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

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

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ISACS12: Challenges in Chemical Renewable Energy
Cambridge, UK
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

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

45% $\text{H}_2\text{O}$
45% $\text{CO}_2$
10% $\text{H}_2$
Solid oxide electrochemical cells

Electrolysis mode
electricity $\rightarrow$ fuels

Fuel cell mode
fuels $\rightarrow$ electricity

$\text{O}_2$

$\text{2O}_2^-$

$\text{2H}_2$ $\text{2CO}$

$\text{2H}_2$ $\text{2H}_2\text{O}$ $\text{2CO}_2$

$\text{4e}^-$

$\text{2H}_2\text{O}$ $\text{2CO}_2$

$\text{4e}^-$
Using solid oxide cells as batteries

Electrolysis (charge) mode

- Porous oxygen-electrode: \( \frac{1}{2}O_2 \rightarrow \frac{1}{2}O_2 + 2e^- \)
- Dense electrolyte: \( O^{2-} \) conduction
- Porous fuel-electrode:
  - \( H_2O + 2e^- \rightarrow H_2 + O^{2-} \)
  - \( CO_2 + 2e^- \rightarrow CO + O^{2-} \)
- \( H_2 + CO_2 \leftrightarrow H_2O + CO \)
- \( 3H_2 + CO \leftrightarrow CH_4 + H_2O \)
- \( 4H_2 + CO_2 \leftrightarrow CH_4 + 2H_2O \)

Fuel-cell (discharge) mode

- \( \frac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \)
- \( O^{2-} \) conduction
- \( H_2 + O^{2-} \rightarrow H_2O + 2e^- \)
- \( CO + O^{2-} \rightarrow CO_2 + 2e^- \)
- \( H_2O + CO \leftrightarrow H_2 + CO_2 \)
- \( CH_4 + H_2O \leftrightarrow 3H_2 + CO \)
- \( CH_4 + 2H_2O \leftrightarrow 4H_2 + CO_2 \)
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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

*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**
- **Charge**: Energy stored in metal atoms on electrodes
- **Discharge**: Energy stored in metal atoms on electrodes

**Flow battery**
- **Charge**: 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)
- **Discharge**: Energy stored in hydrogen/carbon atoms in reservoirs, not in electrolyte or electrodes

**Reversible fuel cell**
- **Charge**: 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 infrastructure
- **Discharge**: Energy stored in hydrogen/carbon atoms in reservoirs, not in electrolyte or electrodes

**Examples:**
- **Battery**
  - Lithium-ion
  - Lead-acid
  - Sodium-sulfur
- **Flow battery**
  - Vanadium redox
  - Zinc-bromine
  - Iron-chromium
- **Reversible fuel cell**
  - CO+O2 / CO2
  - CH4+O2 / CO2+H2O
  - CH3OH+O2 / CO2+H2O
  - C+O2 / CO2

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 H₂ 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 H₂O → H₂ + O₂ 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

Briefly, more about categorization:

Is this a reversible fuel cell or a battery?


Fig. 4. Keringum diagram of Fe–O2 and P02 in charge and discharge.
• 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)...
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6. Case study of an island in Denmark powered by 100% wind
Possible redox chemistries

• Selecting from the entire periodic table is possible...

• 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

\[ \text{H}_2, \text{CH}_4, \text{CO}, \text{C} \]
Possible redox chemistries - thermodynamics

\[ \text{H}_2 \text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2} \text{O}_2 \]
\[ \text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2} \text{O}_2 \]
\[ \text{FeO} \rightleftharpoons \text{Fe} + \frac{1}{2} \text{O}_2 \]

\[ \text{CO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \]
\[ \text{CO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{CH}_4 + 2\text{O}_2 \]
\[ \text{CO}_2 \rightleftharpoons \text{C} + \text{O}_2 \]

\[ 3\text{H}_2\text{O} + \text{N}_2 \rightleftharpoons 2\text{NH}_3 + \frac{3}{2} \text{O}_2 \]
\[ 2\text{HCl} \rightleftharpoons \text{H}_2 + \text{Cl}_2 \]
\[ 2\text{HBr} \rightleftharpoons \text{H}_2 + \text{Br}_2 \]

Universities involved:
- Univ. S. Carolina
- Kyushu Univ.
- DTU
- Northwestern
- Univ. Kansas
- MIT
- Harvard
- Dalian, China
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).

- $\text{Li}_2\text{O} = 2\text{Li} + \frac{1}{2}\text{O}_2$
- $\frac{1}{2}\text{Li}_2\text{O}_2 = \text{Li} + \frac{1}{2}\text{O}_2$
- $\text{Na}_2\text{S}_4 = 2\text{Na} + 4\text{S}$
Possible redox chemistries – max. roundtrip efficiencies

$H_2$ and CO

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

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

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

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

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

$Na_2S_4 = 2Na + 4S$
Possible redox chemistries – max. roundtrip efficiencies

\[ \text{CH}_4 \]

\[ \begin{align*}
\text{H}_2\text{O}(l) &= \text{H}_2 + \frac{1}{2}\text{O}_2 \\
\text{H}_2\text{O}(g) &= \text{H}_2 + \frac{1}{2}\text{O}_2 \\
\text{CO}_2 &= \text{CO} + \frac{1}{2}\text{O}_2 \\
\text{CO}_2 + 2\text{H}_2\text{O}(l) &= \text{CH}_4 + 2\text{O}_2 \\
\text{CO}_2 + 2\text{H}_2\text{O}(g) &= \text{CH}_4 + 2\text{O}_2 \\
\text{Li}_2\text{O} &= 2\text{Li} + \frac{1}{2}\text{O}_2 \\
\frac{1}{2}\text{Li}_2\text{O}_2 &= \text{Li} + \frac{1}{2}\text{O}_2 \\
\text{Na}_2\text{S}_4 &= 2\text{Na} + 4\text{S}
\end{align*} \]
Possible redox chemistries – max. roundtrip efficiencies

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

HCl and HBr
Possible redox chemistries – max. roundtrip efficiencies

C and Fe
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: $\text{H}_2$ vs $\text{CH}_4$ at 700°C

$\eta = 0.1 \text{ V}$ for all cells (e.g. $0.5 \text{ A/cm}^2 \times 0.2 \text{ } \Omega \text{ cm}^2$) 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 $\approx 10^{-20}\%$.

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 $\varepsilon(\text{CH}_4)$ because both modes are exothermic, but it does not affect $\varepsilon(\text{H}_2)$ until electrolysis operation rises above thermoneutral.

• Efficiencies estimated by full-system energy balance studies
  – Prof. Braun (Colorado) is working on one, for the “partial CH$_4$” chemistry.
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: $\text{H}_2$ vs $\text{CH}_4$ at 600 °C
  - $\eta = 0.1$ V for all cells (e.g. $0.5 \text{ A/cm}^2 \times 0.2 \Omega \text{ cm}^2$) 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 $\sim10$-$20\%$. 
Possible redox chemistries

• Maximum theoretical efficiency → 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 $\sim$10-20%.
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because both modes are exothermic, but it does not affect $\varepsilon(H_2)$ until
electrolysis operation rises above thermoneutral.
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Resource Use

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

![Bar chart showing 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%
- Misc: 14%
- Power electronics: 28%
- Recuperator: 19%
- Blowers: 11%
- Gas conditioning: 20%
- Vessel Cost: 6%
- Electrode cost: 4%
- Balance of stack: 4%
- Power electronics: 25%
- Misc: 29%
- Assembly labor: 5%
- Recuperator: 19%
- Power electronics: 25%
- Misc: 29%
- Assembly labor: 5%

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

**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:
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
## 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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   Article submitted, in review
Long-term testing of 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 \( \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{O}_2 \)

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

1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0

U [V]

0 100 200 300 400

0 100 200 300 400

t [hr]

-1.0 A/cm² electrolysis mode

R_s [Ω cm²]

0.3
0.2
0.1
0.0

0 100 200 300 400

t [hr]

constant electrolysis
reversible operation
Results – impedance

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

- Impedance of the cell operated in constant electrolysis increased dramatically at \(\sim 10^1-10^5\) 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.
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

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

- 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
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 CO₂)

• 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.)