Redox Flow Batteries

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Energy Storage

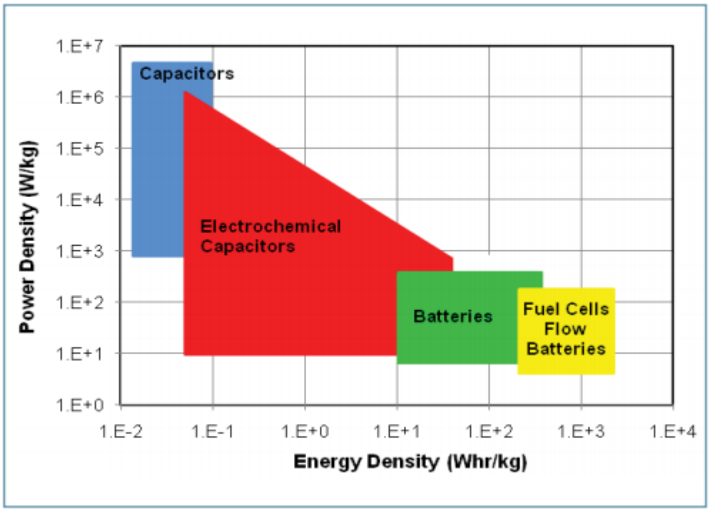
Problem: Fossil Fuels depletes very fast and emits GHGs

Solution: Solar Energy and Wind Energy

Problem: Highly dependent on climate and surplus energy

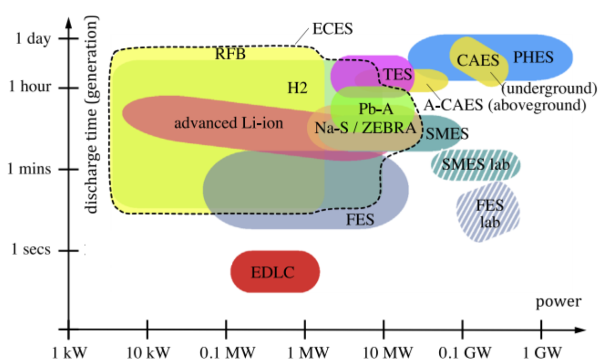
Solution: Energy Storage to store surplus energy

Flow Batteries VS Other Energy Storages



Power and Energy Density of various EES

Flow Batteries VS Other Energy Storages



Power duration diagram of energy storage system

LEGEND:

ECES: Electrochemical Energy Storage

RFB: Redox Flow Battery

TES: Thermal Energy Storage

CAES: Compressed Air Energy Storage

PHES: Pumped Hydro Energy Storage

H2: Electrolyzer-Fuel Cell

Li-ion: Lithium Ion

Pb-A: Lead Acid

Na-S: Sodium Sulfur

SMES: Superconducting Magnetic Energy Storage

FES: Flywheel Energy Storage

EDLC: Electric Double Layer Capacitor

Comparison of Energy Storages

Small scale energy storage

- ✓Simple and efficient
- ✓Portable power
- ✓Transportation systems application
- ✓Sizing and volume are very critical
- ➢Conventional Rechargeable Batteries

Large scale energy storage

- ✓Durable for large number of charge/discharge cycles
- ✓Ability to respond to sudden change in load
- ✓Sizing and volume are not very critical
- ✓Solution to customer's fluctuating demand for energy
- ➢Flow Batteries

Redox Flow Batteries

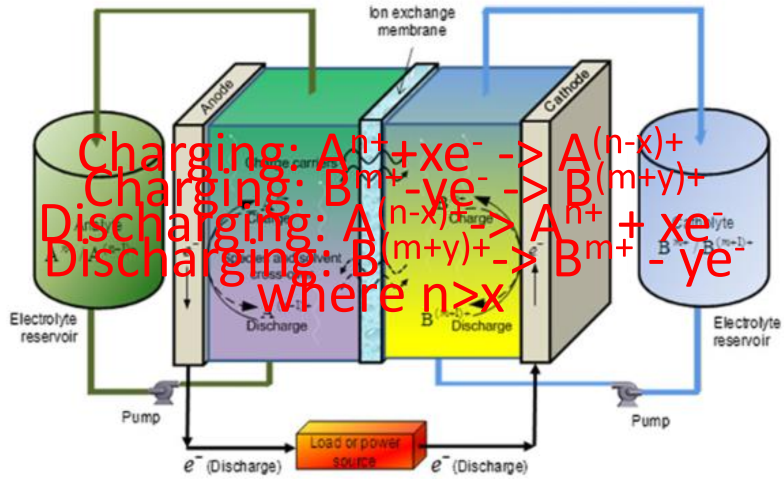
Advantages

- Instant recharge
- Low demand (store energy), High demand (consume energy)
- Long service life
- No self-discharge
- Electrolytes are recyclable
- Scalability of power and energy
- Low environmental impact
- Suitable for large scale storage application

Disadvantages

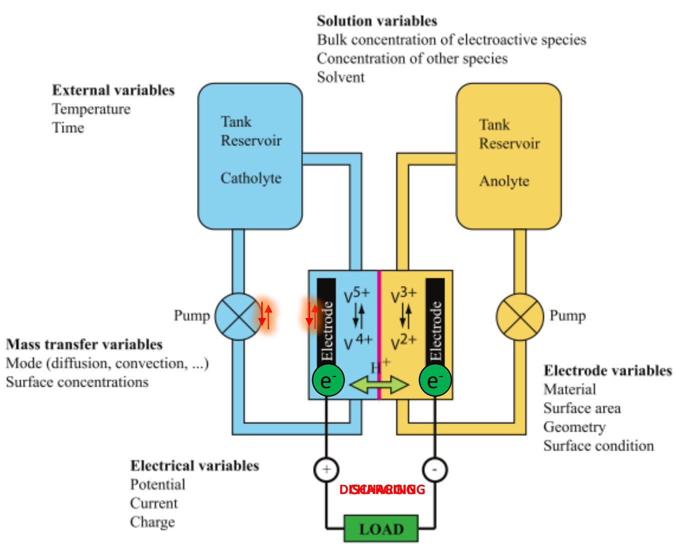
- Low power density vs other energy storages
- Requires good temperature control system (prevent precipitation of solution)
- Many system requirements (i.e. pumps, sensors, flow and power management)

Flow Battery Concept



Schematic diagram of redox flow battery with electric transport in the circuit, ion transport in the electrolyte and across the membrane, active specie crossover, and mass transport in the electrolyte

Flow Battery Concept



Schematic representation of VRB with a list of variables affecting the rate of redox reaction (Bard & Faulkner, 2001).

History Overlook

Vanadium redox couple mentioned and patented in 1933 by P.A. Pissoort

Titanium Chloride Flow Cell registered by Walter Kango in Germany in 1954

Thaller studied Fe-Ti and Fe-Cr electrolytes in 1970s until 1984

Fe-Cr redox system in HCl solution were studied in Japan around 1980s

First successful RFB is employing vanadium electrolyte by Skyllas-Kozacos in 1986

In 1989, R&D for VRFB boosted and commercial installation began in 2001

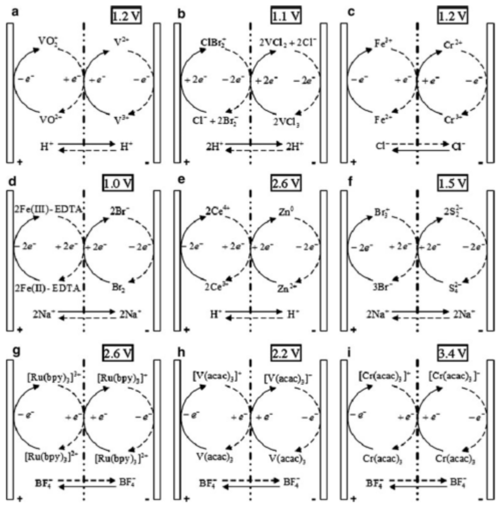
Present Technologies in RFB

Types of RFB system	Positive Findings	Negative Findings
Iron/Chromium	-Open circuit is 1V -iron redox couple is reversible -low voltage output and efficiency	-slow Cr ion reaction -membrane aging -cell degradation (cross contamination) -low energy density
Bromine/polysulfide	-electrolytes are very abundant and inexpensive	-prone to crossover and mixing of electrolyte -prone to precipitation of H_2S and formation of Br_2
VRB	-most successful RFB -commercially available -same metal ion for both the cathodic and anodic electrolyte -longer lifespan due to no cross contamination -E^0=1.26V at 25 °C -current density 25-35 Wh/L	-must exist in 4 different oxidation states -energy density limited by solubility of vanadium leading to precipitates

Vanadium/bromine	-enhanced the solubility of vanadium due to presence of halides -higher energy density (35-70Wh/L) VS all-vanadium (25-35 Wh/L)	-emission of Br_2 gases that are toxic (complexing agents added such as tetrabutylammonium bromide to minimize the emission)
Hydrogen based systems Hydrogen/Oxygen	-better mass transfer since its gaseous -smaller required tank volume	-oxygen reaction is very slow resulting to large overpotential and low overall efficiency
Zinc/bromide	-high concentration of Br^- and Br_2 enhances the kinetics and energy density -high cell voltage -good reversibility -low material costs	-Br_2 is a toxic gas -material corrosion -dendrite formation -electric shorting -high self-discharge rates -short cycle life
All-iron	-same metal ions -low cost	-low current efficiency -overall cell voltage is low -hydrogen generation occurs

Zinc/cerium	-cell potential of 2.5V -energy density of 37.5 to 120 Wh/L -high acid concentration for better cerium (IV) solubility	-cerium redox couple is slow -cerium has low diffusivity -high acid concentration for lower solubility of cerium (III)
Ruthenium/bipyridine	-open circuit voltage of 2.6V -energy efficiency of 40%	
Ruthernuim acetylacetonate	-cell potential 1.77V	

Redox couples



Schematic of charge transport in various redox-flow systems (values give potential of the redox couple)

LEGEND:

a. All vanadium
b. Vanadium/bromide
c. Iron/chromium
d. Fe-EDTA/bromide
e. Zinc/cerium
f. Bromine/polysulphide
g. Non-aqueous ruthenium/bipyridine
h. Non-aqueous vanadium/acetylacetonate
i. Non-aqueous chomium/acetylacetonate

All-Chromium Redox Flow Batteries

- Chromium: 3 common oxidation states
  - $Cr(II), Cr(III), Cr(VI)$
- Main Reactions Involved:

  A: $2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14\ H^+ + 6e^-$

  E= -1.33V

  C: $6Cr^{3+} + 6e^- \rightarrow 6Cr^{2+}$

  E= -0.41V

All-Chromium Redox Flow Batteries

Advantages

- Identical anodic and cathodic solution
- High open circuit voltage (2.1V)

Disadvantages

- Slow kinetics of Cr(III)/Cr(VI) redox couple (irreversible reaction)

Electrolytes with Additives compared to Blank in RFBs

System	Additives	Results
All Chromium RFB (Bae et al. 2011)	EDTA	-enhanced kinetics but considered sluggish
All Vanadium RFB (Peng et al 2012)	TRIS	-better stability -better electrochemical activity

Current Study in DLSU:

System	Additives	Results
All Chromium RFB	TRIS	-

All Chromium-TRIS RFB Research

General Objective

To develop an all-chromium redox flow battery using trishydroxymethyl aminomethane as stabilizing agent.

All Chromium-TRIS RFB Research

Specific Objectives

1. To fabricate, and assemble a laboratory scale all-chromium redox flow battery.

2. To determine the effect of the following factors on the cycle stability of the all chromium-TRIS redox flow battery using cyclic voltammetry:

a. Concentration of chromium solution

b. Concentration of TRIS

c. Temperature of the electrolyte

3. To optimize the cycle stability based mainly on the least sum of the current deviation and high current peak as secondary response using full factorial design.

4. To determine the voltage efficiency, energy efficiency and power output of the RFB based on the optimized factors.

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