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

Graves, Christopher R.

Publication date: 2013

Citation (APA): Graves, C. R. (Author). (2013). Are reversible fuel cells better batteries for large-scale renewable energy storage?. Sound/Visual production (digital)
Are reversible fuel cells better batteries for large-scale renewable energy storage?

Chris Graves, cgra@dtu.dk
PhD, Scientist
Technical University of Denmark

6th September 2013
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

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

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

45% H\textsubscript{2}O

+ 45% CO\textsubscript{2}

+ 10% H\textsubscript{2}
Solid oxide electrochemical cells

Electrolysis mode

Electricity $\rightarrow$ fuels

$$4e^- \rightarrow 2H_2O \rightarrow 2H_2 + 2CO_2$$

Fuel cell mode

Fuels $\rightarrow$ electricity

$$2H_2 + 2CO \rightarrow 2H_2O + 2CO_2$$
Using solid oxide cells as batteries

**Electrolysis (charge) mode**

- **O₂ / air**
- Porous oxygen-electrode: \( \text{O}_2^- \rightarrow \frac{1}{2}\text{O}_2 + 2\text{e}^- \)
- Dense electrolyte: \( \text{O}_2^- \) conduction
- Porous fuel-electrode:
  - \( \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + \text{O}_2^- \)
  - \( \text{CO}_2 + 2\text{e}^- \rightarrow \text{CO} + \text{O}_2^- \) [electrochemical]
  - \( \text{H}_2 + \text{CO}_2 \leftrightarrow \text{H}_2\text{O} + \text{CO} \)
  - \( 3\text{H}_2 + \text{CO} \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \)
  - \( 4\text{H}_2 + \text{CO}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O} \) [catalytic]

\( 2\text{e}^- \rightarrow \) export as needed

**Fuel-cell (discharge) mode**

- \( \frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{O}_2^- \)
- \( \text{O}_2^- \) conduction
- \( \text{H}_2 + \text{O}_2^- \rightarrow \text{H}_2\text{O} + 2\text{e}^- \)
- \( \text{CO} + \text{O}_2^- \rightarrow \text{CO}_2 + 2\text{e}^- \)
- \( \text{H}_2\text{O} + \text{CO} \leftrightarrow \text{H}_2 + \text{CO}_2 \)
- \( \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow 3\text{H}_2 + \text{CO} \)
- \( \text{CH}_4 + 2\text{H}_2\text{O} \leftrightarrow 4\text{H}_2 + \text{CO}_2 \)

\( 2\text{e}^- \rightarrow \) import as needed
1. **Background**

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

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

4. **Resource use**

5. **Economics**

6. **Recent experimental results**
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**
- **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 infrastructure

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

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

- **Reversible fuel cell**
  - $H_2O_2 / H_2O$
  - $H_2O_2 / HBr$
  - $NH_3O_2 / N_2 + H_2O$
  - $CO + O_2 / CO_2$
  - $CH_4O_2 / CO_2 + H_2O$
  - $CH_2OH + O_2 / CO_2 + H_2O$
  - $C + O_2 / CO_2$
  - $Li^+; Na^+; H^+; OH^-; O^-; CO_3^-$

Note: For each, the charge carrier in the electrolyte need not necessarily be a positive species.
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 \( \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}_2 \) 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
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.


• 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

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...

• 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

Relative abundance of the chemical elements in Earth’s upper continental crust

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

\[
\begin{align*}
\text{H}_2 & \quad \text{CO} \\
\text{CH}_4 & \quad \text{C}
\end{align*}
\]
Possible redox chemistries - thermodynamics

\[
\begin{align*}
\text{H}_2 & \Leftrightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \\
\text{CO} & \Leftrightarrow \text{CO} + \frac{1}{2} \text{O}_2 \\
\text{FeO} & \Leftrightarrow \text{Fe} + \frac{1}{2} \text{O}_2 \\
\text{CO}_2 + 2\text{H}_2\text{O} & \Leftrightarrow \text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \\
\text{CO}_2 + 2\text{H}_2\text{O} & \Leftrightarrow \text{CH}_4 + 2\text{O}_2 \\
\text{CO}_2 & \Leftrightarrow \text{C} + \text{O}_2 \\
3\text{H}_2\text{O} + \text{N}_2 & \Leftrightarrow 2\text{NH}_3 + \frac{3}{2} \text{O}_2 \\
2\text{HCl} & \Leftrightarrow \text{H}_2 + \text{Cl}_2 \\
2\text{HBr} & \Leftrightarrow \text{H}_2 + \text{Br}_2 \\
\text{NH}_3 & \\
\text{H}_2/\text{Cl}_2 & \\
\text{H}_2/\text{Br}_2 &
\end{align*}
\]
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

$H_2$ and CO
Possible redox chemistries – max. roundtrip efficiencies

\[ \text{CH}_4 \]

Graph showing the maximum round-trip efficiency as a function of temperature (T) for different chemistries, including:

- \( \text{H}_2\text{O}(l) = \text{H}_2 + \frac{1}{2}\text{O}_2 \)
- \( \text{H}_2\text{O}(g) = \text{H}_2 + \frac{1}{2}\text{O}_2 \)
- \( \text{CO}_2 = \text{CO} + \frac{1}{2}\text{O}_2 \)
- \( \text{CO}_2 + 2\text{H}_2\text{O}(l) = \text{CH}_4 + 2\text{O}_2 \)
- \( \text{CO}_2 + 2\text{H}_2\text{O}(g) = \text{CH}_4 + 2\text{O}_2 \)
- \( \text{Li}_2\text{O} = 2\text{Li} + \frac{1}{2}\text{O}_2 \)
- \( \frac{1}{2}\text{Li}_2\text{O}_2 = \text{Li} + \frac{1}{2}\text{O}_2 \)
- \( \text{Na}_2\text{S}_4 = 2\text{Na} + 4\text{S} \)
Possible redox chemistries – max. roundtrip efficiencies

NH₃
Possible redox chemistries – max. roundtrip efficiencies

HCl and HBr
Possible redox chemistries – max. roundtrip efficiencies

- $\text{H}_2\text{O}(l) = \text{H}_2 + \frac{1}{2}\text{O}_2$
- $\text{H}_2\text{O}(g) = \text{H}_2 + \frac{1}{2}\text{O}_2$
- $\text{CO}_2 = \text{CO} + \frac{1}{2}\text{O}_2$
- $\text{CO}_2 + 2\text{H}_2\text{O}(l) = \text{CH}_4 + 2\text{O}_2$
- $\text{CO}_2 + 2\text{H}_2\text{O}(g) = \text{CH}_4 + 2\text{O}_2$
- $3\text{H}_2\text{O}(l) + \text{N}_2 = 2\text{NH}_3 + \frac{3}{2}\text{O}_2$
- $3\text{H}_2\text{O}(g) + \text{N}_2 = 2\text{NH}_3 + \frac{1}{2}\text{O}_2$
- $2\text{HCl} = \text{H}_2 + \text{Cl}_2$
- $2\text{HBr} = \text{H}_2 + \text{Br}_2 (l)$
- $2\text{HBr} = \text{H}_2 + \text{Br}_2 (g)$
- $\text{CO}_2 = \text{C} + \text{O}_2$
- $\text{FeO} = \text{Fe} + \frac{1}{2}\text{O}_2$
- $\text{Li}_2\text{O} = 2\text{Li} + \frac{1}{2}\text{O}_2$
- $\frac{1}{2}\text{Li}_2\text{O}_2 = \text{Li} + \frac{1}{2}\text{O}_2$
- $\text{Na}_2\text{S}_4 = 2\text{Na} + 4\text{S}$
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 700° 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%.

– 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
  - \( \eta = 0.1 \) 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 \( \varepsilon(\text{H}_2) = 69\% \) and \( \varepsilon(\text{CH}_4) = 86\% \). Heat and system losses \( \sim 10-20\% \).
Possible redox chemistries

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

• Example: $\text{H}_2$ vs $\text{CH}_4$ at 600 °C
  – $\eta = 0.1$ V for all cells (e.g. 0.5 A/cm$^2$ x 0.2 $\Omega$ 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 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.
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
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](attachment:material_per_kWh.png)

  - 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)
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
Economics – capital cost breakdowns

Solid oxide cell

- Power electronics: 28%
- Recuperator: 19%
- Blowers: 11%
- Misc: 14%
- Anode support material: 1%
- Interconnect: 6%
- Other materials: 1%

Alkaline fuel/electrolysis cell

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

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><strong>Cell</strong></td>
<td>734.53</td>
<td>23.15</td>
</tr>
<tr>
<td><strong>Module</strong></td>
<td>771.79</td>
<td>26.77</td>
</tr>
<tr>
<td><strong>Pack</strong></td>
<td>864.38</td>
<td>31.68</td>
</tr>
</tbody>
</table>

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


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
### 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>
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
   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
H₂O ↔ H₂ + O₂

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]

Rₛ [Ω cm²]

t [hr]

constant electrolysis
reversible operation
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 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.)