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Advances in Redox-Flow Batteries

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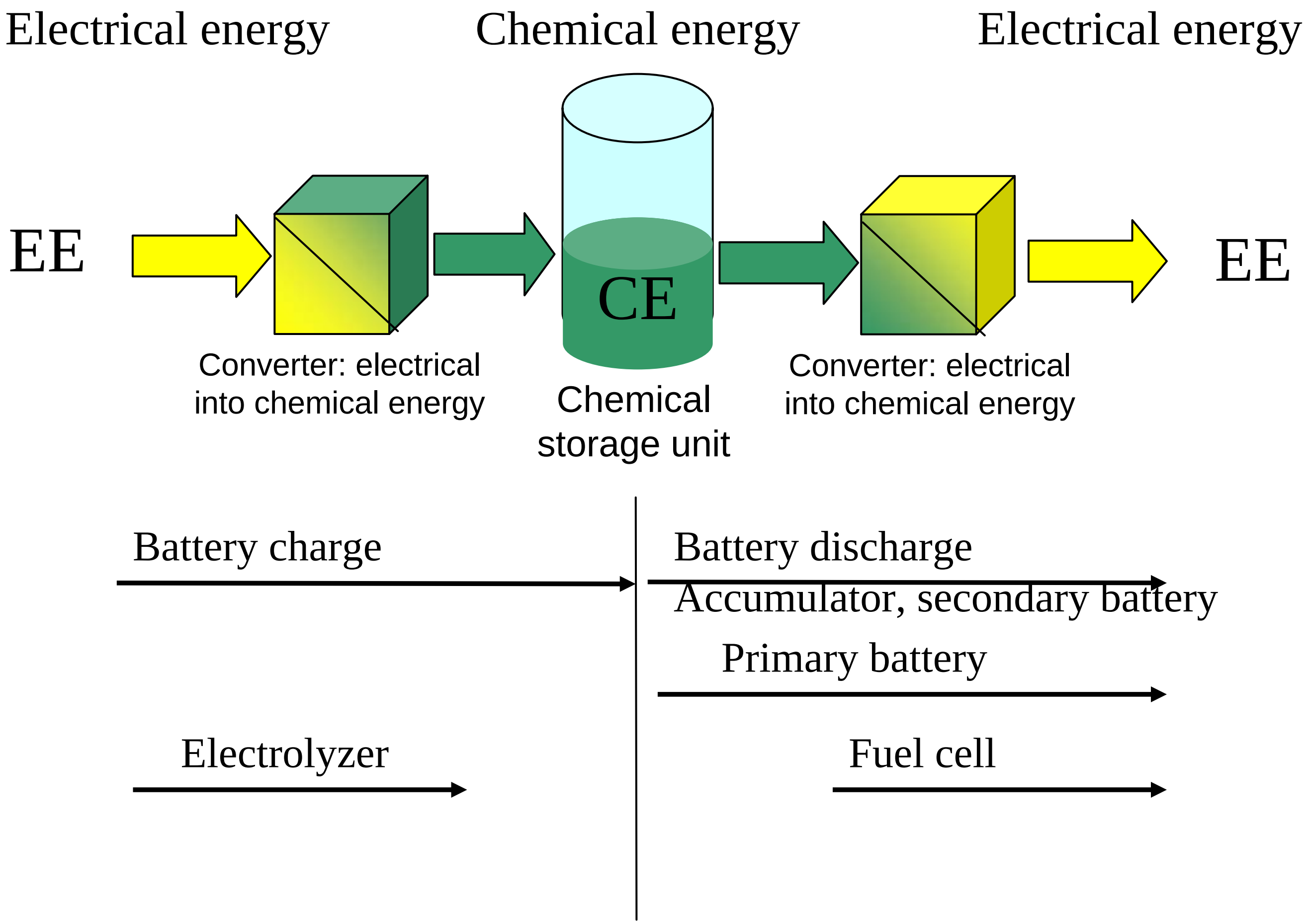
Overview

- The principle of redox-flow batteries
- Electrochemical systems used for redox-flow batteries
- Characteristics in comparison with other batteries
- State of the art systems
- R&D required
- Costs

Principle of electrochemical storage systems



Electrical energy

Chemical energy

Electrical energy

EE

CE

EE

Converter: electrical into chemical energy

Chemical storage unit

Converter: electrical into chemical energy

Battery charge

Battery discharge

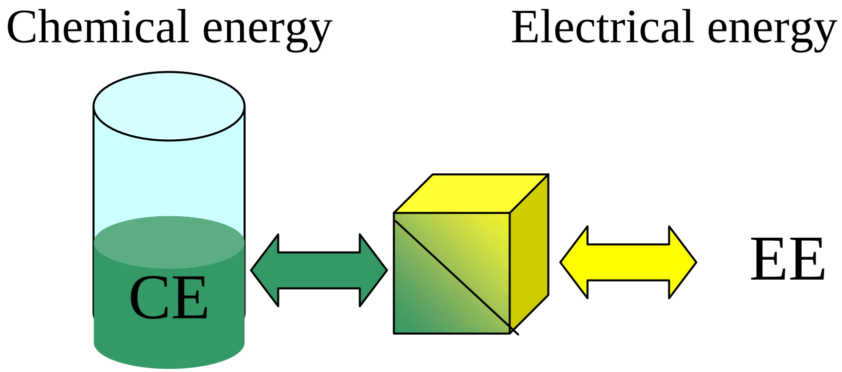
Accumulator, secondary battery

Primary battery

Electrolyzer

Fuel cell

Principle of redox-flow batteries



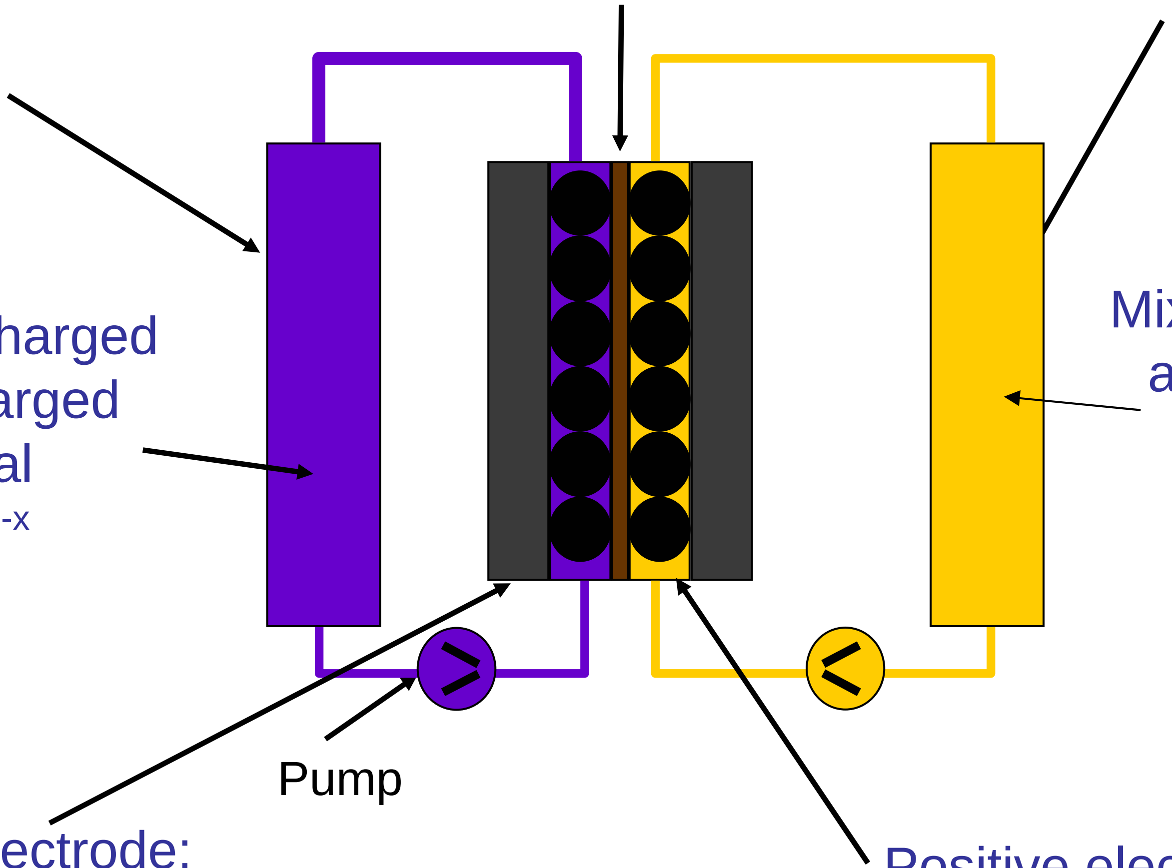
Chemical storage unit

- liquid phase
- storage in tanks
- Typically two tanks are required

Converter: electrical into chemical energy

- Electrochemical cells
- To increase the voltage a large number of cells is necessary → Stack

Principle of redox-flow batteries



Membrane

Tank

Tank

Mixture of charged and discharged Material
A^n / A^{n-x}

Mixture of charged and discharged Material
C^n / C^{n+y}

Pump

Negative electrode:

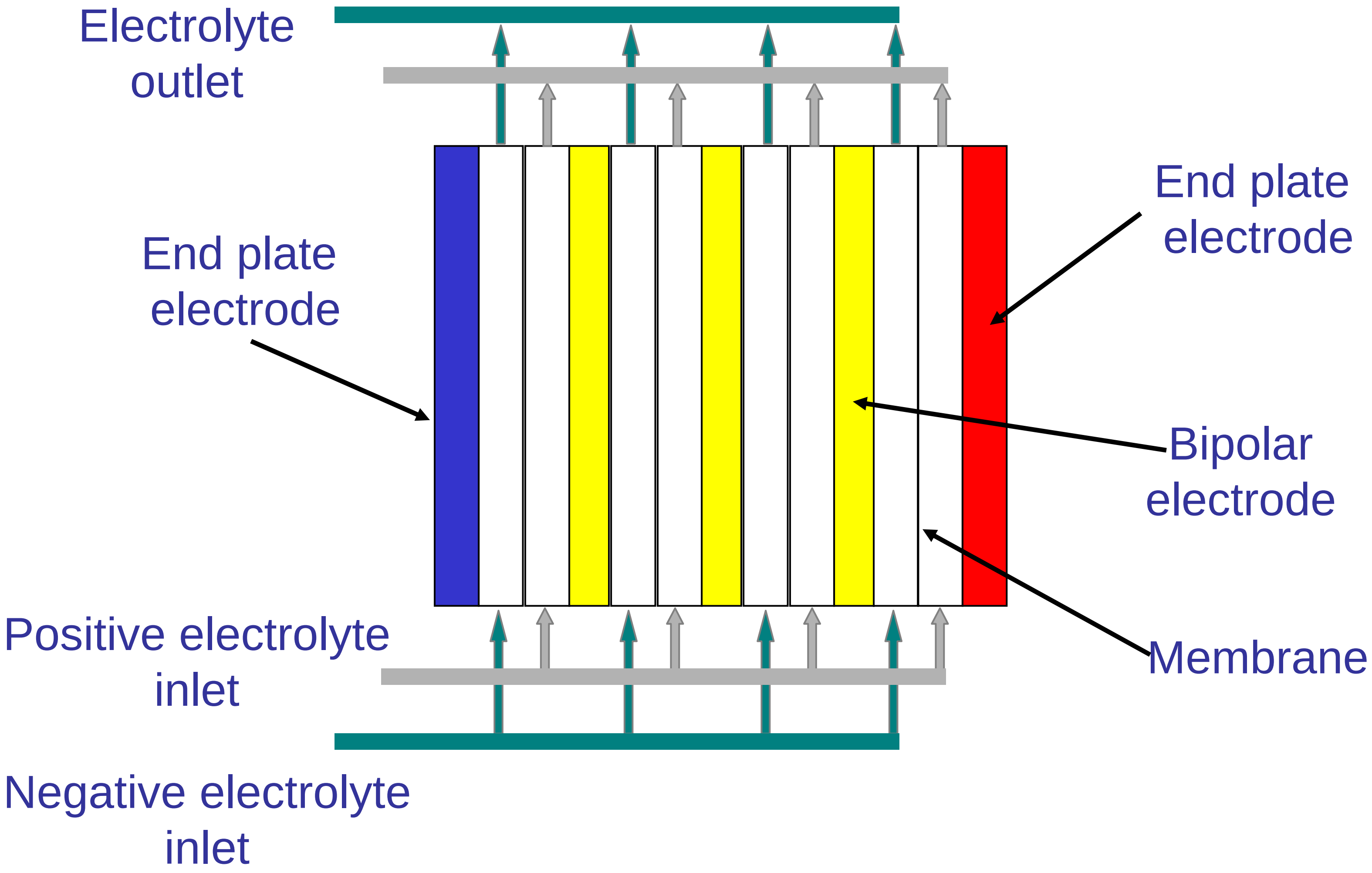
$$A^n \xrightarrow{\text{discharge}} A^{n-x} + x\,e^-$$

Positive electrode:

$$C^n + y\,e^- \xrightarrow{\text{discharge}} C^{n+y}$$

Stack design

- four cells in a bipolar arrangement -

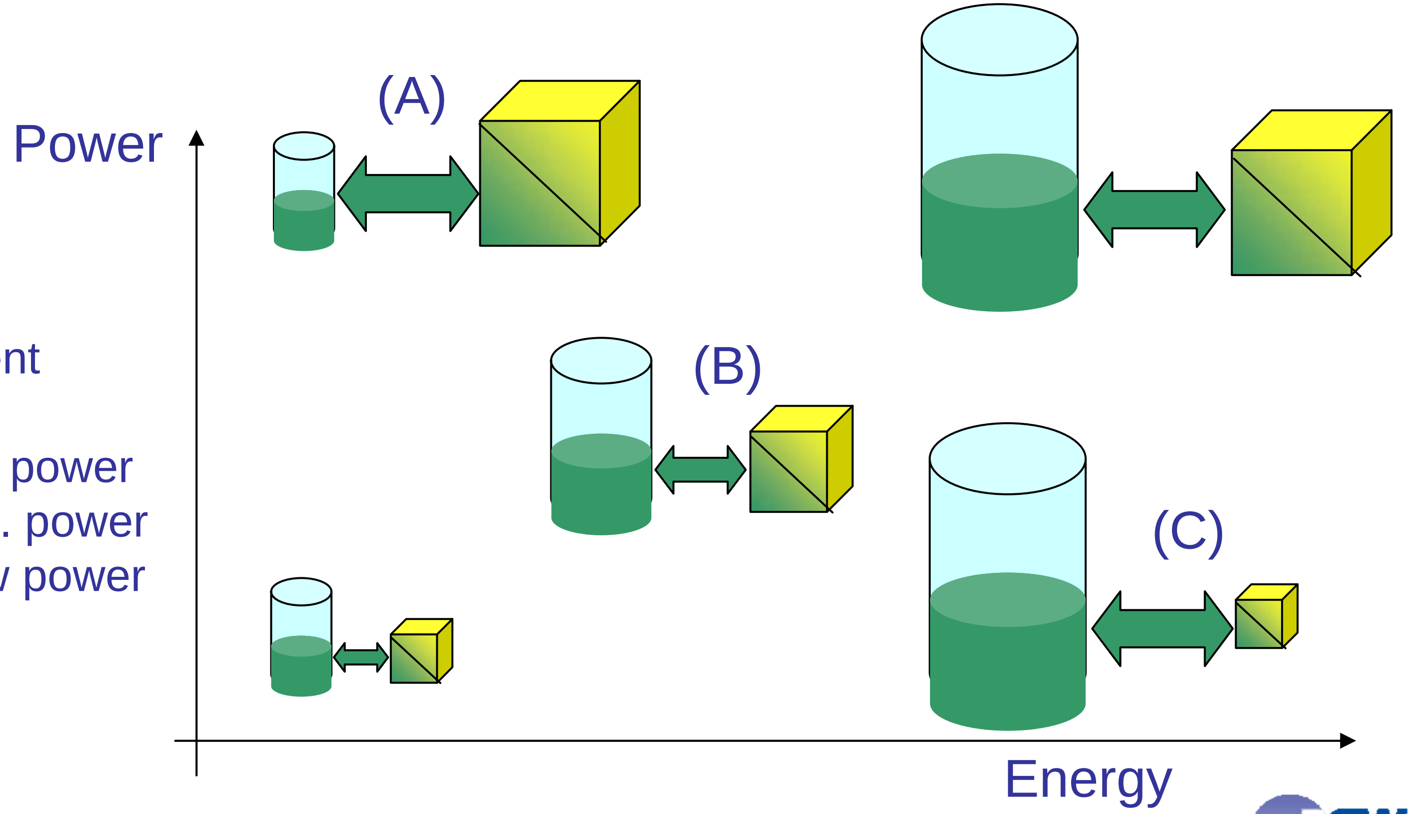


Important Characteristics

- The two components converter (Stack) and the storage (tank) are separate.

→ Flexible sizing, possible, but as the converter is complex and expensive the systems are sized for high energy and low power (C).

Size of storage and converter for different configurations.
(A) short term, high power
(B) Med. term, med. power
(C) High energy low power

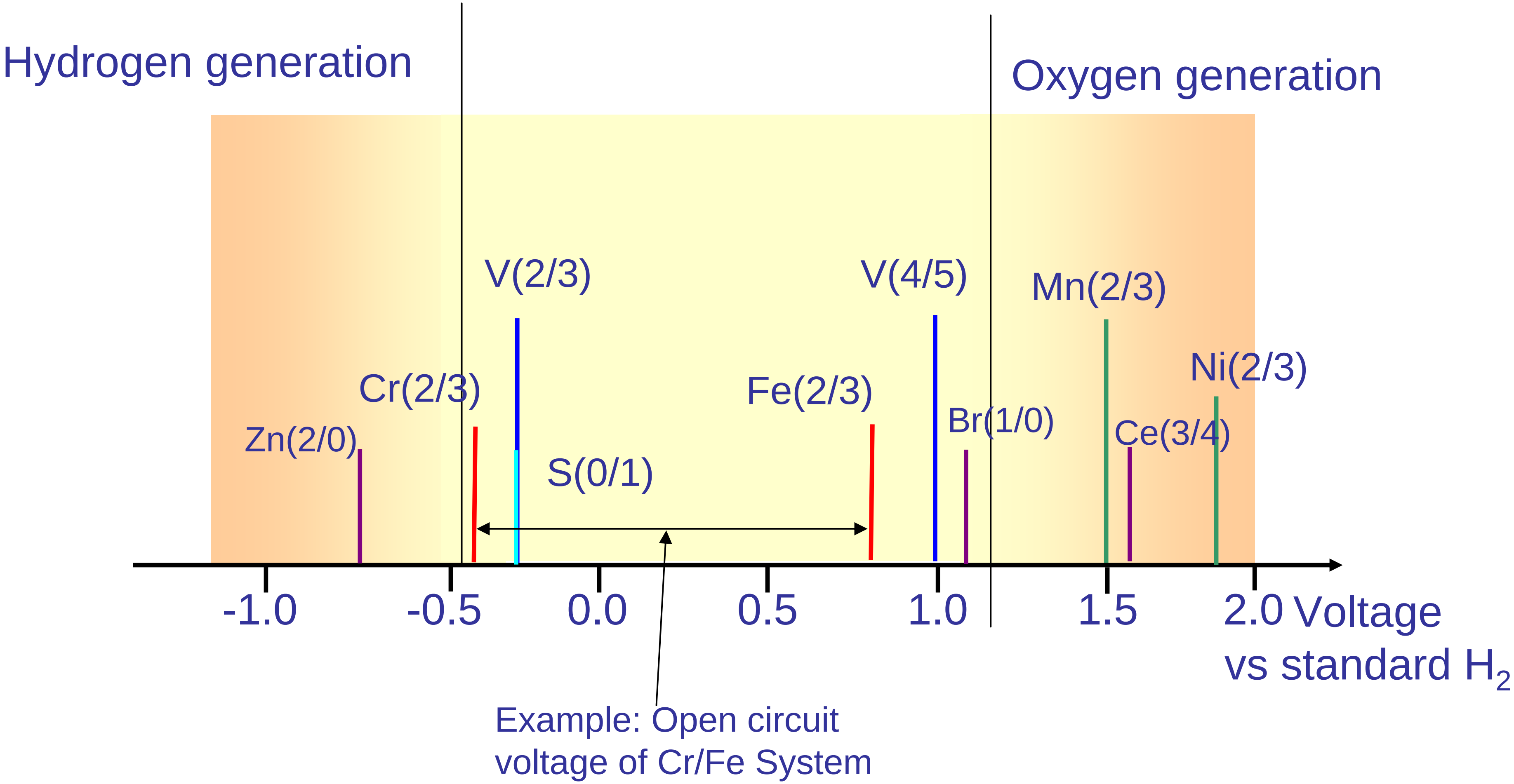


The history of redox-flow batteries

- Researche concerning redox-flow battery began in the 70's with the Fe-Ti couple, using $FeCl_3$ as the oxidising agent and $TiCl_2$ as the reducing one, both in an alkaline electrolyte.
- Then Ti^{2+} was replaced by Cr^{2+}, leading to better performances.
- During the 80's, a lot of work have been carried out by the NASA on the Fe-Cr system, as well as on the zinc/alkaline/sodium ferricyanide ($Na_3Fe(CN)_6,H_2O$) couple.
- 10 kW systems have been built with the Fe-Cr couple
- Problems of the Fe-Cr system:
  - expensive, ion selective membrane needed
  - high maintenance to avoid clogging up of the membrane
- Other redox-flow systems were developed
- Today we have some manufacturers of redox-flow batteries

Possible chemistries

Half cell voltages and cell voltages



Possible chemistries

Some data from different sources

System	E Cell in V	Current densities in mA/cm²	Ah efficiency in %	Energy efficiency
Fe/Cr	1.03V	6.5	81	66
Bromine/ Polysulfide	1.53	60	90	67
Vanadium/ Vanadium	1.7	80	90	72

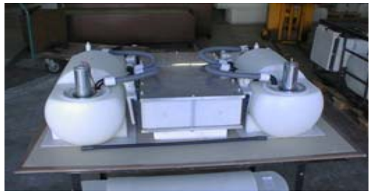
The Vanadium redox flow battery (VRB)
- The most common redox flow technology -

PacifiCorp (Moab, Utah) 2MWh VRB-ESS

Pos: $VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$
Neg: $V^{2+} \rightarrow V^{3+} + e^-$

Lifetime: Estimated by more than
10 000 cycles 20 – 80 % dod

Manufacturer / develop companies:
VRB Power Systems Inc. (Vancouver, Canada)
Sumitomo Electric Industries (Japan)
Cellennium limited (Thailand)



ZSW Vanadium redox flow battery

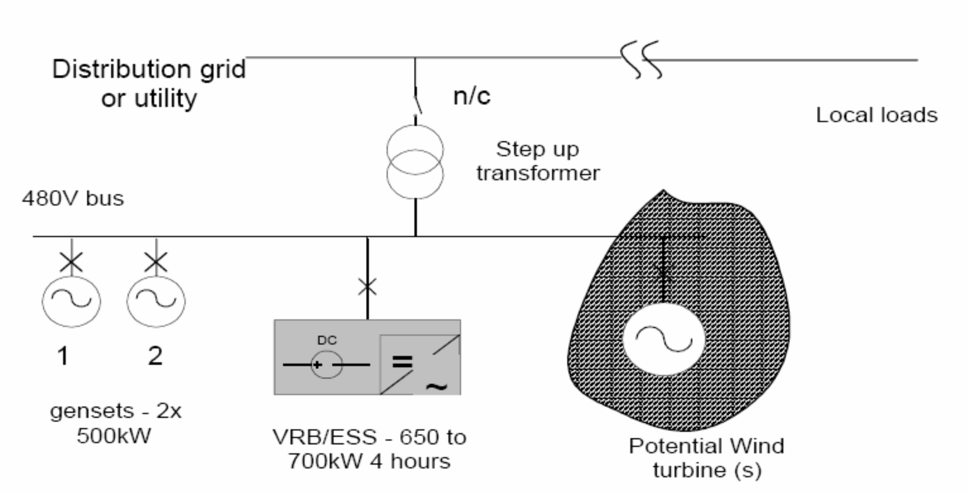
VRB Projects in Japan

- Sumitomo Electric -

Place	Applications	Specifications	Start of operation
Office building	Load leveling (Demonstration)	100kW x 8h	2000/02
Semi-conductor factory	1) Voltage sag protection 2) Load leveling	1) 3000kW x 1.5sec. 2) 1500kW x 1h	2001/04
Wind power station	Stabilization of wind turbine output (Field test)	170kW x 6h	2001/04
Golf course	Load leveling (Photovoltaic hybrid system)	30kW x 8h	2001/04
University	Load leveling	500kW x 10h	2001/07

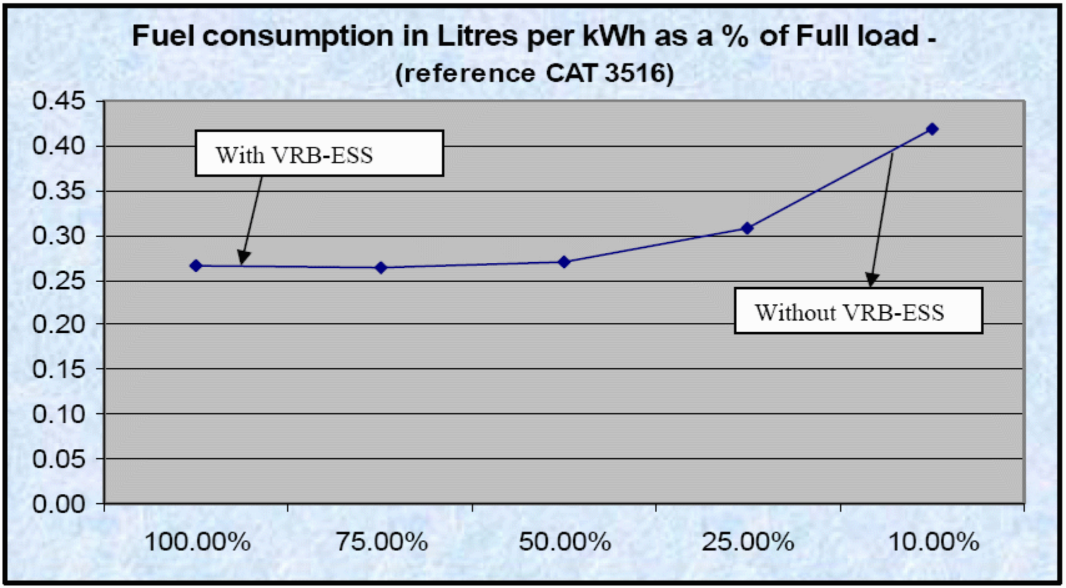
VRB for use in a Remote Area Power Supply

- Result of a case study -



Comparison of a RAPS system with and without a VRB.

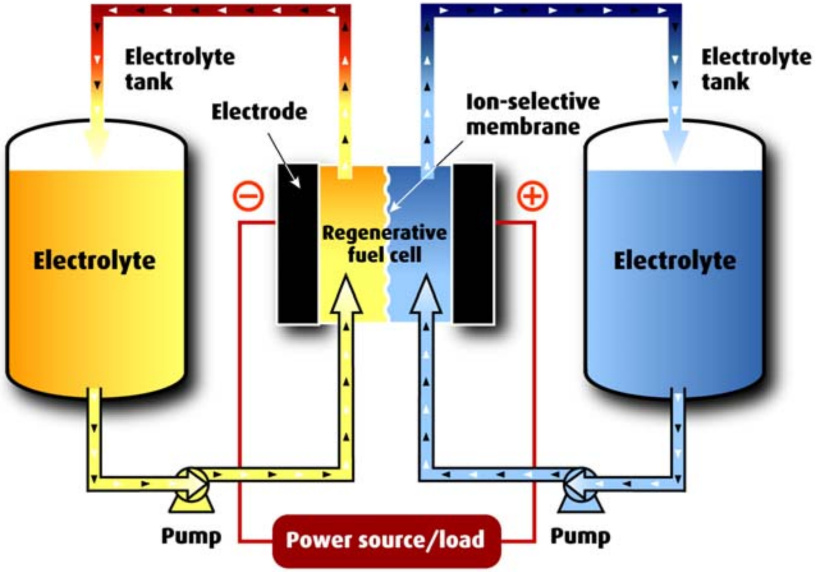
Efficiency of VRB: 75%



Source: VRB Power Systems

Bromine/polysulfide flow battery

- The Regenesys-system -



Negative:
$Na_2S_4 \rightarrow 2\ Na_2S_2$

Positive:
$3\ NaBr \rightarrow NaBr_3$

- Energy efficiency ~ 70 %
- Estimated costs: 175 €/kWh

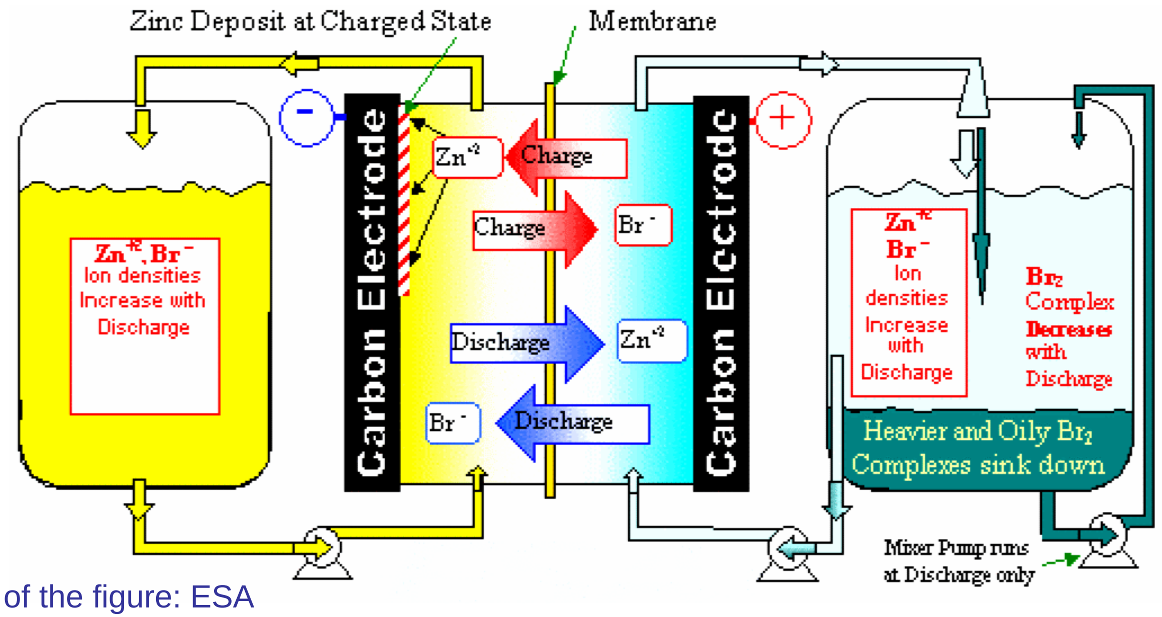
Bromine/polysulfide flow battery
- The Regenesys-system -

Little Barford, South England
120MWh / 15 MW

The XL-Modules
with 100 kW each
Total planed: 120 Modules

Project was stopped in Dec. 2003

The zinc / bromine system



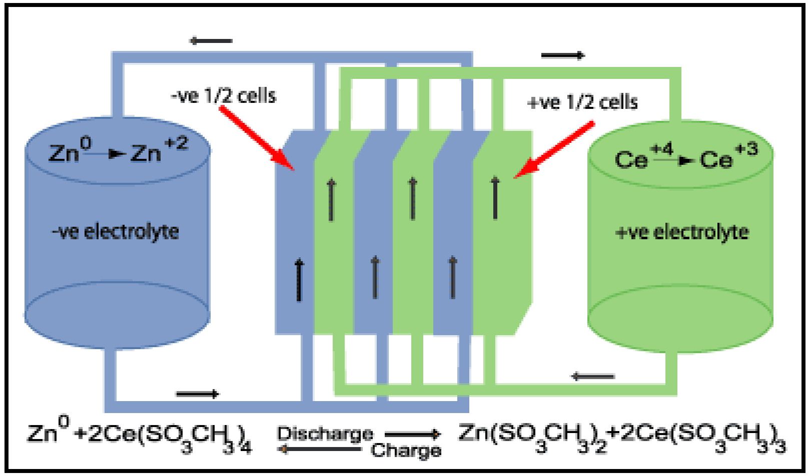
Source of the figure: ESA

Just a “hybrid” redox-flow battery,
As zinc is in the charged state
plated on the negative electrode.
→ Stack size influences
energy content, too.

- Commercialized system by different manufacturers.
- Applications like telecom and ups are known.
- Zinc is critical for lifetime

The cerium / zinc system
- Plurion´s redox-flow battery -

The bromine is exchanged by cerium. Environmentally friendly System, but only “hybrid system” and limitations by zinc.



$$Zn^0 + 2Ce(SO_3CH_3)_4 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Zn(SO_3CH_3)_2 + 2Ce(SO_3CH_3)_3$$

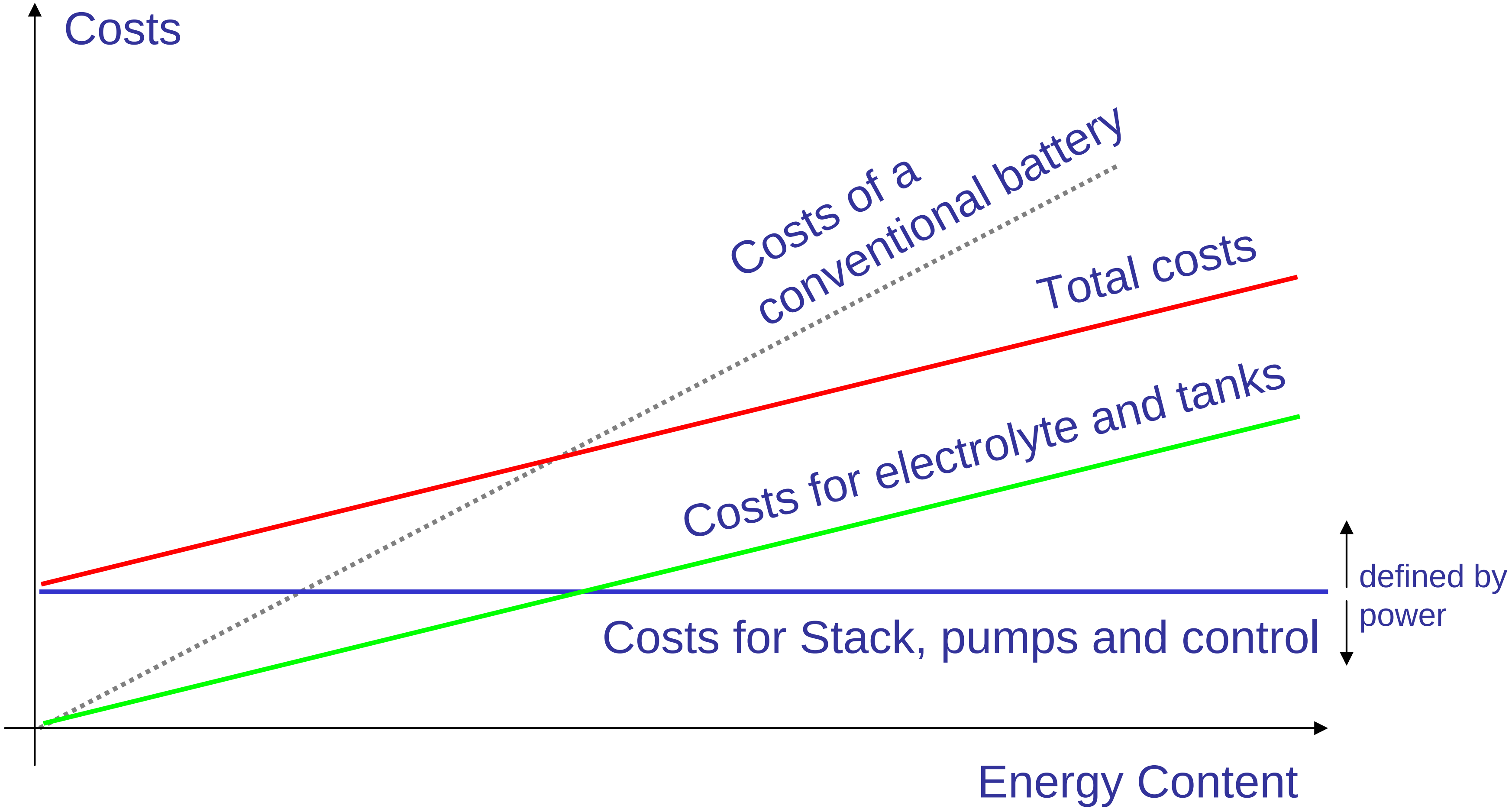
Electrolyte (solvent):
Methane Sulfonic Acid (CH_3SO_3H)

Open circuit voltage: 2.4V
Discharge voltage: ~ 2.0V


1 m² pilot cell, 2002

Costs of redox-flow batteries

- Principle -



The vanadium redox-flow system

- a cost estimation for a 2 kW / 30 kWh system-

	Data	cost per unit	Total costs
Current density	52mA/cm^2		
Electrode area	1.75m^2/kW		
V_2O_5- Energy	6.0kg/kWh		
Activation layer	3.5m^2/kW	50 €/m^2	350 €
Bipolar plate		65 €/kW	130 €
Frame, etc.		435 €/kW	870 €
Membrane	2.1 m^2 / kW	25 €/m^2	105 €
Tanks	Each 550 l	185 € each	370 €
Pumps		160 € each	320 €
Control		500 €	500 €
V_2O_5	180 kg	8.0 €/kg	1440 €
Electrolyte manuf.		3 €/kg	540 €
Tanks	Each 550 l	185 € each	370 €
TOTAL			**4665 € → 155 € / kWh**

Converter costs

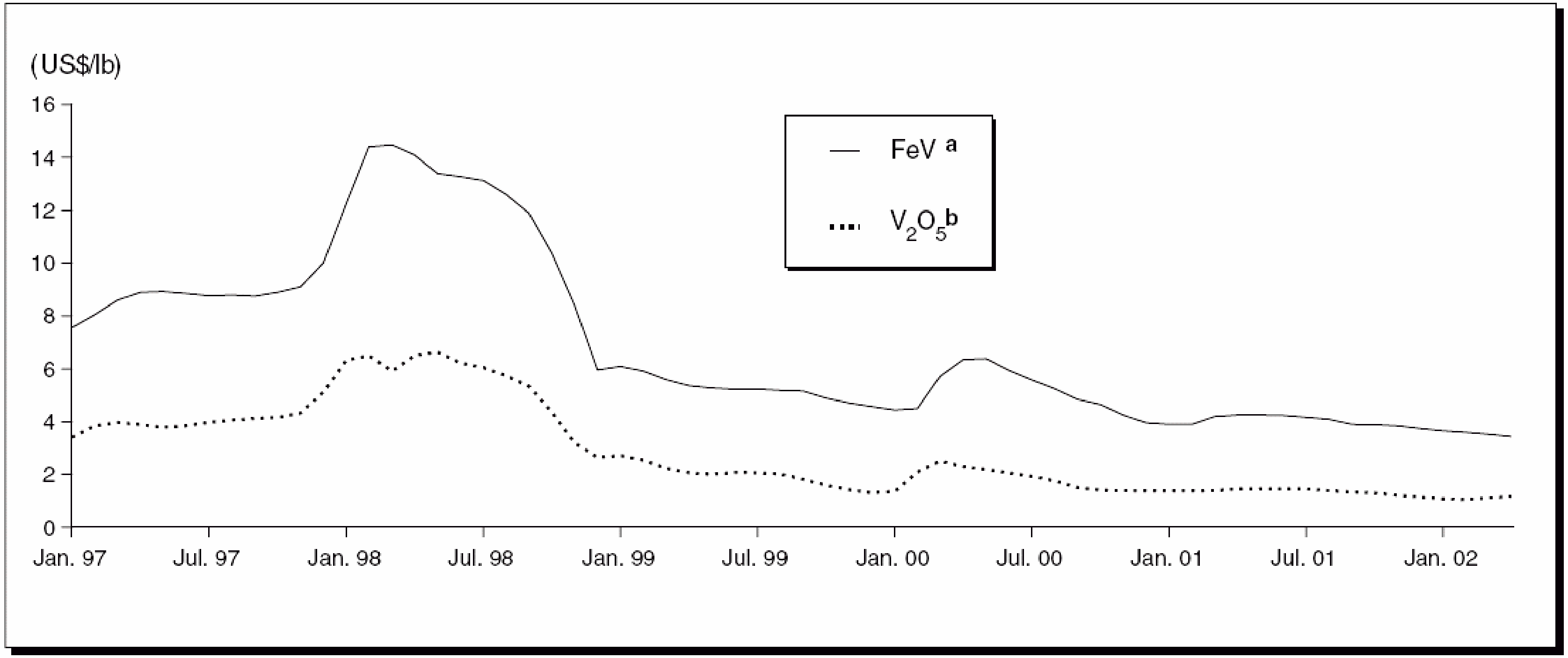
2315 €
→ 1157 €/kW

Storage costs

2350 €
→ 78 €/ kWh

According L. Jörissen, ZSW

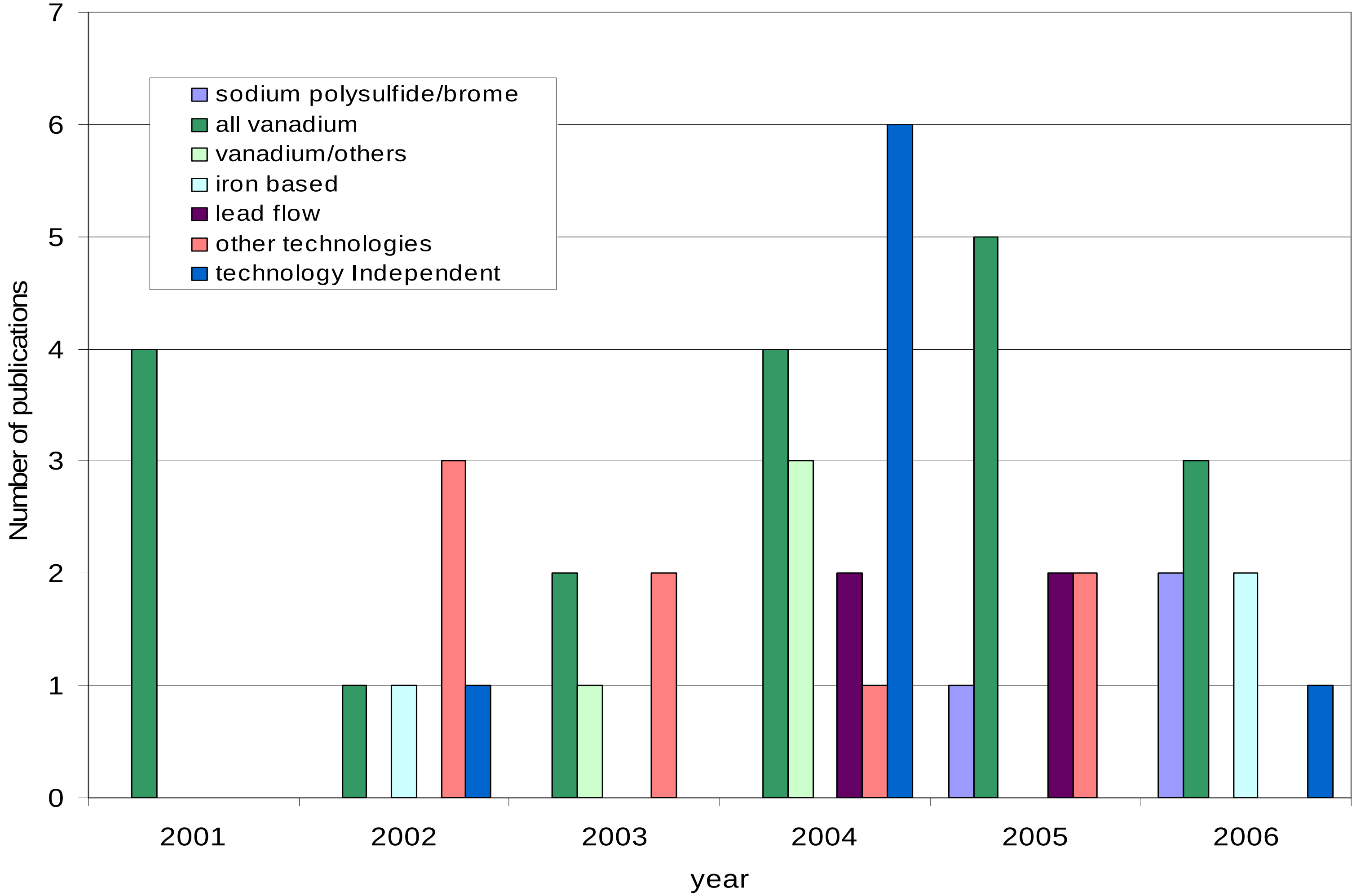
Vanadium products price variation



Source: *Metal Bulletin*.

[a] Price per pound of contained vanadium, U.S. free market 70-80% V in warehouse, Pittsburgh. [b] Price per pound V_2O_5, Europe, min. 98%.

Publications about redox-flow batteries



Search for “redox flow battery” in the title or the abstract at www.scorpus.com

Important factors

- potential for further improvement -

- Shunt currents (bypass or leakage) result in a reduced efficiency
- Hydraulic characteristic, especially for larger systems is the flow distribution a critical point. Unbalanced cells will generate side products (gasses) what finally will damage the cell and the stack.
- Sealing of large cells/stacks is complex
- Reactant mixing results in reduced cell voltage during discharge.
- Ions crossing the membrane result in unwanted species and change of the concentration. A special treatment is necessary to maintain the redox couple concentrated and pure.

Summery

- Different systems are possible and investigated by R&D teams
- All vanadium and zinc/bromine are commercialized
- The flexible independent sizing of storage capability and power is an important advantage in comparison to other battery technologies.
- The most continuous activities are in the all vanadium technology
- The “Regenesys Problem” increases the scepticism in redox flow technology. Finally it shows that commercializing of electrochemical storage systems needs more than a decade.
- The electrolyte costs are strongly related to the raw material costs (V_2O_5 changed within months by a factor of 4)
- Up-scaling from small to large systems is a important but a difficult task. Systems in the 100 MW class are possible.
- Potential for cost reductions are in more efficient electrodes, larger stacks and lower electrolyte manufacturing costs.
- Environmental aspects must be taken into account.