Redox flow batteries - Hydrogen Production

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Analytical Chemistry

Electrophoresis
Electroanalysis
Mass Spectrometry
Electrochemical Microscopy

Physical Chemistry

Energy Conversion
Supercritical CO₂ Reduction
Electron Transfer at Soft Interfaces
Redox Flow Batteries

H₂O → H₂ + D₂ + H⁺
Supercritical CO₂ phase
Water Phase

EPFL École Polytechnique Fédérale de Lausanne
The beginning of a new era…
Solar irradiation and energy consumption

Solar radiation is higher at the equator, and lower further north and south. If covered in solar panels, each blue spot would provide more than the world's current energy demand.

The Sheffield Solar Farm

NASA
Photovoltaic Solar Electricity Potential in European Countries

Yearly sum of global irradiation incident on optimally-inclined south-oriented photovoltaic modules

Global irradiation [kWh/m²]

<600  800  1000  1200  1400  1600  1800  2000  2200

Yearly sum of solar electricity generated by 1 kWp system with optimally-inclined modules and performance ratio 0.75

Solar electricity [kWh/kWp]

<450  600  750  900  1050  1200  1350  1500  1650

© European Communities, 2006

http://re.jrc.ec.europa.eu/pvgis/
The new turbine at Gries, Switzerland, is higher than any other in Europe. The site was chosen because of the good electrical connection at the adjacent hydro-dam. Photo: obs/SIG Services Industriels de Genève
Swiss Electricity
German Electricity production
Swiss Storage
Les barrages sont de gigantesques batteries, avec des rendements de l’ordre de 80%. «Ce sont les batteries les plus efficaces du monde», Eric Wuilloud, Directeur de Nant de Drance SA.

Avec un coût d’environ deux milliards de francs, les conditions actuelles du marché ne lui permettraient pas d’être rentable.

«La durée de vie d’une telle installation est d’environ 80 ans.»
1. Sendai Substation Lithium Ion Battery Pilot Project
   Sendai, Miyagi, Japan
   Lithium Ion Battery
   Rated Power: 40,000 kW

2. Duke Energy Business Services Notrees Wind Storage Demonstration Project
   Goldsmith, Texas
   Advanced Lead Acid Battery
   Rated Power: 36,000 kW

3. Rokkasho Village Wind Farm
   Rokkasho, Japan
   Sodium Sulfur Battery
   Rated Power: 34,000 kW
Citigroup estimates a 240GW global market for energy storage worth more than $400 billion by 2030. That is excluding car batteries.
Technology
Wall mounted, rechargeable lithium ion battery with liquid thermal control.

Models
10 kWh $3,500
For backup applications
7 kWh $3,000
For daily cycle applications

Warranty
Ten year warranty with an optional ten year extension.

Efficiency
92% round-trip DC efficiency

Power
2.0 kW continuous, 3.3 kW peak

Voltage
350 – 450 volts

Current
5 amp nominal, 8.5 amp peak output

Compatibility
Single phase and three phase utility grid compatible.

Operating Temperature
-4°F to 110°F / -20°C to 43°C

Enclosure
Rated for indoor and outdoor installation.

Installation
Requires installation by a trained electrician. AC-DC inverter not included.

Weight
220 lbs / 100 kg

Dimensions
52.1" x 33.9" x 7.1"
130 cm x 86 cm x 18 cm

Certifications
UL listed
Mercedes-Benz takes on Tesla with a home battery of its own

Each pack only holds 2.5kWh of electricity, but you can combine up to eight of them to hold 20kWh

http://www.engadget.com/2015/06/09/mercedes-benz-home-battery/
The following powers can be selected directly:

<table>
<thead>
<tr>
<th>Power</th>
<th>Connection voltage</th>
<th>Battery capacity</th>
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<tbody>
<tr>
<td>100 kW</td>
<td>400 V / AC / 50 Hz</td>
<td>&gt;= 60 kWh</td>
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<tr>
<td>150 kW</td>
<td>400 V / AC / 50 Hz</td>
<td>&gt;= 60 kWh</td>
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<tr>
<td>200 kW</td>
<td>400 V / AC / 50 Hz</td>
<td>&gt;= 100 kWh</td>
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<tr>
<td>500 kW</td>
<td>Mittelspannung 10 kV / 20 kV</td>
<td>&gt;= 250 kWh</td>
</tr>
<tr>
<td>650 kW</td>
<td>Mittelspannung 10 kV / 20 kV</td>
<td>&gt;= 300 kWh</td>
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<tr>
<td>1.000 kW</td>
<td>Mittelspannung 10 kV / 20 kV</td>
<td>&gt;= 500 kWh</td>
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<tr>
<td>1.300 kW</td>
<td>Mittelspannung 10 kV / 20 kV</td>
<td>&gt;= 600 kWh</td>
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</table>
Megabatteries vs Gas turbines

Average cost of generating electricity over the lifetime of the system
Economy of scale
vs
Economy of mass production

Centralised production
Power Plants
Emission & Waste

Distributed Production & Storage
Many different types of Chemistry
Many Suppliers
Price decreases with volume
Does it still make sense?
Extra-high voltage in the transmission system (level 1)
The transmission grid absorbs the electricity produced by the big power plants or in neighbouring countries. The electricity is transported at a voltage of 380 kV or 220 kV to the vicinity of the consumer. Here it is fed into the lower grid levels, the distribution grids. The Swiss transmission grid is the property of Swissgrid.

High voltage in the supra-regional distribution system (level 3)
In the high voltage level electricity is distributed for supra-regional supply at 50 to 150 kV to cantonal, regional and municipal distribution grid operators and to major industrial plants.

Medium voltage in the regional distribution system (level 5)
Medium voltage from 10 kV to 35 kV is used for the regional distribution of electricity. Local distribution grids supply individual suburbs or villages and small and medium-sized industrial enterprises.

Low voltage in the local distribution system (level 7)
The electricity arrives as low voltage at 400 V or 230 V in homes and agricultural and commercial businesses.
Redox Flow Battery

Charge, reduction of $V(III)$ to $V(II)$ & oxidation of $V(IV)$ to $V(V)$

Discharge, oxidation of $V(II)$ to $V(III)$ & reduction of $V(V)$ to $V(IV)$

Maria Skyllas-Kazacos (1985)
University of New South Wales, Australia
Vanadium chemistry

- In aqueous solutions $V^{2+}, V^{3+}, V^{4+} (VO^{2+})$ and $V^{5+} (VO_2^{+})$ with $V^{4+}$ dominating as the most stable in ambient air.

- $V^{3+/2+} E^\circ = -0.26 \text{ V vs SHE}$
- $V^{5+/4+} E^\circ = 1.00 \text{ V vs SHE}$

- The various vanadium species have relatively fast kinetics at carbon electrodes with little overpotentials required to drive the reactions.

- Hydrogen and oxygen evolution are nearly negligible at carbon electrodes.
Vanadium redox flow battery
Vanadium redox flow battery

2015 Uni.System.AC™: 500kW/4h; 600kW_{peak}; 2.2MWh_{max}

- Temperature Agnostic
  -40 °C to +50 °C

- SOC Agnostic
  100% capacity access
  no capacity fade

- Cycle Agnostic
  20-year design life

- Factory integration
  precision assembly & QC

- Parallel Architecture
  array sizes over 20MW/acre

- Inherently Safe
  integrated 2ndry containment
  no thermal runaway

- Plug & Play
  rapid incremental deployment

- 97% Availability
  no stripping or equalizing

- 100% recyclable
  disposal contract included
Sumitomo Yokohama Works

- 2012/7 -
- LL & Peak shaving, Smoothing PV output and Time shift of PV output
- Maximum AC Output : 1 MVA = 0.5 MVA + 0.25 MVA + 0.25 MVA
- Rated Energy Capacity : 5 MWh = 2.5 MWh + 1.25 MWh + 1.25 MWh
Company Overview

Market Focus:
*Long-duration = 4-12+ hours discharge*
"Grid Scale" = power in megawatts

Customer Benefits:
Full rated power for full rated discharge time
Unparalleled safety, reliability, and low cost
Power and energy matched to application
Rechargeable zinc hybrid cathode battery technology

Eos’s standard Aurora 1000|4000 product, a containerized 1 MW DC battery system providing four continuous hours of discharge, offers a cost-effective energy storage solution competitive with gas peaking generation and utility distribution infrastructure. The Aurora 1000|4000 will be sold at a price of $160/kWh in volume.

EnergyCell zinc-flow battery
Zinc-Iron redox flow battery

“By 2018 the CapEx of ViZn Energy’s 4-hour flow battery storage solution, which Energy Strategies Group uses as a proxy for the lowest cost flow battery technologies now being commercialized, is projected to be $974 per kW, or $244 per (installed) kWh, essentially the same as a conventional simple cycle combustion turbines (CT).

Storage will be a disruptive winner against simple cycle gas-fired CTs at that point, assuming a typical mid-range cost for competing fossil-based CT generation resources.”
How an Aquion Energy Aqueous Hybrid Ion (AHI™) Battery is Manufactured

- **Cathode**: Manganese Oxide spinel structure hosts intercalation reaction
- **Separator**: Non-woven cellulosic material
- **Anode**: Activated carbon composite with pseudocapacitive and intercalation reactions
- **Electrolyte**: Sodium sulfate in an aqueous solution
Pilot Plant
Full control
Redox Flow Batteries

**Advantages**

- Power independent of the energy capacity
- High flexibility
- Easy use
- Long lifetime
- **Safe**
- Short response time

**Limitations**

- **Low specific and volumetric energy**
- Electrode stability under deep charge and deep discharge
- Cross over through the membrane

*Tesla Model S worth about $70,000, caught fire when a metallic object directly impacted the battery pack.*
V–Ce RFB for water electrolysis

Ce-V redox flow battery: conventional electrochemical discharge

Dual-circuit system: discharge via two catalysed chemical reactions
Indirect water electrolysis

Slow electrode reactions cause kinetic overpotentials

Can thermodynamic overpotentials compete with kinetic ones?
**Catalyst Preparation**

- **Spray coating**: Denstone 2000 beads with MoO₂(acac)_2
- **Coated beads**
- **Calcination**: 2h, 450 °C
  - MoO₃ coated beads
- **Reduction**: H₂, 2h, 850 °C
  - Mo coated beads
- **Carburization**: 20% CH₄/H₂, 2h, 675 °C
  - Mo₂C coated beads
Mo$_2$C on ceramics
Catalytic hydrogen generation from V(II)

\[ 2V^{2+} + 2H^+ \xrightarrow{\text{Mo}, \text{C}} 2V^{3+} + H_2 \]

Conversion efficiency:

- Shake-flask tests for various \([V^{2+}]\)
- \(V^{2+}\) full conversion to \(V^{3+}\)
- Detection of hydrogen by gas chromatography

\[ \rightarrow \] Conversion efficiency of about 100 %, stoichiometric reaction
Catalytic water oxidation from Ce(IV)

\[
4\text{Ce}^{4+} + 2\text{H}_2\text{O} \xrightarrow{\text{RuO}_2} 4\text{Ce}^{3+} + 4\text{H}^+ + \text{O}_2
\]

Catalyst screening:
IrO\textsubscript{2}\textsuperscript{1}, RuO\textsubscript{2} prepared as nanoparticles then bound to SiO\textsubscript{2} microparticles, and dried commercial RuO\textsubscript{2} powder\textsuperscript{2}

\[ \leftrightarrow \text{Ru}_2\text{O catalyst microparticles,} \]
\[ \leftrightarrow 20 \text{mM Ce(IV) in 1 M H}_2\text{SO}_4 \text{ solution from the RFB} \]

\textsuperscript{2} Hara M. et al., Chem. Mater. 2001, 13(12), 4668
Hydrogen Production Reactor
Hydrogen Production Reactor

- H₂ compressor
- P. cylindre
- H₂ storage
- Proportional valve
- Mo₂C Reactor catalytic
- Pump electrolyte charged
- Electrolyte charged
- Electrolyte discharged
- Pompe électrolyte déchargé
Reactor Control
Hydrogen Production

The graph shows the production of hydrogen over time, with the volume of hydrogen produced, $V$, in dm$^3$, plotted against time, $t$, in seconds. Different lines represent different concentrations, with labels indicating the percentage of a certain component. The graph illustrates how the rate of hydrogen production changes with varying concentrations and time.
Hydrogen Production

![Graph showing the relationship between charge level of the battery and volumetric flow of H2, in dm3 h⁻¹. The graph indicates a linear increase as the charge level increases from 0% to 100%.]

Volumetric flow of H₂, dm³ h⁻¹

Charge Level of the Battery, %
Electric cars could help save power utilities from a “death spiral”

Today, Americans’ daily spending on energy can be split into two large chunks: about $1 billion on electricity and $1.4 billion on fuel for their vehicles. In the past, electricity providers had no way to tap into the latter market. Plug-in cars (and fuel cell cars) should change that.
How to fuel electric cars?
Battery Based Service Station

For example, a VW e-Golf can be charged in less than 30 minutes, enough for 150 km.

Fast-charge in less than 30 min.

up to 200 kW

50 kW

Type 2
43 kW AC
CHAdeMO
50 kW DC
CCS
50 kW DC

Fast-charge
From electricity to fuel

1 kWh = 20 g of hydrogen
eGallon: Compare the costs of driving with electricity

What is eGallon?
It is the cost of fueling a vehicle with electricity compared to a similar vehicle that runs on gasoline.

Did you know?
On average, it costs about half as much to drive an electric vehicle.

Find out how much it costs to fuel an electric vehicle in your state

<table>
<thead>
<tr>
<th>Type</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regular Gasoline</td>
<td>2.78</td>
</tr>
<tr>
<td>Electric egallon</td>
<td>1.22</td>
</tr>
</tbody>
</table>

Data and Methodology

http://energy.gov/maps/egallon
In the twenties, there was still no viable electrolyzer outfit for industrial-scale production of hydrogen. It was only with the discovery and development of water electrolyzers by Pechkranz, an engineer at Lonza's Valais works, that the way was opened. The electrolyzers at the Ackersand electrolysis plant were fed with direct current from appropriately equipped generators at the company's power station. Altogether, Visp and Ackersand produced 5800 m$^3$ hydrogen per hour.
Six major companies will invest about 350 million Euros (US$500 million) on a network of hydrogen filling stations for fuel-cell electric vehicles (FCEVs) in Germany over the next 10 years, they announced on Monday. Fuel-cell cars are seen by many in the industry as the best long-term solution to lowering carbon emissions from road transport, but a major problem remains in the lack of a refuelling infrastructure. "By 2023 there should be more hydrogen filling stations than conventional ones on the autobahn (highway) today," Daimler Research and Development Chief Thomas Weber said in a statement. The initiative includes Daimler and petrochemical groups OMV, Shell and Total as well as industrial gas producers Air Liquide and Linde. The group - dubbed "H₂ Mobility" - is aiming to have about 400 hydrogen filling stations in Germany by 2023, the first 100 of which will be working within the next four years. Germany has about 15 such stations now. Once the scheme is complete, every 90 km (56 miles) of German motorway will offer a hydrogen station, the group said.
Fuel cells useful as range extenders for electric cars...
Citaro FuelCELL Hybrid offers significant innovations: hybridisation with energy recovery and storage in lithium-ion batteries, powerful electric motors fitted in the wheel hubs with a continuous output of 120 kW, electrified PTO units.

35 kg of hydrogen

The operating range of the fuel-cell bus is over 250 kilometres.
Electric cars

Tank to wheel efficiency: 18% petrol - 22% diesel
Well to wheel efficiency: 15% petrol - 18% diesel

DOI: 10.1109/JPROC.2006.883715

Smart cars will not run on petrol or gas...

Smart cars never park...
Last year, a total of 140 electric cars were sold.

Gas stations all across Russia have been ordered to adapt their facilities to provide chargers for the country’s electric vehicles — which number just a few hundred in total.

Prime Minister Dmitry Medvedev signed a decree on Aug. 27 requiring the owners of gas stations to equip their facilities with chargers for electric cars by Nov. 1, 2016, according to a copy of the document published on the official government website last Monday.
La RATP veut 80 % de bus électriques dans dix ans

Le Monde.fr | 09.06.2015 à 20h38 • Mis à jour le 09.06.2015 à 20h43 |
« Art. L. 224-7.-

« 1° Pour l'Etat et ses établissements publics, dans la proportion minimale de 50 % de ce renouvellement, des véhicules à faibles émissions définis comme les véhicules électriques ou les véhicules de toutes motorisations et de toutes sources d'énergie produisant de faibles niveaux d'émissions de gaz à effet de serre et de polluants atmosphériques, fixés en référence à des critères définis par décret ;
« 2° Pour les collectivités territoriales et leurs groupements ainsi que pour les entreprises nationales, dans la proportion minimale de 20 % de ce renouvellement, des véhicules définis au 1°.
« Sans être inclus dans le champ des obligations définies aux 1° et 2°, les véhicules utilisés pour les missions opérationnelles, notamment ceux de la défense nationale, de la police, de la gendarmerie et de la sécurité civile ainsi que ceux nécessaires à l'exploitation des réseaux d'infrastructures et à la sécurité des transports terrestres et maritimes, peuvent contribuer à atteindre les objectifs définis aux mêmes 1° et 2° avec des solutions existantes adaptées aux spécificités de ces missions.
Conclusions

• Towards distributed production, storage and consumption of electricity

• Megabatteries are coming fast

• Indirect water electrolysis provides hydrogen on demand

• Service stations can be used to regulate the grid and provide energy for mobility
Acknowledgements:

Veronique Amstutz, Pekka Peljo, Kathryn Toghill
Heron Vrubel

EOS Holdings, CREM, Sinergy

Office Fédéral de l’énergie,
Fonds National Suisse