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

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

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Sustainable Fuels from Renewable Energies workshop
IASS Potsdam Germany
Outline

• Background

• What is a reversible fuel cell

• vs Batteries

• vs Electrolysers

• Case study of 100% wind/solar using RFCs

Efficiency

Resource use

Capital cost & lifetime
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

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

O₂

4e⁻

2H₂O → 2H₂ + 45% H₂O + 45% CO₂ + 10% H₂

2CO₂

2O²⁻

Electricity mode

fuels → electricity

4e⁻

2H₂ + 45% H₂O + 45% CO₂ + 10% H₂
Solid oxide electrochemical cells

Electrolysis mode
electricity $\rightarrow$ fuels

Fuel cell mode
fuels $\rightarrow$ electricity

supply $>$ demand

supply $<$ demand

\[
\begin{align*}
4e^- &\rightarrow 2H_2O + 2CO_2 \\
2H_2O &\rightarrow 2H_2 + 2CO \\
2H_2 &\rightarrow 2H_2O + 2CO_2
\end{align*}
\]
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<table>
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</tr>
</thead>
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<tr>
<td>Resource use</td>
</tr>
<tr>
<td>Capital cost &amp; lifetime</td>
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</table>
Battery
“A device consisting of one or more* electro-chemical cells that convert stored chemical energy into electrical energy” – Merriam-Webster dictionary

*originally only >1

Galvanic/voltaic cell
“A simple device with which chemical energy is converted into electrical energy”
– Columbia Electronic Encyclopedia

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
- Examples:
  - Lithium-ion
  - Lead-acid
  - Sodium-sulfur

**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)
- Examples:
  - Vanadium redox
  - Zinc-bromine
  - Iron-chromium

**Reversible fuel cell**
- Energy stored in hydrogen/carbon atoms in reservoirs, not in electrolyte or electrodes
- Separates energy and power density
- Less expensive material used to store energy
- Energy storage medium can be energy-dense liquid hydrocarbon fuels useable in existing infrastructure
- Independent level of charging and discharging (e.g. can discharge more than, and before, charging)
- Examples:
  - $\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$
  - $\text{H}_2 + \text{Br}_2 \rightarrow \text{HBr}$
  - $\text{NH}_4\text{H}_2\text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{OH} + \text{O}_2 + \text{H}_2\text{O}$
  - $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$

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

Examples: Li⁺, Na⁺, H⁺, OH⁻, O₂⁻, CO₃⁻
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\textsubscript{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 \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{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
Is this a reversible fuel cell or a battery?


Fig. 4. Keringum diagram of Fe–O2 and P02 in charge and discharge.
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?

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

• 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
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.


• 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.

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

\[
\begin{align*}
H_2 & \quad CO \\
CH_4 & \quad C
\end{align*}
\]
Possible redox chemistries - thermodynamics

\[ \text{H}_2 \text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2} \text{O}_2 \]
\[ \text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2} \text{O}_2 \]
\[ \text{FeO} \rightleftharpoons \text{Fe} + \frac{1}{2} \text{O}_2 \]
\[ \text{CO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \]
\[ \text{CO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{CH}_4 + 2\text{O}_2 \]
\[ \text{CO}_2 \rightleftharpoons \text{C} + \text{O}_2 \]
\[ 3\text{H}_2\text{O} + \text{N}_2 \rightleftharpoons 2\text{NH}_3 + \frac{3}{2} \text{O}_2 \]
\[ 2\text{HCl} \rightleftharpoons \text{H}_2 + \text{Cl}_2 \]
\[ 2\text{HBr} \rightleftharpoons \text{H}_2 + \text{Br}_2 \]

\[ \text{NH}_3 \]
\[ \text{H}_2/\text{Cl}_2 \]
\[ \text{H}_2/\text{Br}_2 \]
Possible redox chemistries - thermodynamics

- $\text{H}_2 \rightleftharpoons \text{H}_2 + \frac{1}{2} \text{O}_2$
- $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2} \text{O}_2$
- $\text{FeO} \rightleftharpoons \text{Fe} + \frac{1}{2} \text{O}_2$

- $\text{CO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2$
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- $2\text{HBr} \rightleftharpoons \text{H}_2 + \text{Br}_2$

- $\text{NH}_3$
- $\text{H}_2/\text{Cl}_2$
- $\text{H}_2/\text{Br}_2$
Possible redox chemistries – max. roundtrip efficiencies

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).

Li-air and Na-S batteries

- $Li_2O = 2Li + \frac{1}{2}O_2$
- $\frac{1}{2}Li_2O_2 = Li + \frac{1}{2}O_2$
- $Na_2S_4 = 2Na + 4S$
Possible redox chemistries – max. roundtrip efficiencies

$H_2$ and CO

$H_2O(l) = H_2 + \frac{1}{2}O_2$

$H_2O(g) = H_2 + \frac{1}{2}O_2$

$CO_2 = CO + \frac{1}{2}O_2$

$Li_2O = 2Li + \frac{1}{2}O_2$

$\frac{1}{2}Li_2O_2 = Li + \frac{1}{2}O_2$

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Possible redox chemistries – max. roundtrip efficiencies

\[ \text{CH}_4 \]

\[ \begin{align*}
H_2O(l) &= H_2 + \frac{1}{2}O_2 \\
H_2O(g) &= H_2 + \frac{1}{2}O_2 \\
CO_2 &= CO + \frac{1}{2}O_2 \\
CO_2 + 2H_2O(l) &= CH_4 + 2O_2 \\
CO_2 + 2H_2O(g) &= CH_4 + 2O_2 \\
Li_2O &= 2Li + \frac{1}{2}O_2 \\
\frac{1}{2}Li_2O_2 &= Li + \frac{1}{2}O_2 \\
Na_2S_4 &= 2Na + 4S
\end{align*} \]
Possible redox chemistries – max. roundtrip efficiencies

\[ \text{NH}_3 \]
Possible redox chemistries – max. roundtrip efficiencies

HCl and HBr
Possible redox chemistries – max. roundtrip efficiencies
Efficiency

• 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 700°C

$\eta = 0.1 \text{ V for all cells (e.g. } 0.5 \text{ A/cm}^2 \times 0.2 \text{ }\Omega \text{ cm}^2 \text{) 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$^{-20}\%$.

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.

• Efficiencies estimated by full system energy balance studies

Prof. Braun (Colorado) is working on one, for the "partial CH₄" chemistry
Efficiency

- Maximum theoretical efficiency → practical efficiency $\varepsilon$
  - Overpotentials $\eta$ to actually produce current
  - Heat losses
  - Energy consumed by balance of system
- Example: $\text{H}_2$ vs $\text{CH}_4$ 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 $\varepsilon(\text{H}_2) = 69\%$ and $\varepsilon(\text{CH}_4) = 86\%$. + Heat and system losses ~10-20%.
Efficiency

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- Example: $\text{H}_2$ vs $\text{CH}_4$ at 600 °C
  - $\eta = 0.1 \text{ V}$ 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 $\varepsilon(\text{H}_2) = 69\%$ and $\varepsilon(\text{CH}_4) = 86\%$. + 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 $\varepsilon(\text{CH}_4)$ because both modes are exothermic, but it does not affect $\varepsilon(\text{H}_2)$ 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)

![Graph showing material per kWh storage](image)

- NiMH battery
- Ni-YSZ based solid oxide cell

- 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**
- Anode support material: 1%
- Other materials: 1%
- Interconnect: 6%
- Misc: 14%
- Power electronics: 28%
- Recuperator: 19%
- Blowers: 11%
- Gas conditioning: 20%
- Capital charge: 8%
- Labor & utilities: 6%
- Maintenance: 2%
- Balance of stack: 4%

**Alkaline fuel/electrolysis cell**
- Vessel Cost: 6%
- Plastic cost: 12%
- Electrode cost: 4%
- Gas conditioning: 20%
- Misc: 29%
- Power electronics: 25%
- Assembly labor: 5%
- Blowers: 11%
- Recuperator: 19%

**Balance of system dominates!**

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

Data collected from:
Economics – capital cost breakdowns ($/kWh)

Solid oxide cell

- Anode support material: 2%
- Other materials: 1%
- Interconnect: 9%
- Capital charge: 13%
- Labor & utilities: 9%
- Maintenance: 3%
- Balance of stack: 6%
- Blowers: 9%
- Recuperator: 15%
- Power electronics: 22%
- Misc: 11%

Assuming BoS life is 2x that of stack.

Li-ion battery

- Other: 20%
- Materials: 77%
- Manuf.: 3%


Opposite!

Li-ion mass production is optimized and cost reduction potential is relatively limited.
## Simple economics estimations

<table>
<thead>
<tr>
<th>Battery</th>
<th>CAPEX (U.S. cents/kWh elec)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb-acid</td>
<td>15 – 40</td>
<td># cycles (700-1800), DOD</td>
</tr>
<tr>
<td>Li-ion</td>
<td>5 – 17</td>
<td># cycles (1000-8500), DOD</td>
</tr>
<tr>
<td>NiMH</td>
<td>15 – 20</td>
<td># cycles (1000-3000), DOD</td>
</tr>
<tr>
<td>V redox</td>
<td>16</td>
<td>10 000 cycles</td>
</tr>
<tr>
<td>SOC</td>
<td>1.5 – 9</td>
<td>5-10 yr, $500-2000/kW</td>
</tr>
</tbody>
</table>
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Efficiency
Resource use
Capital cost & lifetime
Denmark’s need for energy storage

4% storage capacity factor

13% storage capacity factor
If we will turn around and convert it right back to electricity, need not be convenient, portable, high energy density and plug into existing infrastructure – need not be liquid hydrocarbon storage.

Electrolytic CO$_2$-to-fuels economics

Reversible fuel cell capacity factor

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

<table>
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<tr>
<th></th>
<th>Sell electricity (spot market arbitrage)</th>
<th>Sell fuel (e.g. transportation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Battery</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Electrolyser</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Reversible fuel cell</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

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
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

Dense YSZ electrolyte | Porous LSM-YSZ electrode

YSZ grain

nano-sized pores

YSZ grain

100 nm
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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 \( \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{O}_2 \)
  – 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 \( \text{CO}_2 \))

• 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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