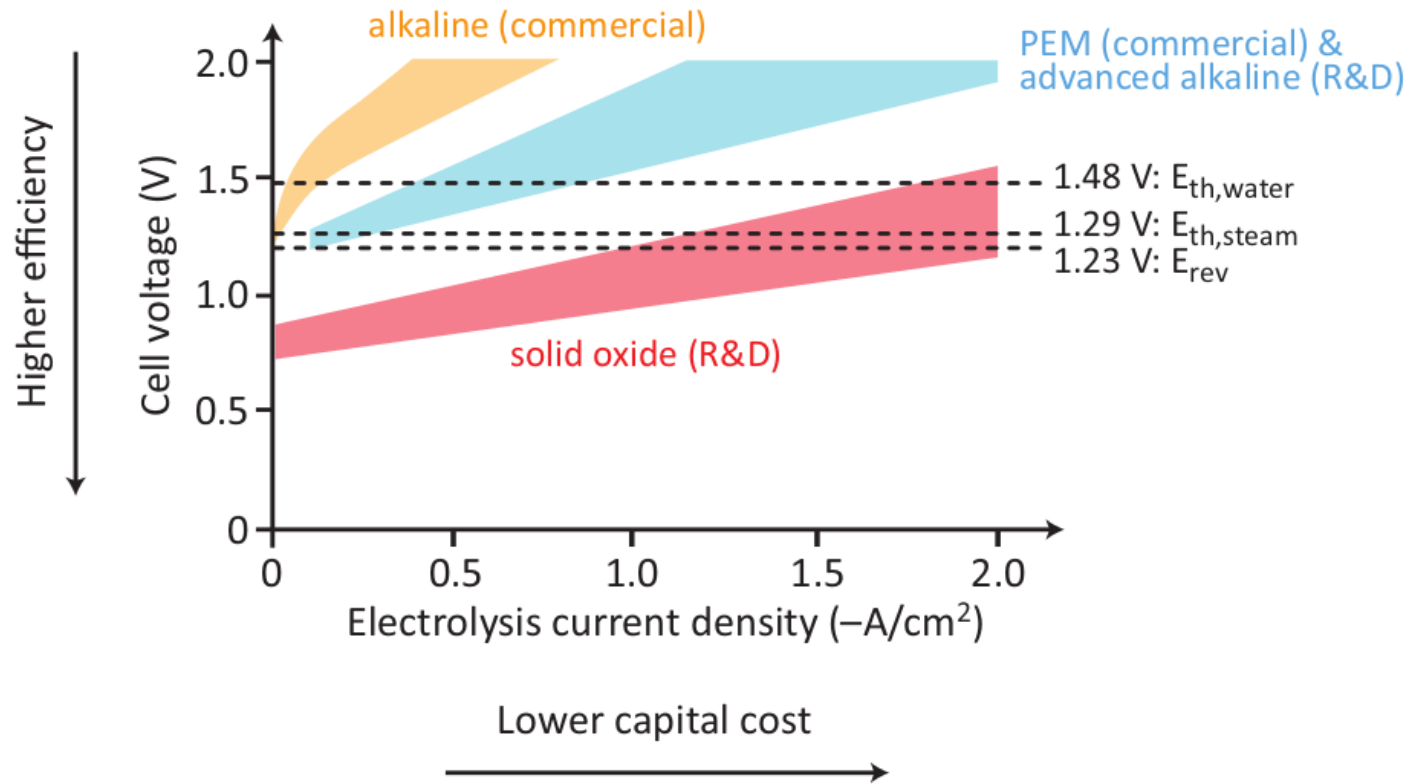
# Solid oxide electrochemical cells
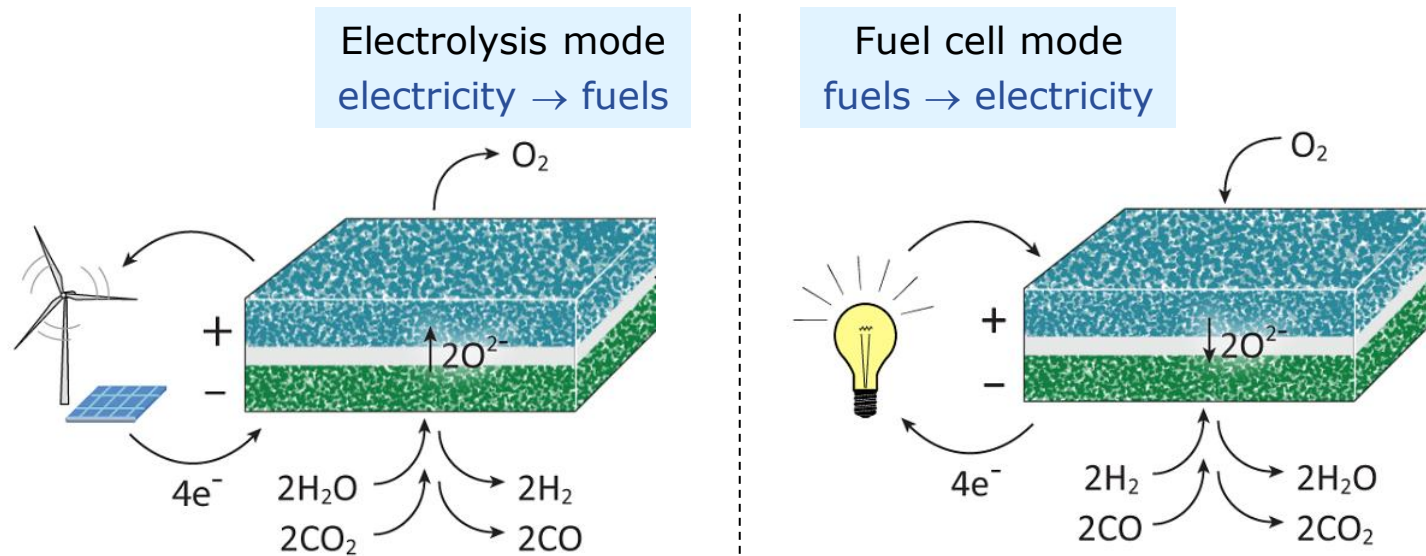
# Using solid oxide cells as batteries



Electrolysis (charge) mode

$O_2$ / air

Porous oxygen-electrode
$O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$

Dense electrolyte
$O^{2-}$ conduction

Porous fuel-electrode
$H_2O + 2e^- \rightarrow H_2 + O^{2-}$
$CO_2 + 2e^- \rightarrow CO + O^{2-}$ } electro-chemical

$H_2 + CO_2 \leftrightarrow H_2O + CO$
$3H_2 + CO \leftrightarrow CH_4 + H_2O$
$4H_2 + CO_2 \leftrightarrow CH_4 + 2H_2O$ } catalytic

$H_2O$ $CO_2$

$CH_4$ $H_2$ $CO$

$2e^-$

export as needed
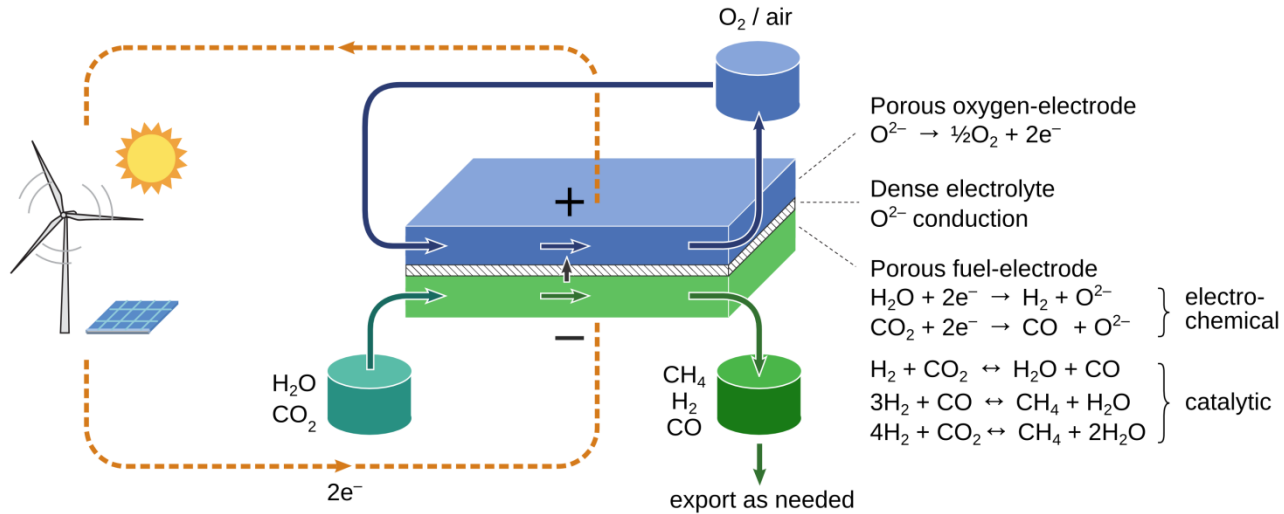
Fuel-cell (discharge) mode
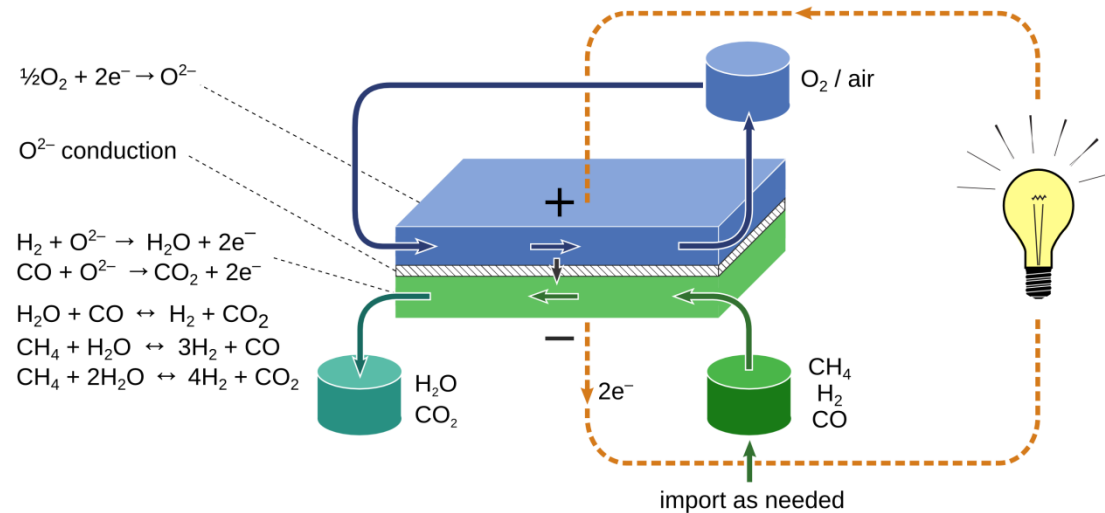
$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$

$O^{2-}$ conduction

$H_2 + O^{2-} \rightarrow H_2O + 2e^-$
$CO + O^{2-} \rightarrow CO_2 + 2e^-$

$H_2O + CO \leftrightarrow H_2 + CO_2$
$CH_4 + H_2O \leftrightarrow 3H_2 + CO$
$CH_4 + 2H_2O \leftrightarrow 4H_2 + CO_2$

$O_2$ / air

$H_2O$ $CO_2$

$2e^-$

$CH_4$ $H_2$ $CO$

import as needed

# Outline

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2. **Batteries, flow batteries, & reversible fuel cells**

3. Possible redox chemistries, thermodynamics & efficiencies

4. Resource use
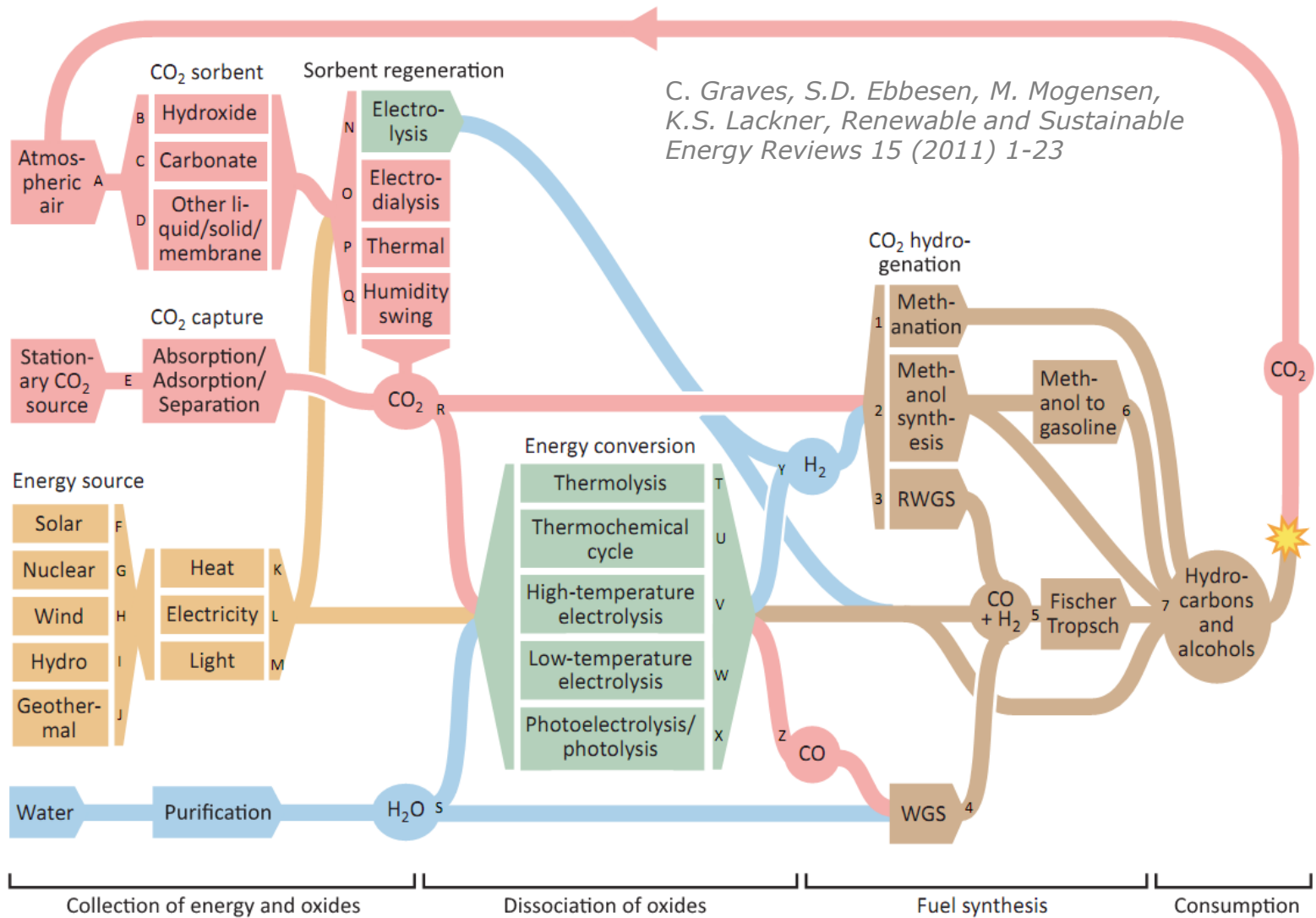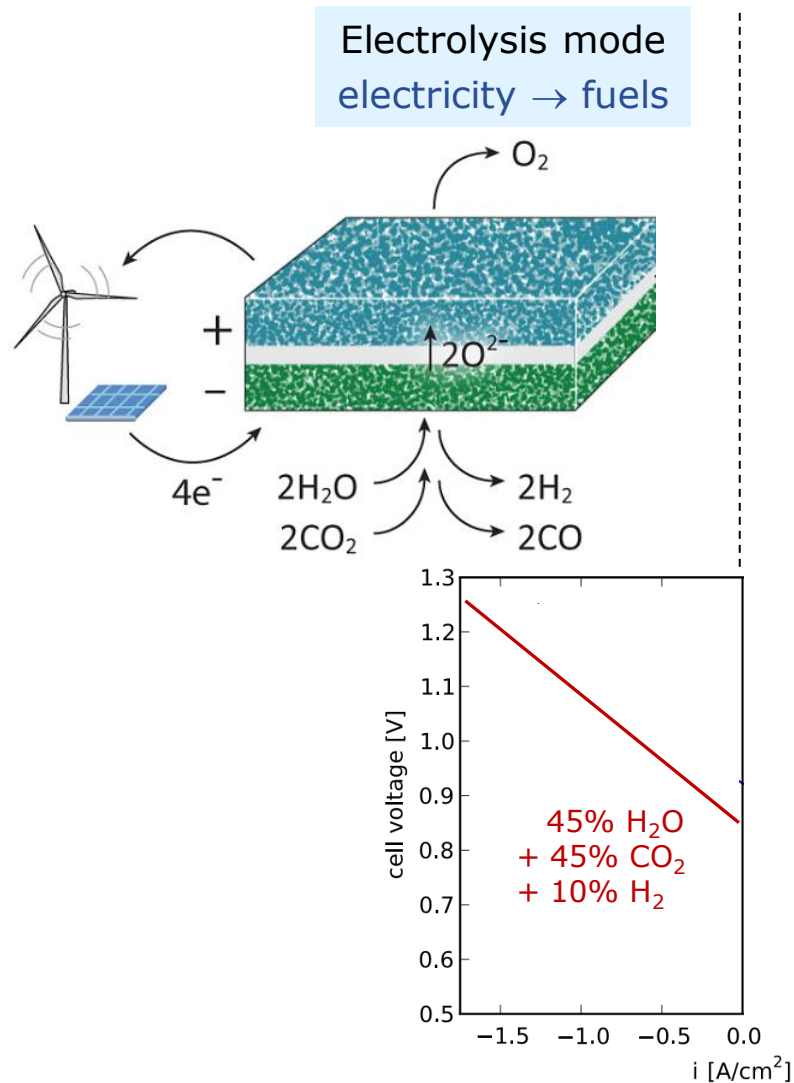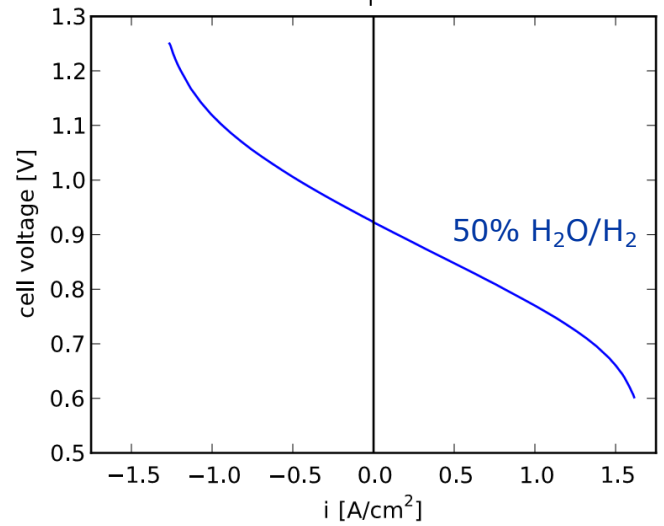
5. Economics

6. Recent experimental results

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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
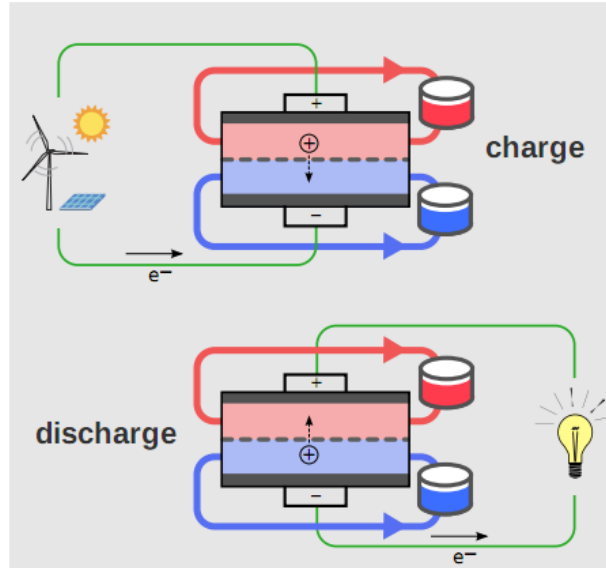
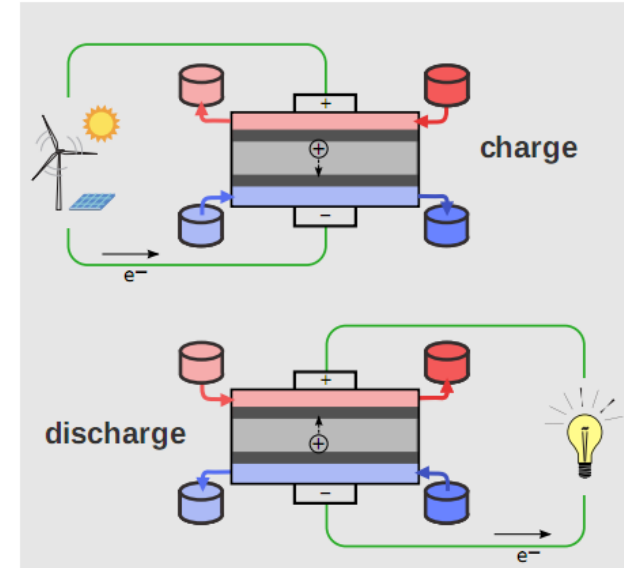# Batteries, flow batteries, & reversible fuel cells



**Battery**

charge

discharge
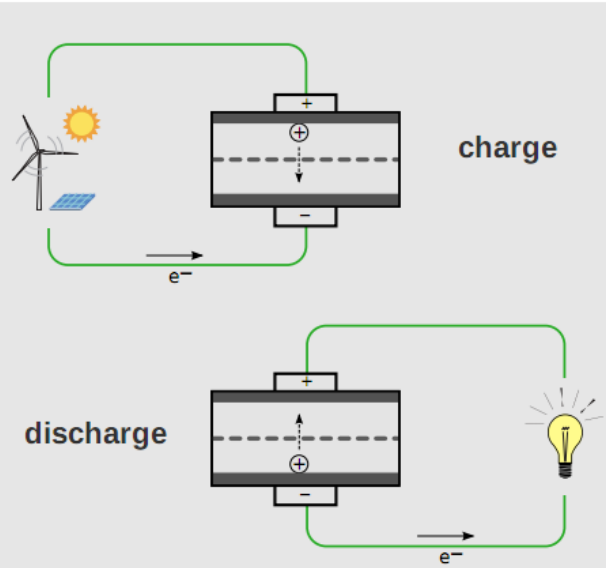
Energy stored in metal atoms on electrodes

**Flow battery**

charge

discharge

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**

charge

discharge

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

**Examples:**

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

Note: For each, the charge carrier in the electrolyte need not necessarily be a positive species.

**Examples:**

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

Examples: $Li^+$, $Na^+$, $H^+$, $OH^-$, $O^{--}$, $CO_3^{--}$

**Examples:**

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

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# 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

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# Batteries, flow batteries, & reversible fuel cells

Briefly, more about categorization:

Is this a reversible fuel cell or a battery?
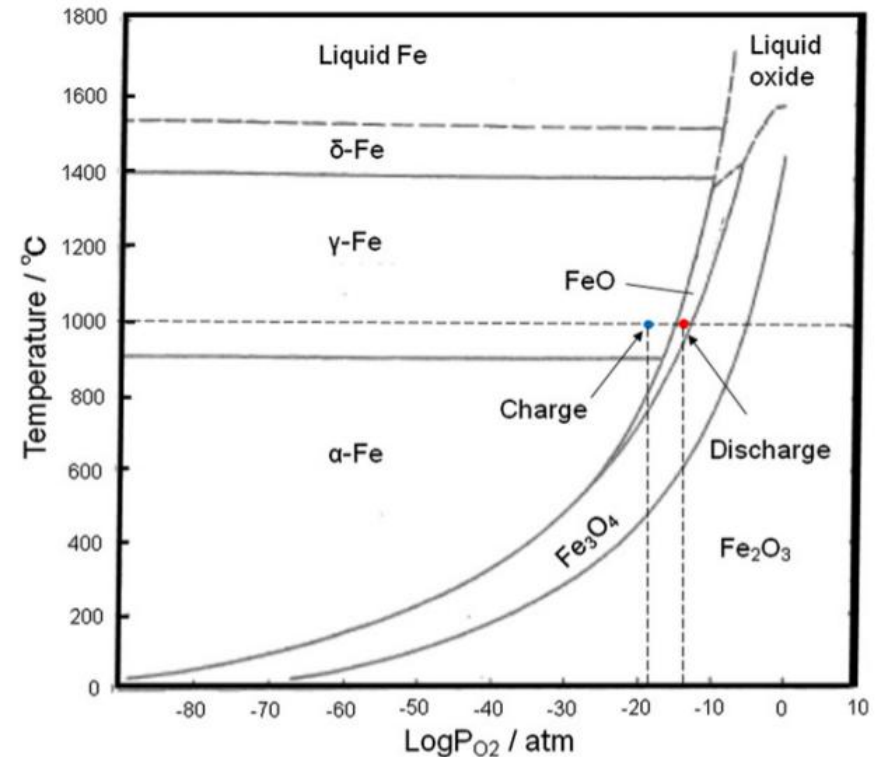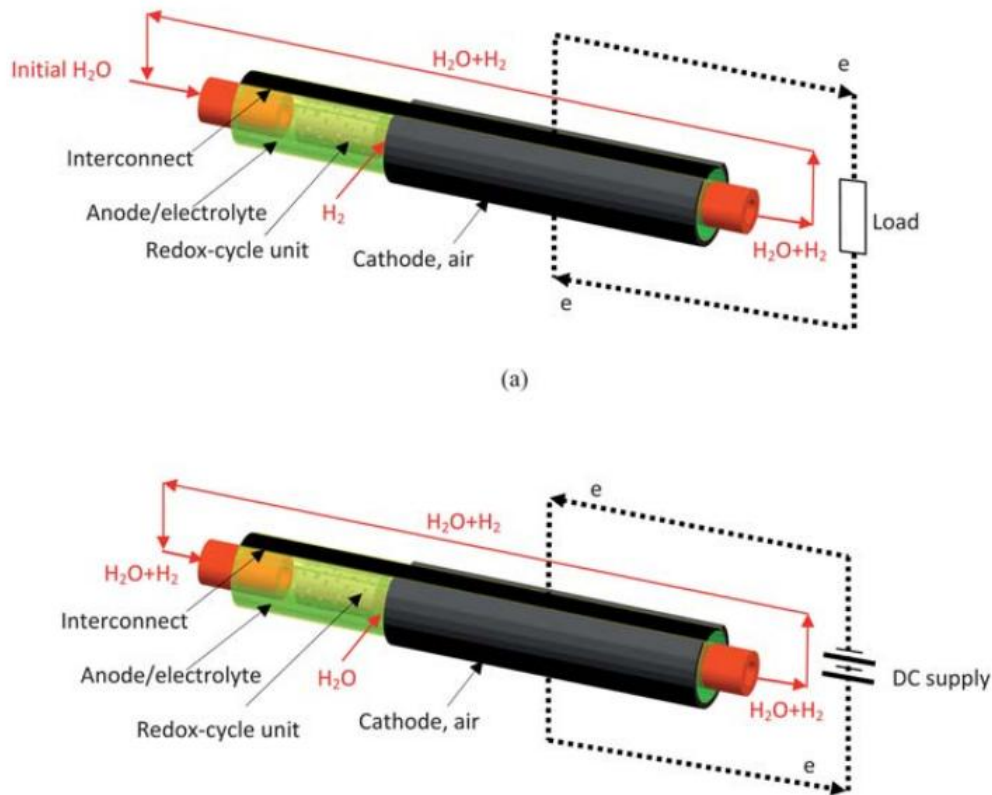


Fig. 4. Keringum diagram of Fe–$O_2$ and $P_{O_2}$ in charge and discharge.

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?
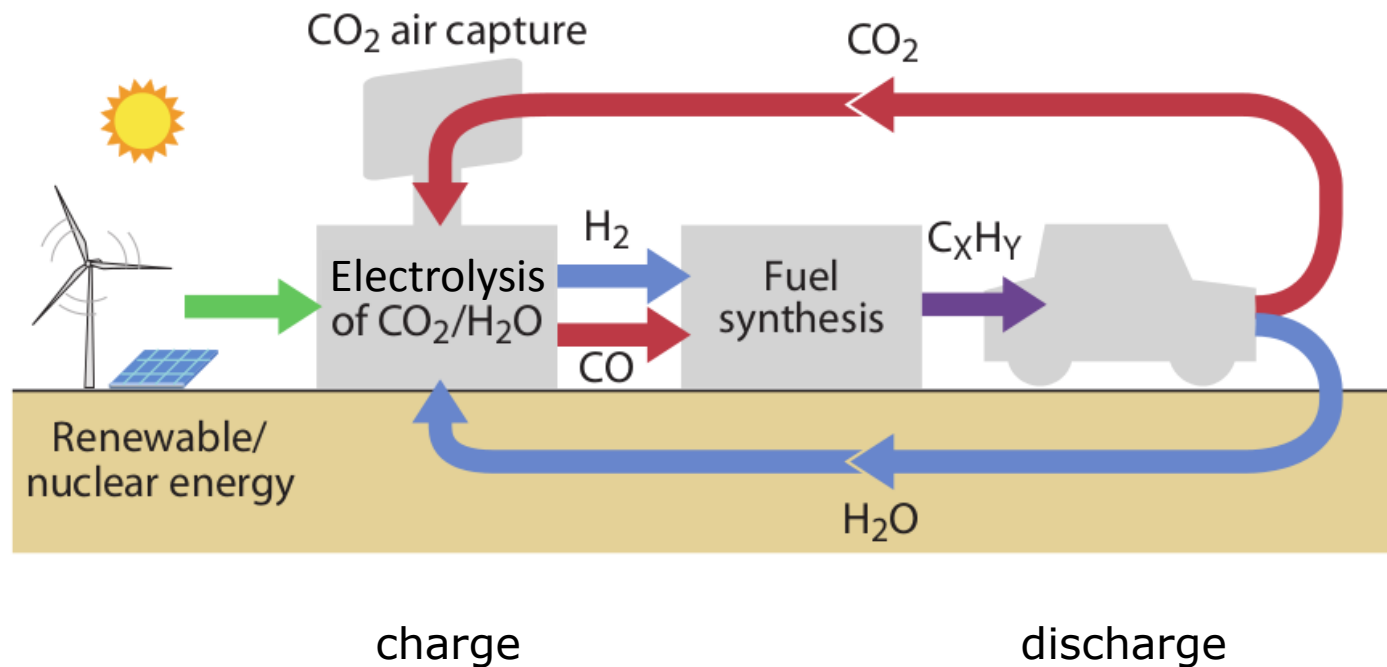


charge                                    discharge

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)…

# Outline

1. Background

2. Batteries, flow batteries, & reversible fuel cells

3. **Possible redox chemistries, thermodynamics & efficiencies**

4. Resource use

5. Economics

6. Case study of an island in Denmark powered by 100% wind

# 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/

http://pubs.usgs.gov/fs/2002/fs087-02/
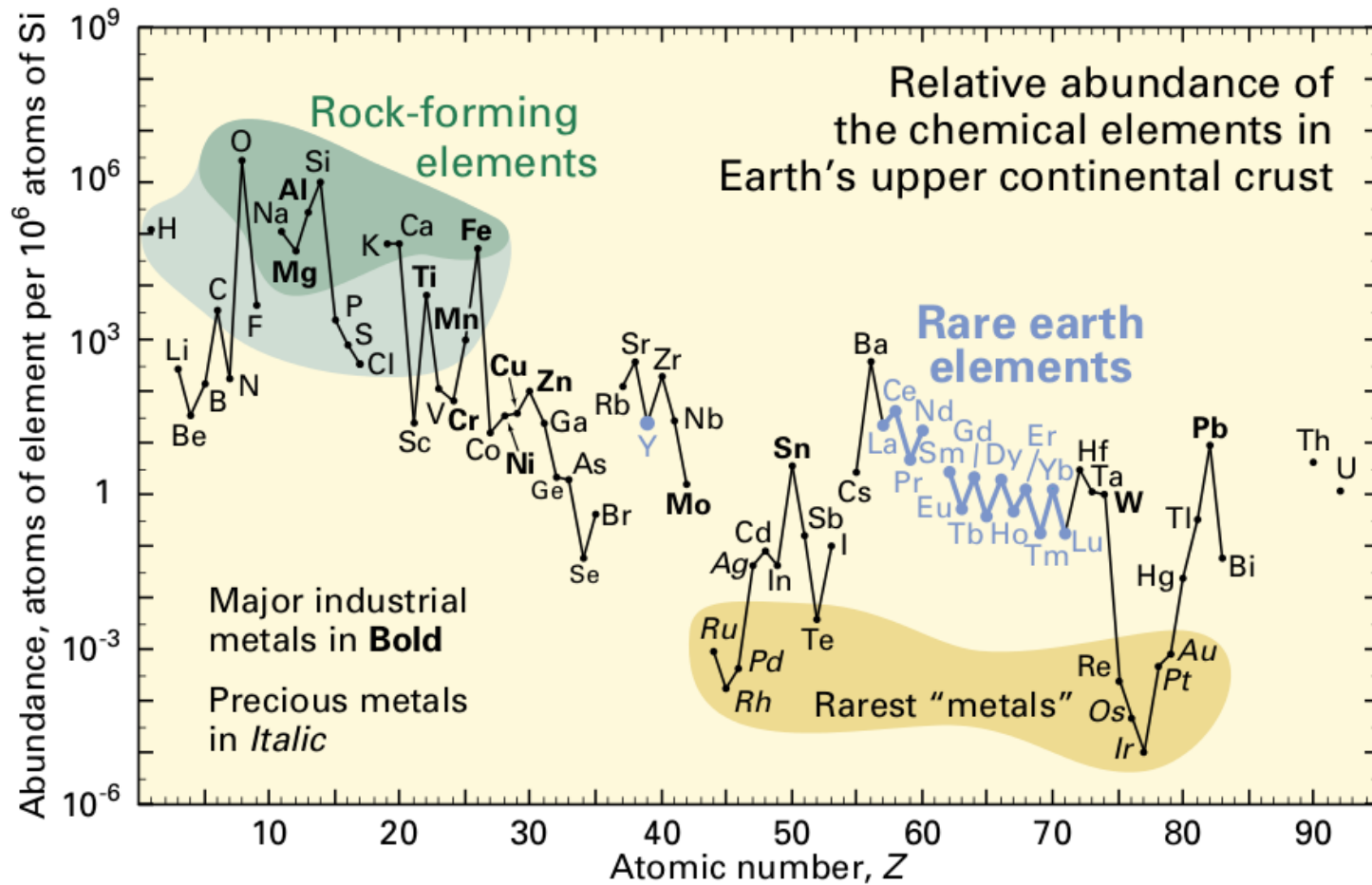
Raw materials costs and abundance
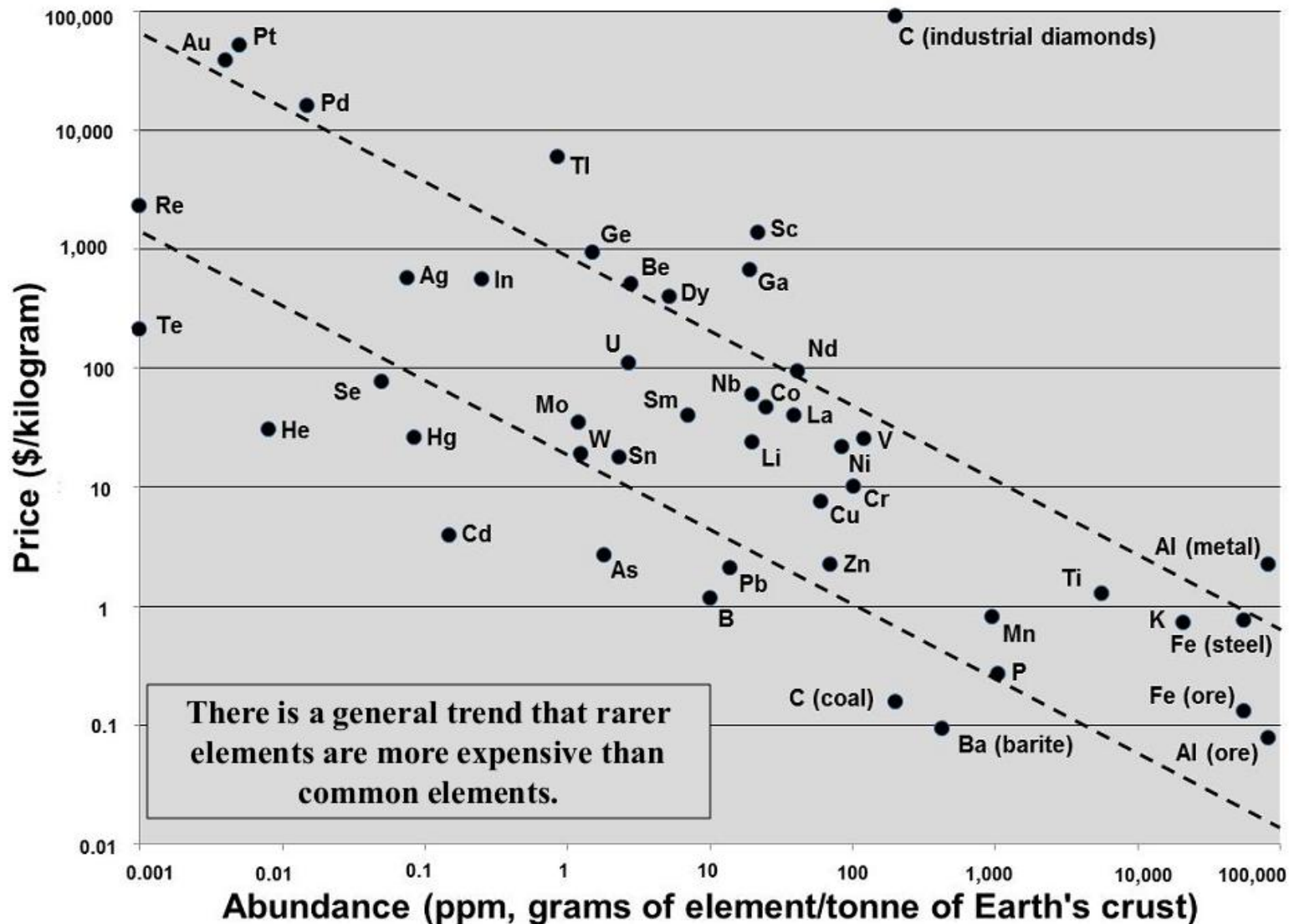
# Possible redox chemistries

- Most abundant elements include H, C, Fe, Na, Si, Al, Ca

- Besides low cost, they are also the lightest $\rightarrow$ high energy density

- Focus first on H and C

  | $H_2$ | CO |
  | $CH_4$ | C |

# Possible redox chemistries - thermodynamics

Li-air and Na-S batteries

Based on losing T$\Delta$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).

$$-- \quad Li_2O \rightleftharpoons 2Li + \tfrac{1}{2}O_2$$

$$\cdots \quad \tfrac{1}{2}Li_2O_2 \rightleftharpoons Li + \tfrac{1}{2}O_2$$
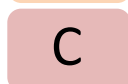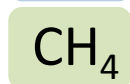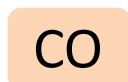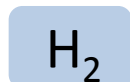
$$-- \quad Na_2S_4 \rightleftharpoons 2Na + 4S$$
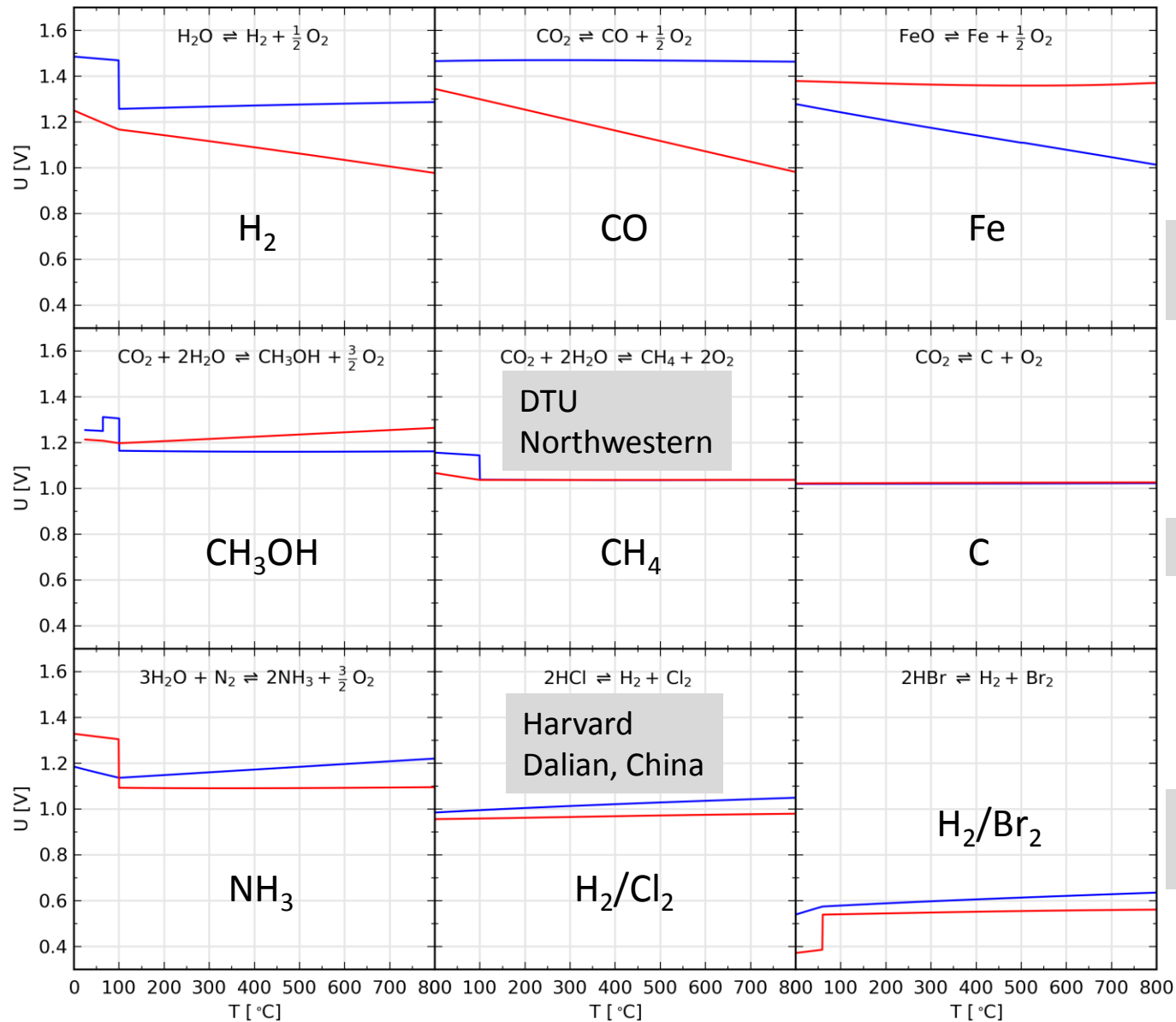
# Possible redox chemistries – max. roundtrip efficiencies
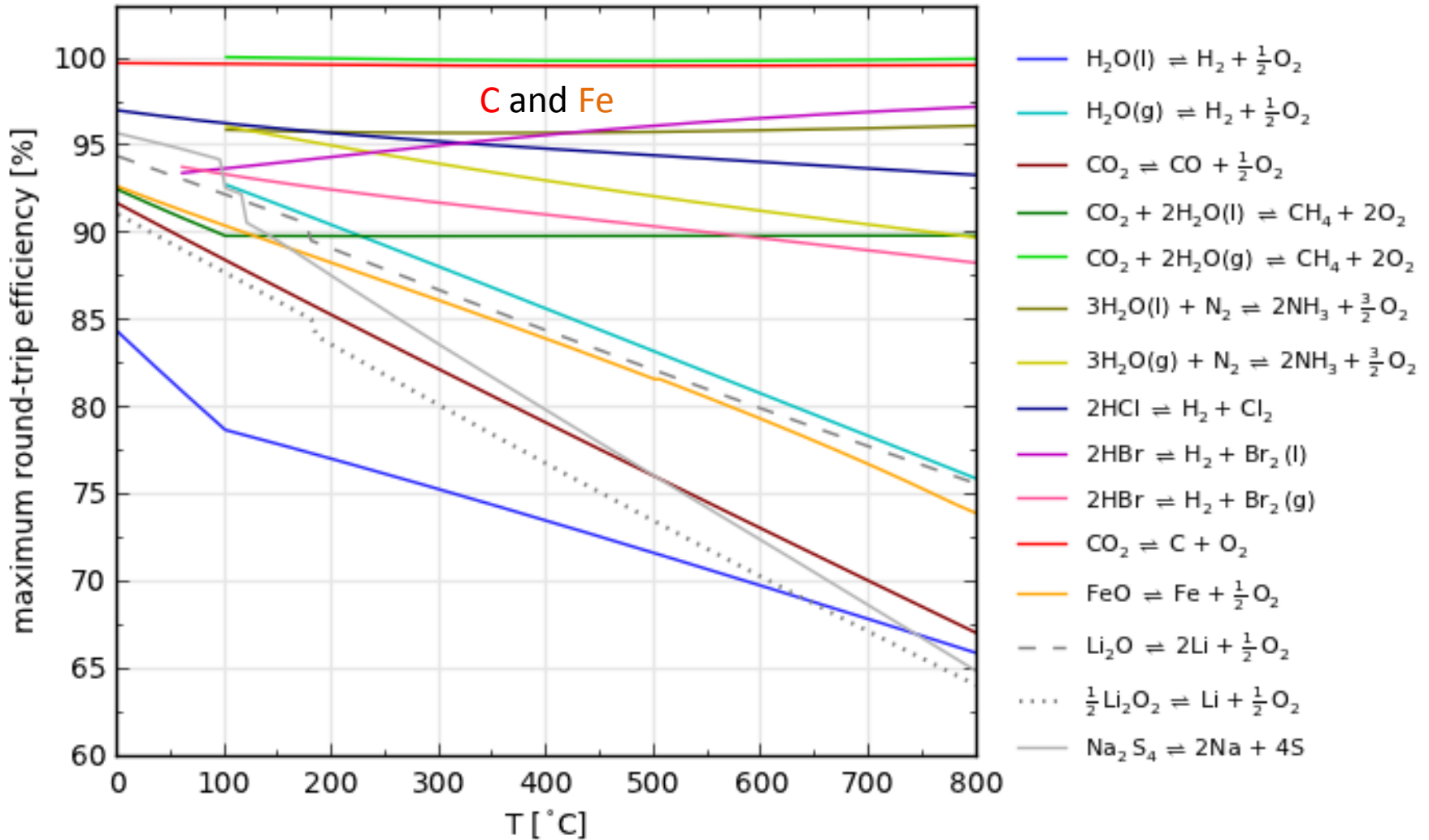
HCl and HBr

Legend:
- $H_2O(l) \rightleftharpoons H_2 + \frac{1}{2}O_2$
- $H_2O(g) \rightleftharpoons H_2 + \frac{1}{2}O_2$
- $CO_2 \rightleftharpoons CO + \frac{1}{2}O_2$
- $CO_2 + 2H_2O(l) \rightleftharpoons CH_4 + 2O_2$
- $CO_2 + 2H_2O(g) \rightleftharpoons CH_4 + 2O_2$
- $3H_2O(l) + N_2 \rightleftharpoons 2NH_3 + \frac{3}{2}O_2$
- $3H_2O(g) + N_2 \rightleftharpoons 2NH_3 + \frac{3}{2}O_2$
- $2HCl \rightleftharpoons H_2 + Cl_2$
- $2HBr \rightleftharpoons H_2 + Br_2(l)$
- $2HBr \rightleftharpoons H_2 + Br_2(g)$
- $Li_2O \rightleftharpoons 2Li + \frac{1}{2}O_2$
- $\frac{1}{2}Li_2O_2 \rightleftharpoons Li + \frac{1}{2}O_2$
- $Na_2S_4 \rightleftharpoons 2Na + 4S$

Axis labels: maximum round-trip efficiency [%] vs $T$ [°C]

C and Fe

Legend:
- $H_2O(l) \rightleftharpoons H_2 + \frac{1}{2}O_2$
- $H_2O(g) \rightleftharpoons H_2 + \frac{1}{2}O_2$
- $CO_2 \rightleftharpoons CO + \frac{1}{2}O_2$
- $CO_2 + 2H_2O(l) \rightleftharpoons CH_4 + 2O_2$
- $CO_2 + 2H_2O(g) \rightleftharpoons CH_4 + 2O_2$
- $3H_2O(l) + N_2 \rightleftharpoons 2NH_3 + \frac{3}{2}O_2$
- $3H_2O(g) + N_2 \rightleftharpoons 2NH_3 + \frac{3}{2}O_2$
- $2HCl \rightleftharpoons H_2 + Cl_2$
- $2HBr \rightleftharpoons H_2 + Br_2(l)$
- $2HBr \rightleftharpoons H_2 + Br_2(g)$
- $CO_2 \rightleftharpoons C + O_2$
- $FeO \rightleftharpoons Fe + \frac{1}{2}O_2$
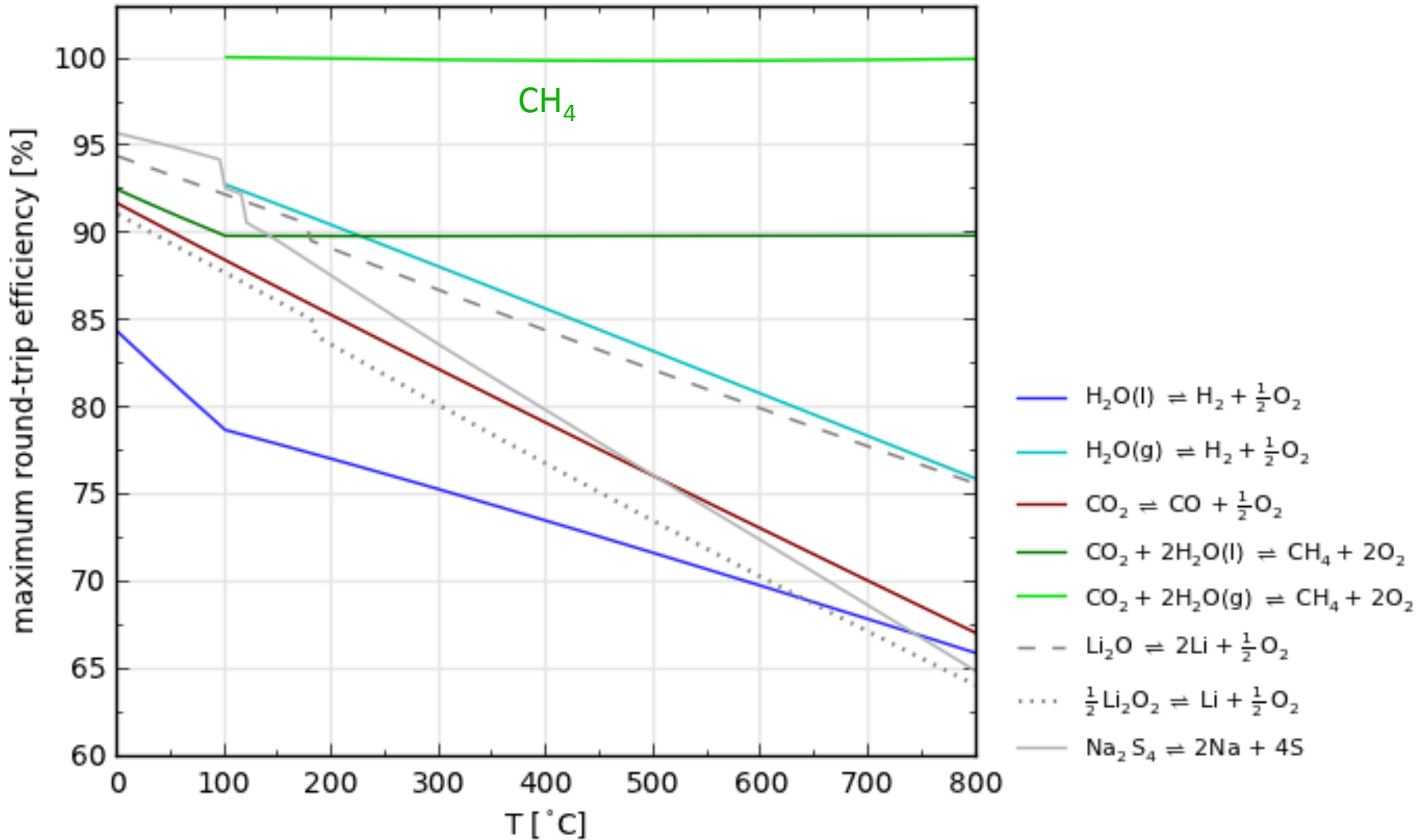- $Li_2O \rightleftharpoons 2Li + \frac{1}{2}O_2$
- $\frac{1}{2}Li_2O_2 \rightleftharpoons Li + \frac{1}{2}O_2$
- $Na_2S_4 \rightleftharpoons 2Na + 4S$

x-axis: $T\ [°C]$

y-axis: maximum round-trip efficiency [%]

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

# Possible redox chemistries

- Maximum theoretical efficiency $\rightarrow$ practical efficiency $\varepsilon$
  - Overpotentials $\eta$ to actually produce current
  - Heat losses
  - Energy consumed by balance of system
- 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 $\Omega$ 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%.

# Possible redox chemistries

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  - However, the difference could become smaller or larger depending on the required operating profile: For example, energy balancing intermittent renewable energy with a low 20-30% capacity factor requires operating at higher electrolysis current density for a shorter time than in fuel-cell mode, which lowers $\varepsilon(CH_4)$ because both modes are exothermic, but it does not affect $\varepsilon(H_2)$ until electrolysis operation rises above thermoneutral.

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3. Possible redox chemistries, thermodynamics & efficiencies

4. **Resource use**

5. Economics

6. Recent experimental results

# Resource Use

- **Amount of material tied up in a kWh of stored electricity**
  - → Cost, Sustainability, Ability to scale-up (and toxicity)

g material per kWh storage
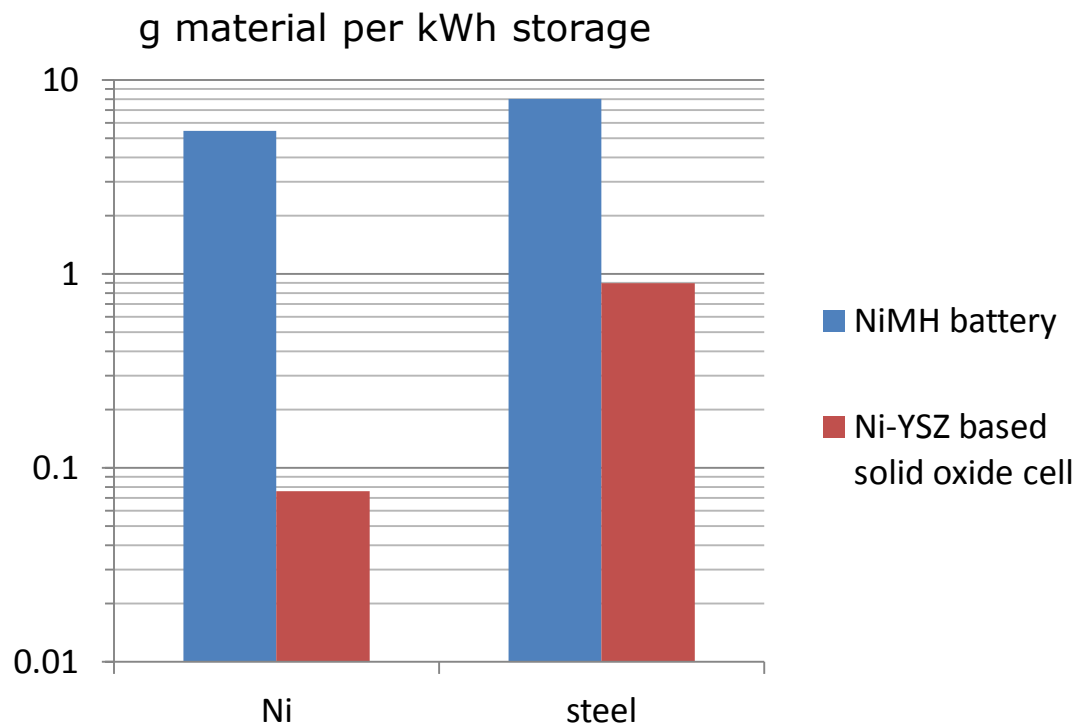


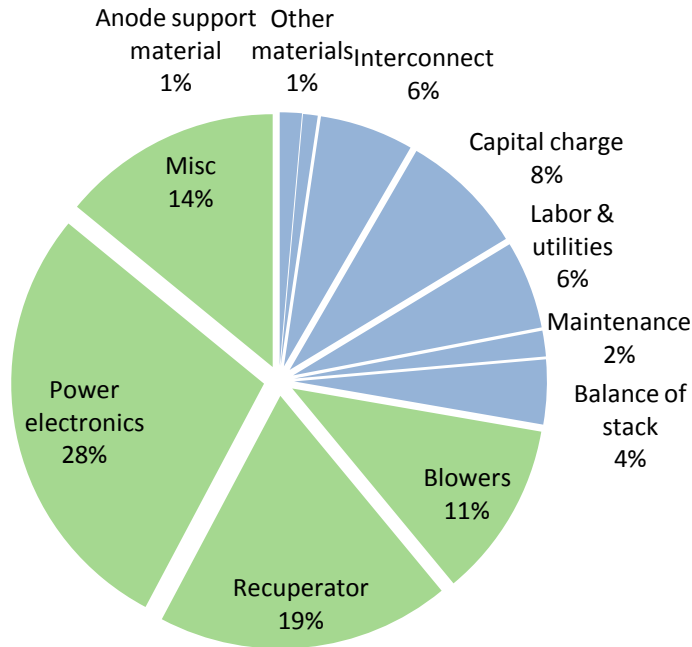- Similar magnitudes of Li+Co for Li-ion and Pb for Pb-acid batteries
- Using life cycle analysis from literature and device lifetimes
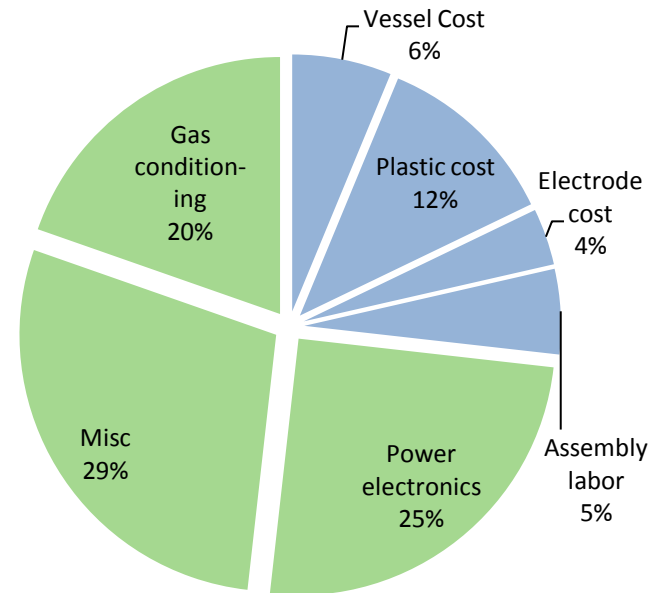  - NiMH battery 2000 cycles at 50% DOD; SOC 5-yr (1800 daily cycles)

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# Economics – capital cost breakdowns

## Solid oxide cell

Anode support material 1%
Other materials 1%
Interconnect 6%
Capital charge 8%
Labor & utilities 6%
Maintenance 2%
Balance of stack 4%
Blowers 11%
Recuperator 19%
Power electronics 28%
Misc 14%

## Alkaline fuel/electrolysis cell

Vessel Cost 6%
Plastic cost 12%
Electrode cost 4%
Assembly labor 5%
Power electronics 25%
Misc 29%
Gas conditioning 20%

**Balance of system dominates!**

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

The estimates are based on mass production of the cells+stacks, but what about the BoS components?

Data collected from:

Saur (2008) NREL technical report - Wind-To-Hydrogen Project- Electrolyzer Capital Cost Study
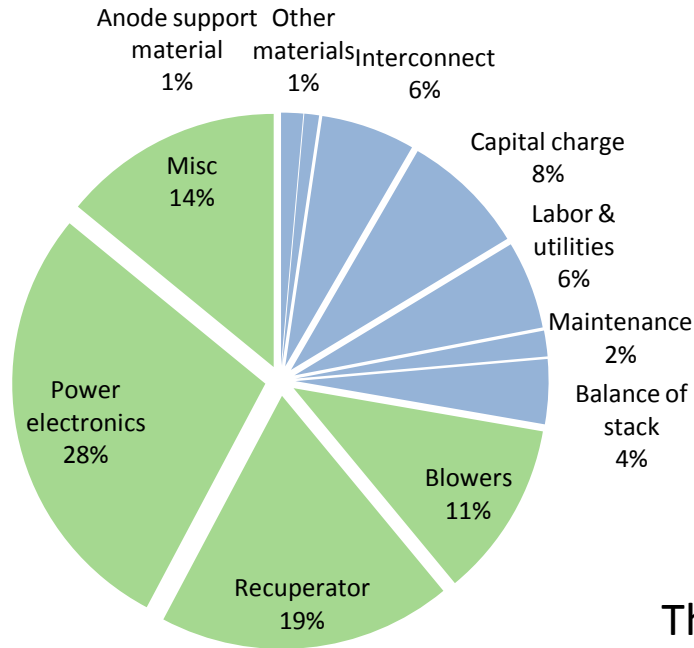
Thijssen, Jan. The Impact of Scale-Up and Production Volume on SOFC Manufacturing Cost. J. Thijssen, LLC. Prepared for National Energy Technology Laboratory, U.S. DOE, A pril 2, 2007.

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

## Solid oxide cell



- Anode support material 1%
- Other materials 1%
- Interconnect 6%
- Capital charge 8%
- Labor & utilities 6%
- Maintenance 2%
- Balance of stack 4%
- Blowers 11%
- Recuperator 19%
- Power electronics 28%
- Misc 14%

## Li-ion battery

| Level of Integration | Cost Category | | | Total ($/kWh) |
|---|---|---|---|---|
| | Materials | Manufacturing | Other | |
| Cell | 734.53 | 23.15 | 86.90 | 844.59 |
| Module | 771.79 | 26.77 | 86.90 | 885.47 |
| Pack | 864.38 | 31.68 | 230.27 | 1126.33 |

**Costs for High-Energy Li-Ion Batteries ($/kWh) in Year 2000**

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

## Opposite!

This means:

- Li-ion cost reduction potential is relatively limited

- Solid oxide cell BoS cost reductions should be possible, and since raw materials are estimated at ~2% of the total cost, small use of more expensive materials are not out of the question

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# 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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6. **Recent experimental results**
   Article submitted, in review

# Long-term testing of solid oxide cells

**Electrolysis mode**
electricity → fuels

**Fuel cell mode**
fuels → electricity

$O_2$

$2O^{2-}$

$4e^-$    $2H_2O$ → $2H_2$
          $2CO_2$ → $2CO$

$O_2$

$2O^{2-}$

$4e^-$    $2H_2$ → $2H_2O$
          $2CO$ → $2CO_2$

cell voltage [V]

50% $H_2O/H_2$

i [A/cm$^2$]
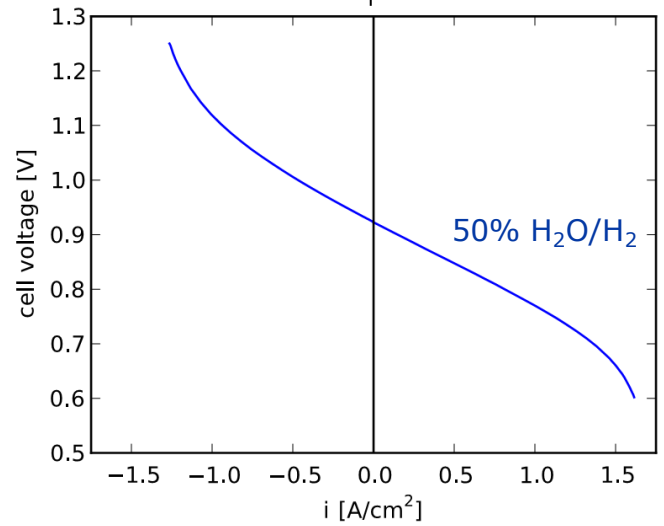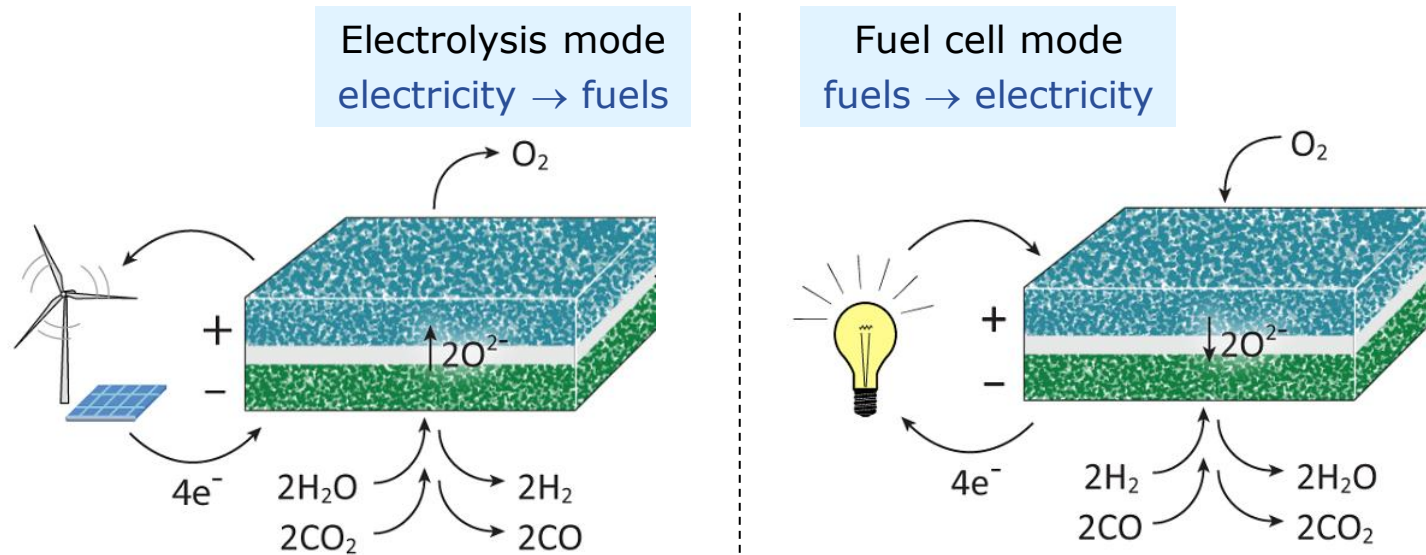
Cell type: most common
Ni–YSZ | YSZ | LSM–YSZ

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

To facilitate interpretation
and comparison with
prior work

# Motivation

- 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

−0.5 A/cm² electrolysis mode

−1.0 A/cm² electrolysis mode
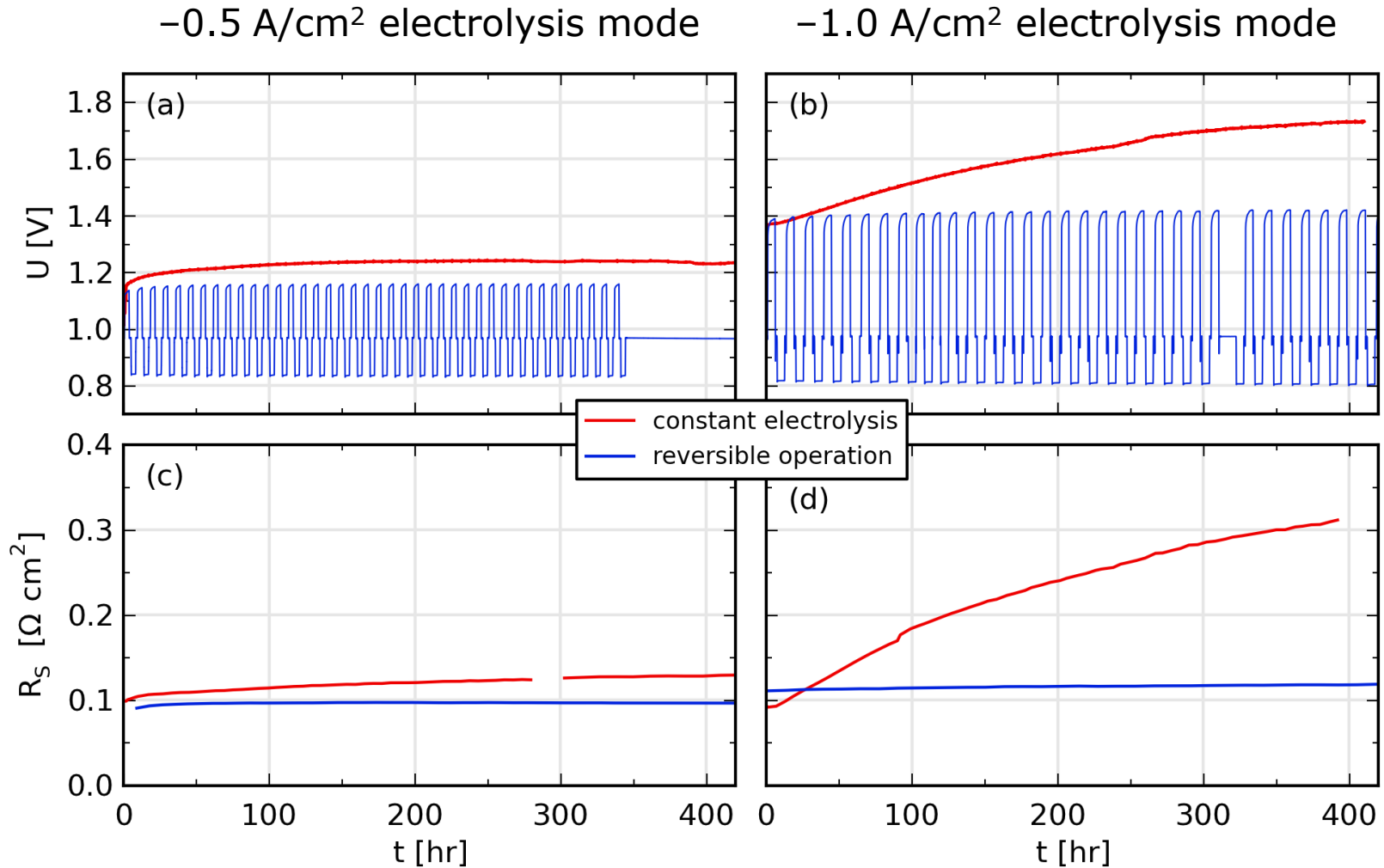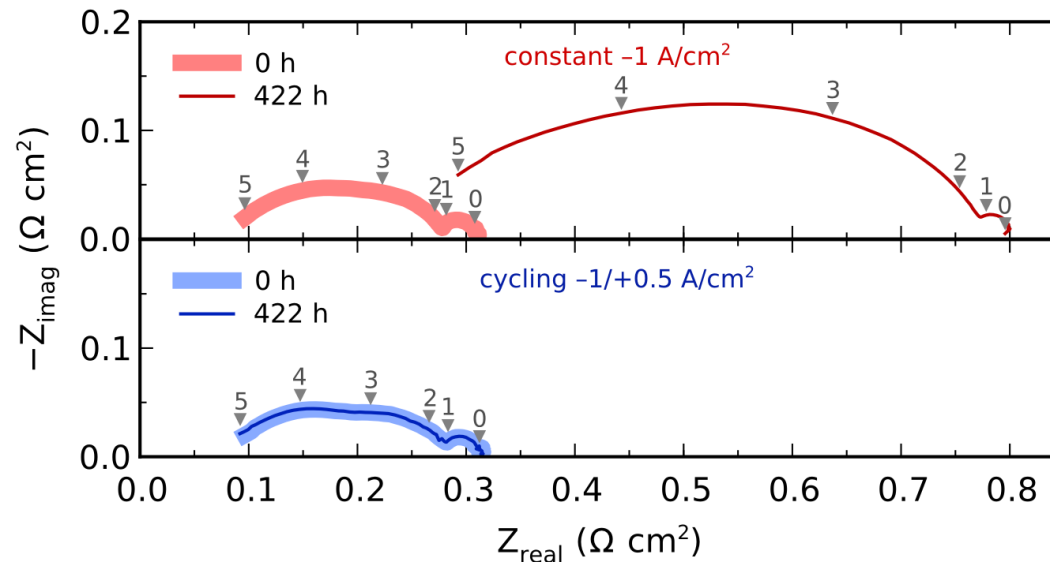
Impedance measured at open-circuit

- Initially, the 2 cells had very similar impedance before the test segments

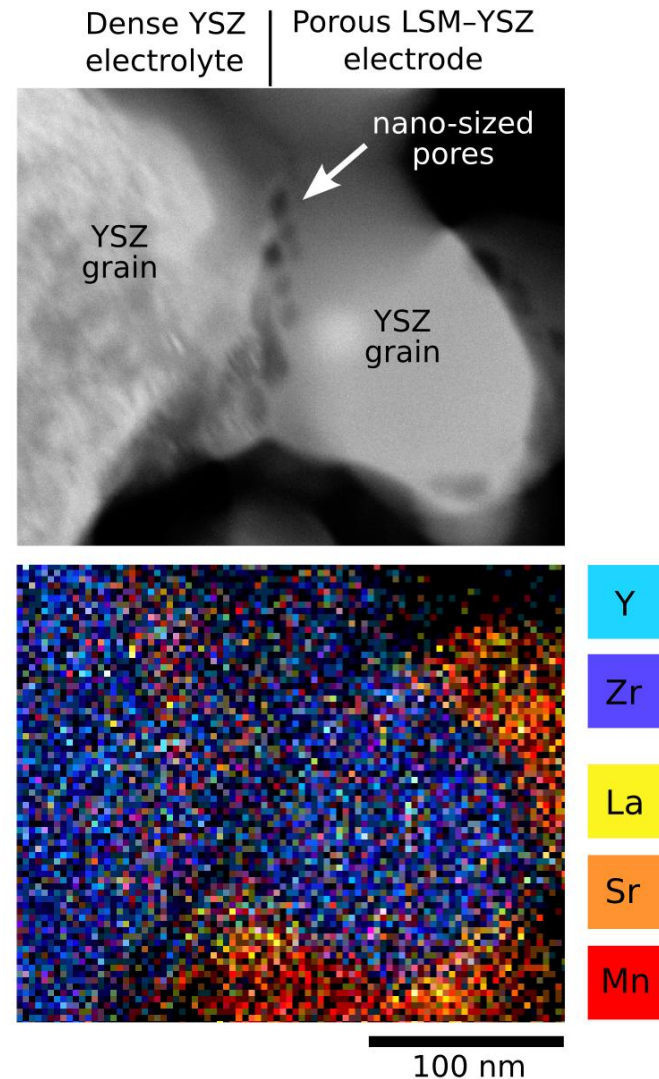- Impedance of the cell operated in constant electrolysis increased dramatically at ~$10^1$-$10^5$ Hz, and the ohmic resistance ($R_S$) increases by a factor of 2.8, showing major degradation

- Impedance of the cell operated in reversible cycling mode was nearly identical after 420 h, showing no degradation

# Mechanism of stability enhancement

- Dividing the impedance measured after constant electrolysis degradation by 2.8 almost perfectly overlays the initial spectrum

- $R_S$ and the impedance of both electrodes increased approximately by the same factor, consistent with internal loss of contact area, which could be caused by delamination at an electrode/electrolyte interface or internal microstructural damage in the electrolyte

- Supported by TEM analysis



Dense YSZ electrolyte | Porous LSM–YSZ electrode

nano-sized pores

YSZ grain

YSZ grain

Y
Zr
La
Sr
Mn

100 nm

# Nano-pore formation

- Believed to be driven by the high anodic overpotential of the oxygen-electrode during high electrolysis polarization

- The high oxygen-electrode overpotential $\eta$ yields a very high internal oxygen pressure at the oxygen-electrode/electrolyte interface

$$pO_{2,\,int} = pO_{2,\,gas} \exp\left(-\eta\,\frac{4F}{RT}\right)$$

- Precipitation of $O_2$ bubbles in closed cavities (mainly in grain boundaries)

- Increase in $R_S$ = increase in the grain boundary resistivity due to the pore formation, since $R_S$ is almost entirely YSZ electrolyte

- Continued operation can lead to even more severe microstructural damage such as complete separation of YSZ grains or delamination of the oxygen-electrode/electrolyte interface

6 September 2013

# Summary of new reversible SOC results

- Demonstrated that operating a SOC in a reversible cycling mode like a rechargeable battery leads to negligible long-term degradation compared with constant electrolysis operation

- Achieved by eliminating the severe grain-boundary breakdown that occurs near the oxygen-electrode/electrolyte interface

- Practical implications:

  - Ohmic resistance actually slightly decreased during 4000 h of reversible cycling – highly promising in terms of application of SOC technology for large-scale energy storage

- Fundamental implications:

  - Perhaps other degradation mechanisms which are considered irreversible when operating a cell solely in fuel-cell mode or electrolysis mode can be reversed when operating in charge-discharge energy storage modes, extending the lifetime or operating range, even for other types of fuel cells or other electrochemical devices

# Overall conclusions

- There are redox chemistries for RFCs with common elements (including H & C) which are competitive with conventional batteries in terms of **efficiency**

- **Resource use** and **cost** per kWh of energy stored – potential to be significantly lower than conventional batteries

- Recent long-term experimental test results show that, remarkably, reversible battery-like operation of solid oxide cells can **enhance cell stability** compared with steady-state electrolysis operation by eliminating microstructural degradation

- 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),

  and perfect capacity sizing is less important since charge mode need not always precede discharge mode (fuels can be imported to the system.)