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

oxidation: $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + 2\text{CO}_2$

reduction: $2\text{O}^2- \rightarrow 2\text{O}_2, 4e^{-}$

45% $\text{H}_2\text{O}$

+ 45% $\text{CO}_2$

+ 10% $\text{H}_2$
Solid oxide electrochemical cells

Electrolysis mode

+ electricity → fuels

Fuel cell mode

fuels → electricity

\[ 2\text{H}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 4e^- + \text{O}_2 \]

\[ 2\text{CO} + \text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 2\text{H}^+ + 2e^- \]

\[ 2\text{H}_2 + 2\text{O}_2 \rightarrow 4\text{H}^+ + 4e^- + 2\text{H}_2\text{O} \]

\[ 2\text{CO} + 2\text{O}_2 \rightarrow 2\text{CO}_2 + 4\text{H}^+ + 4e^- \]

Graph showing the cell voltage [V] vs. current density [A/cm²] with a peak at 50% H₂O/H₂.
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
- \( H_2 + O^{2-} \rightarrow H_2O + 2e^- \)
- \( CO + O^{2-} \rightarrow CO_2 + 2e^- \)
- \( H_2O + CO \leftrightarrow H_2 + CO_2 \)
- \( CH_4 + H_2O \leftrightarrow 3H_2 + CO \)
- \( CH_4 + 2H_2O \leftrightarrow 4H_2 + CO_2 \)

\( H_2 \) and \( CO \) are imported as needed.
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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: 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 metal atoms in reservoirs of electrolyte solutions, not on the electrodes

**Reversible fuel cell**
- Charge: 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 usable 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
  - Nickel metal hydride
  - Nickel-cadmium
  - Metal-air (special case)

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

- **Reversible fuel cell**
  - H₂ + O₂ / H₂O
  - H₂ + Br₂ / HBr
  - NH₃ + O₂ / N₂ + H₂O
  - CO + O₂ / CO₂
  - CH₄ + O₂ / CO₂ + H₂O
  - C + O₂ / CO₂

**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
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...
  – 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

$\text{H}_2$  CO

$\text{CH}_4$  C
Possible redox chemistries - thermodynamics

- **FeO** $\rightleftharpoons$ Fe $+ \frac{1}{2}O_2$
- **CO** $\rightleftharpoons$ CO $+ \frac{1}{2}O_2$
- **H$_2$O** $\rightleftharpoons$ H$_2$ $+ \frac{1}{2}O_2$
- **CO$_2$** $\rightleftharpoons$ CO $+ \frac{3}{2}O_2$
- **H$_2O$** $\rightleftharpoons$ CH$_3$OH $+ \frac{3}{2}O_2$
- **CH$_4$** $\rightleftharpoons$ C $+ 2O_2$
- **H$_2$** $\rightleftharpoons$ 2H
- **H$_2Cl$** $\rightleftharpoons$ H$_2$ $+ Cl_2$
- **NH$_3$** $\rightleftharpoons$ 2NH$_3$ $+ \frac{3}{2}O_2$
- **H$_2Br$** $\rightleftharpoons$ H$_2$ $+ Br_2$
- **FeO** $\rightleftharpoons$ Fe $+ \frac{1}{2}O_2$
- **H$_2Cl$** $\rightleftharpoons$ H$_2$ $+ Cl_2$
- **NH$_3$** $\rightleftharpoons$ 2NH$_3$ $+ \frac{3}{2}O_2$
- **H$_2Br$** $\rightleftharpoons$ H$_2$ $+ Br_2$

Universities:
- 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).

Li-air and Na-S batteries

$\text{Li}_2\text{O} \rightarrow 2\text{Li} + \frac{1}{2}\text{O}_2$

$\frac{1}{2}\text{Li}_2\text{O}_2 \rightarrow \text{Li} + \frac{1}{2}\text{O}_2$

$\text{Na}_2\text{S}_4 \rightarrow 2\text{Na} + 4\text{S}$
Possible redox chemistries – max. roundtrip efficiencies

\[ H_2 \text{ and CO} \]
Possible redox chemistries – max. roundtrip efficiencies

\[ \text{CH}_4 \]
Possible redox chemistries – max. roundtrip efficiencies

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

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

\[
\begin{align*}
2H_2O(l) &= H_2 + \frac{1}{2}O_2 \\
2H_2O(g) &= H_2 + \frac{1}{2}O_2 \\
CO_2 &= CO + \frac{1}{2}O_2 \\
CO_2 + 2H_2O(l) &= CH_4 + 2O_2 \\
CO_2 + 2H_2O(g) &= CH_4 + 2O_2 \\
3H_2O(l) + N_2 &= 2NH_3 + \frac{3}{2}O_2 \\
3H_2O(g) + N_2 &= 2NH_3 + \frac{1}{2}O_2 \\
2HCl &= H_2 + Cl_2 \\
2HBr &= H_2 + Br_2 (l) \\
2HBr &= H_2 + Br_2 (g) \\
CO_2 &= C + O_2 \\
FeO &= Fe + \frac{1}{2}O_2 \\
Li_2O &= 2Li + \frac{1}{2}O_2 \\
\frac{1}{2}Li_2O_2 &= Li + \frac{1}{2}O_2 \\
Na_2S_4 &= 2Na + 4S
\end{align*}
\]
Possible redox chemistries

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

– $\eta = 0.1$ V for all cells (e.g. $0.5$ A/cm$^2 \times 0.2 \Omega$ 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%.

– 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.
Possible redox chemistries

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

  ![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)
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Economics – capital cost breakdowns

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:
Economics – capital cost breakdowns

Solid oxide cell

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

Li-ion battery

<table>
<thead>
<tr>
<th>Level of Integration</th>
<th>Cost Category</th>
<th>Total ($/kWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Materials</td>
<td>Manufacturing</td>
</tr>
<tr>
<td>Cell</td>
<td>734.53</td>
<td>23.15</td>
</tr>
<tr>
<td>Module</td>
<td>771.79</td>
<td>26.77</td>
</tr>
<tr>
<td>Pack</td>
<td>864.38</td>
<td>31.68</td>
</tr>
</tbody>
</table>

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**
- $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + 2\text{CO}_2$
- $4\text{e}^-$

**Fuel cell mode**
- **fuels → electricity**
- $2\text{H}_2 + 2\text{O}_2 \rightarrow 2\text{H}_2\text{O}$
- $4\text{e}^-$

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

-1.0 A/cm² electrolysis mode

(a) (b) (c) (d)

U [V] t [hr]

constant electrolysis reversible operation

R_s [Ω cm²]

0.1 0.2 0.3 0.4

0.0 0.1 0.2 0.3

0 100 200 300 400

0 100 200 300 400

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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 $R_S = \text{increase in the grain boundary resistivity due to the pore formation, since } R_S \text{ is almost entirely YSZ electrolyte}$
- 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.)