Advanced Electroanalytical Chemistry for Energy

Hubert H. Girault
Laboratoire d’Electrochimie Physique et Analytique

Martigny
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
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
German Electricity production

Average Swiss Power  8 GW
World's 10 Biggest Grid-Scale Batteries

1. Sendai Substation Lithium Ion Battery Pilot Project
   - Lithium Ion Battery
   - Sendai, Miyagi, Japan
   - Rated Power: 40,000 kW

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

3. Rokkasho Village Wind Farm
   - Sodium Sulfur Battery
   - Rokkasho, Japan
   - Rated Power: 34,000 kW
A 40 MW battery farm at Dayton Power and Light's (DP&L) Tait generating station, just south of Dayton, Ohio, built by AES Energy Storage.

Courtesy of AES Energy Storage
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
Pump Hydro
Nant de Drance

L'eau est turbinée lorsque les besoins en électricité sont importants pour fournir de l'énergie de pointe.

Lorsque les besoins en électricité sont moindres ou que la production issue des nouvelles énergies renouvelables est excédentaire, l'eau est pompée du barrage inférieur vers le barrage supérieur pour stocker de l'énergie.

1. Lac de Vieux-Emosson
2. Puits verticaux
3. Cavernes (machines et transformateurs)
4. Galerie d'amenée
5. Lac d'Emosson

1. Galerie d'accès principale depuis Châtelard
2. Galerie d'accès et ventilation
3. Galerie d'accès aux installations supérieures
Megabatteries vs Gas turbines

Average cost of generating electricity over the lifetime of the system

http://www.eosenergystorage.com/technology-and-products/
Does it still make sense?
LEPA - Martigny
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)
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
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
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?
Mo$_2$C in alumina

Hydrogen
$\text{Mo}_2\text{C on ceramics}$
Catalytic hydrogen generation from V(II)

\[2V^{2+} + 2H^+ \xrightarrow{\text{Mo}_2\text{C}} 2V^{3+} + H_2\]

Conversion efficiency:

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

→ 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\(_2\)\(^1\), RuO\(_2\) prepared as nanoparticles then bound to SiO\(_2\) microparticles, and dried commercial RuO\(_2\) powder\(^2\)

\(\leftarrow \) Ru\(_2\)O catalyst microparticles, 
\(\leftarrow 20\) mM Ce(IV) in 1 M H\(_2\)SO\(_4\) solution from the RFB

\(^2\) Hara M. et al., Chem. Mater. 2001, 13(12), 4668
Fermi level of the electron in solution

\[ e^{-V} \]

Electron at rest in vacuum

\[ \alpha_{e^{-}}^{S} \]

Electrolyte Solution

Fermi level in solution

\[ E_{F, \text{ox/red}}^{S} \]

\[ -\alpha_{e^{-}}^{S} = e^{\left[ E_{\text{ox/red}}^{S} \right]}_{\text{AVS, } \psi^{S} = 0} = \alpha_{\text{ox}}^{S} - \alpha_{\text{red}}^{S} \]
Charge dependence of the Fermi level

In vacuum:

\[ IE_{NP,ze}^V = \Phi_{Bulk} + \int_{ze}^{(z+1)e} \frac{q}{4\pi \varepsilon_0 r} \, dq = \Phi_{Bulk} + \frac{(2z + 1)e^2}{8\pi \varepsilon_0 r} \]

In solution with an adsorbed monolayer:

\[ e \left[ E_{ze/(z-1)e}^{\phi} \right]_{AVS}^{NP} = \Phi_{Bulk} + \frac{(2z - 1)e^2}{8\pi \varepsilon_0 (r + d)} \left( \frac{d}{\varepsilon_d r} + \frac{1}{\varepsilon_r} \right) \]
Fermi level in redox media

In the presence of a redox couple in excess, the charge of the particle adapts so as to equalise the Fermi levels
In the presence of two “unreacting” redox couples, the Fermi level of the electrons on the nanoparticle is under kinetic control.
Electrochemistry

Electrode potential
$E < E_{eq}$

Fermi level
$E = E_{eq}$

Electrode potential
$E > E_{eq}$

Reduction

Oxidation

PZC?

Solution

$V$

Butler-Volmer equation

$I = I_o \left[ e^{\alpha nF \eta/RT} - e^{-(1-\alpha) nF \eta/RT} \right]$

$\eta = E - E_{eq}$
Electrochemistry on floating spheres

\[ E = E_{H^+/H_2}^\circ + \frac{RT}{F} \ln \left( \frac{a_{H^+}}{\sqrt{f_{H_2}}} \right) \]

\[ i = -nAFk^0 c_{H^+}^{w,s} e^{-\alpha n\left( E_F^{NP} - E_F^w \right)/RT} \]

Equilibration of the Fermi levels

\[ E = E_{V^{3+/2+}}^\circ + \frac{RT}{F} \ln \left( \frac{a_{V^{3+}}}{a_{V^{2+}}} \right) \]

Butler-Volmer

Kinetic regime

The potential difference metal-solution will depend on the charge on the sphere and the capacitance.
Pilot Plant
Full control
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.

From electricity to fuel

1 kWh = 20 g of hydrogen
Electric cars

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

**Energy consumption EV vs. ICE**

- Electric vehicle Nissan Leaf
  - energy consumption 0.21 kWh/km (motoring magazine TM 2012)
  - transmission losses 5%
  - total energy consumption 0.22 kWh/km (well-to-wheel WTW, renewable electricity)
  - total energy consumption 0.55 kWh/km (well-to-wheel WTW, gas turbine power plant)

- Diesel car VW Golf 1.6 D Blue Motion Technology
  - factual fuel consumption 5.0 l/100 km (own experience)
  - energy consumption 1.80 MJ/km (0.50 kWh)
  - total energy consumption 0.60 kWh/km (WTW)

Sources: Ecofys 2010, Climate Counter 2012