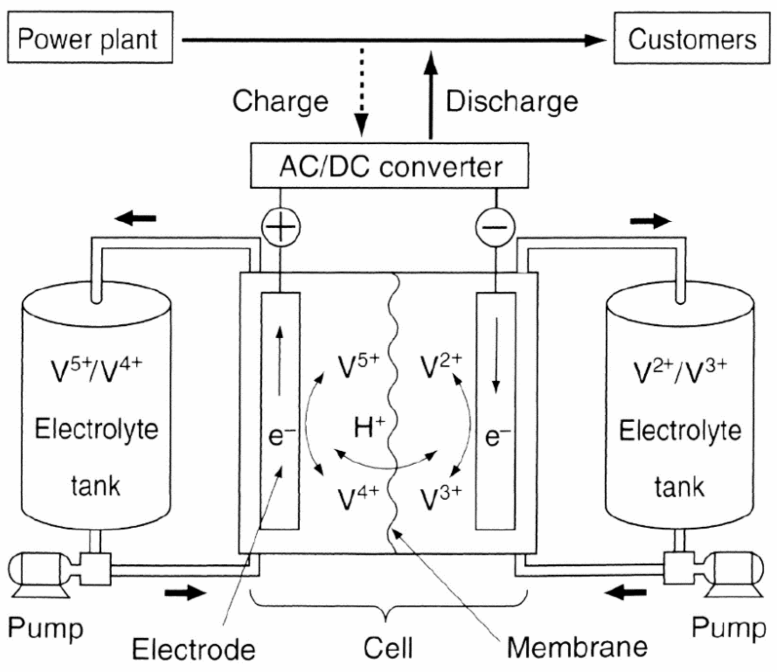
SECTION 5: FLOW BATTERIES

ESE 471 – Energy Storage Systems

Flow Battery Overview

Flow Batteries

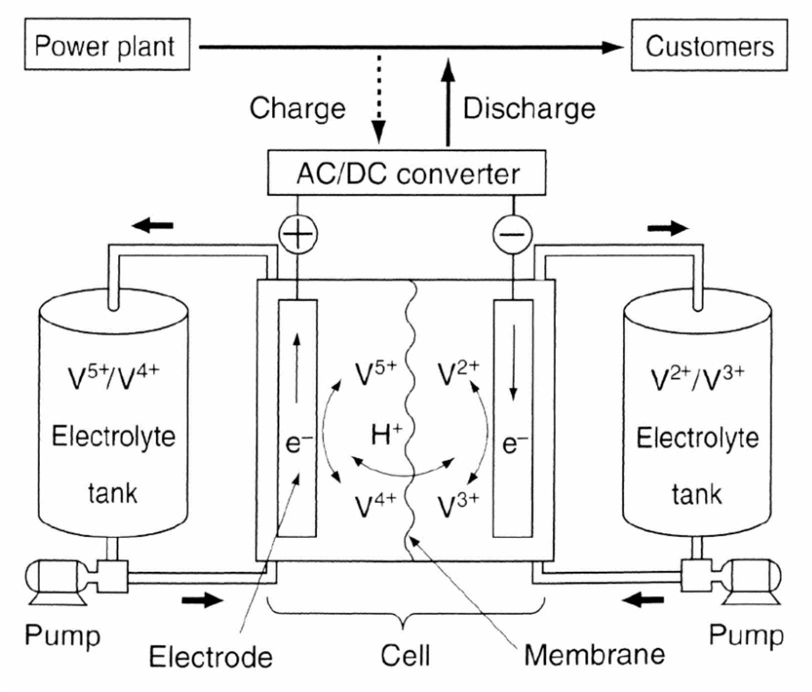
- ***Flow batteries*** are electrochemical cells, in which the reacting substances are stored in electrolyte solutions ***external to the battery cell***
  - Electrolytes are ***pumped*** through the cells
  - Electrolytes flow across the electrodes
  - Reactions occur *at* the electrodes
  - Electrodes do not undergo a physical change



Source: EPRI

Flow Batteries

- Flow batteries comprise two components:
  - **Electrochemical cell**
    - Conversion between chemical and electrical energy
  - **External electrolyte storage tanks**
    - Energy storage



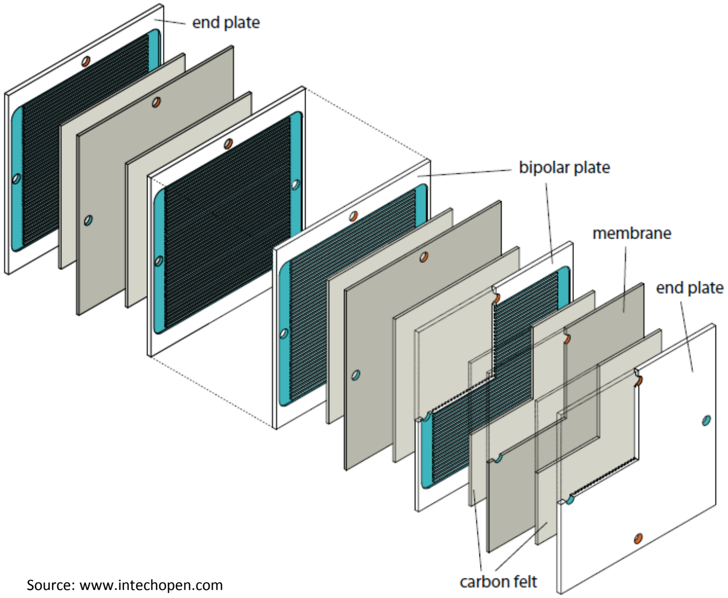
Source: EPRI

Flow Battery Electrochemical Cell

- Electrochemical cell
    - Two ***half-cells*** separated by a ***proton-exchange membrane*** (PEM)
    - Each half-cell contains an ***electrode*** and an ***electrolyte***
        - Positive half-cell: ***cathode*** and ***catholyte***
        - Negative half-cell: ***anode*** and ***anolyte***
- ***Redox reactions*** occur in each half-cell to produce or consume electrons during charge/discharge
- Similar to fuel cells, but two main differences:
    - Reacting substances are all in the liquid phase
    - Rechargeable (secondary cells)

Cell Stacks

- ***Open-circuit voltage*** of an individual cell in the range of 1 V … 2 V
  - Determined by the particular chemistry
- ***For higher terminal voltages, multiple cells are connected in series***
  - Electrolyte flows through cell stack in parallel
- ***Carbon felt electrodes***
  - Porous – high surface area
  - High conductivity
- ***Bipolar plates*** separate individual cells in the stack
  - Shared electrode between adjacent cells
  - Positive electrode for one cell, negative electrode for the neighbor
- Electrodes on the ends are the external electrodes for the stack



Source: www.intechopen.com

Comparison to Other Storage Devices

Flow Battery Characteristics

- Relatively low ***specific power*** and ***specific energy***
  - Best suited for fixed (non-mobile) utility-scale applications
- ***Energy*** storage capacity and ***power*** rating are ***decoupled***
  - Cell stack properties and geometry determine power
  - Volume of electrolyte in external tanks determines energy storage capacity
  - Flow batteries can be tailored for an particular application
- Very ***fast response times*** - < 1 msec
  - Time to switch between full-power charge and full-power discharge
  - Typically limited by controls and power electronics
- Potentially very ***long discharge times***
  - 4 – 10 hours is common

Flow batteries vs. Conventional Batteries

- ***Advantages over conventional batteries***
  - Energy storage capacity and power rating are decoupled
  - Long lifetime
    - Electrolytes do not degrade
    - Electrodes are unaltered during charge/discharge
  - Self-cooling
    - Inherently liquid-cooled
  - All cells in a stack supplied with the same electrolyte
    - All cell voltages are equal
    - Individual cells not susceptible to overcharge/undercharge
    - No need for cell balancing

Flow batteries vs. Conventional Batteries

- ***Advantages over conventional batteries*** (cont'd)
  - Equal charge/discharge rates (power)
  - Bipolar electrodes are possible
    - Convenient for cell stacking

- ***Disadvantages over conventional batteries***
  - Higher *initial* cost
  - Increased complexity associated with pumps and plumbing
  - Lower specific energy and specific power

Flow Battery Applications

- ***Peak shaving/load shifting***
  - Infrastructure upgrade deferral
  - Arbitrage
  - Long duration
- ***Load following***
  - Potentially replace peaker plants
  - Long duration
- ***Integration of renewables***
  - Smooth fluctuating power from wind and solar
  - Improve grid stability
  - Short duration
- ***Frequency or voltage regulation***
  - Accommodate short-term real and reactive power demands
  - Short duration

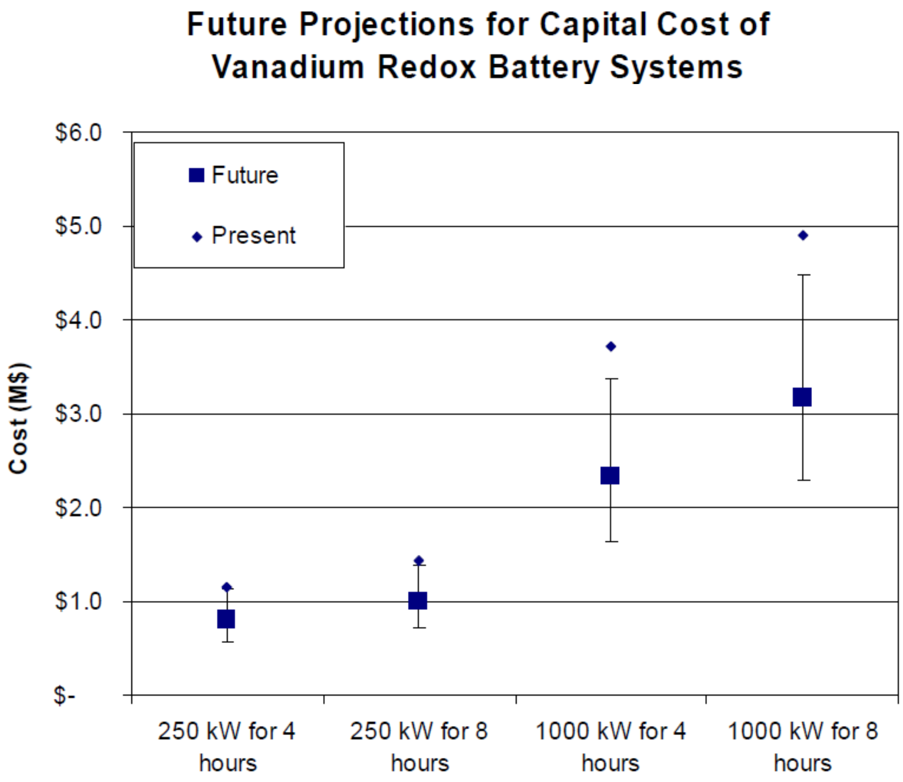
Cost of Flow Batteries

- Cost of storage devices usually reported as either \$/kW or \$/kWh
- The Electric Power Research Institute (EPRI) estimates the cost of energy storages systems with ***three cost components***
  - Costs that scale with ***power*** capacity
  - Costs that scale with ***energy*** storage capacity
  - ***Fixed*** costs
- Total capital cost is given by

$$\begin{aligned} Capital\ Cost = {} & P \cdot (scaled\ power\ cost) \\ & + E \cdot (scaled\ energy\ cost) \\ & + (fixed\ cost) \end{aligned}$$

Cost of Flow Batteries

- In 2007, the EPRI flow battery cost estimates were:
    - Power: $2300/kW
    - Energy: $300/kWh
    - Fixed: $250,000
- EPRI 2007 projections for 2013:
    - Power: $1250/kW
    - Energy: $210/kWh
    - Fixed: $280,000



Source: EPRI

Flow Battery Chemistry

Flow Battery Chemistry

- Several different chemistries used in flow batteries
  - Most employ ***redox*** (oxidation-reduction) ***reactions***
  - Often referred to as redox flow batteries or RFBs
- ***Redox reactions***
  - Chemical reactions pairing a reduction reaction with an oxidation reaction
  - ***Oxidation states*** of reactants are changed
- ***Reduction***
  - Gaining of electrons
  - Oxidation state is decreased (reduced)
- ***Oxidation***
  - Loss of electrons
  - Oxidation state is increased

Redox Flow Battery Chemistry

- Oxidation at one electrode corresponds to reduction at the other
  - Opposite reactions occur during charging and discharging

- **Charging**:
  - Current flows from anode to cathode
  - Electrons flow from cathode to anode
  - Reduction occurs in the anolyte

$$A^{n+} + e^{-} \rightarrow A^{(n-1)+}$$

  - Oxidation occurs in the catholyte

$$B^{m+} \rightarrow B^{(m+1)+} + e^{-}$$

Redox Flow Battery Chemistry

- **Discharging**:
  - Current flows from cathode to anode
  - Electrons flow from anode to cathode
  - Oxidation occurs in the anolyte

$$A^{(n-1)+} \rightarrow A^{n+} + e^-$$

  - Reduction occurs in the catholyte

$$B^{(m+1)+} + e^- \rightarrow B^{m+}$$

Redox Couples

- Different flow batteries use different ***redox couples***
  - Pairs of redox reactants dissolved in electrolyte solution

- Common redox couples
  - Vanadium/vanadium, V/V
  - Zinc/bromine, Zn/Br
  - Iron/chromium, Fe/Cr
  - Bromine/Sulfur, Br/S

- Most common is the ***vanadium redox flow battery*** or ***VRB***

Vanadium

- Abundant
- Inexpensive
- Byproduct of many mining operations

- Vanadium can exist in four different oxidation states
  - V^{2+}, V^{3+}, V^{4+}, and V^{5+}

- In VRB electrolytes:
  - V^{4+} exists as VO^{2+}
  - V^{5+}exists as VO_2^+

- Vanadium in a VRB is dissolved in either:
  - Sulfuric acid
  - Mixture of sulfate and chloride (developed and licensed by PNNL)

Vanadium

- Vanadium changes color as it changes oxidation state

Source: www.eenews.net, David Ferris

- Vanadium flow batteries use only a single element in both half-cells
  - Eliminates the problem of cross-contamination across the membrane

VRB Reactions

- At the anode (charging to the right):

$$V^{3+} + e^- \rightleftharpoons V^{2+}$$

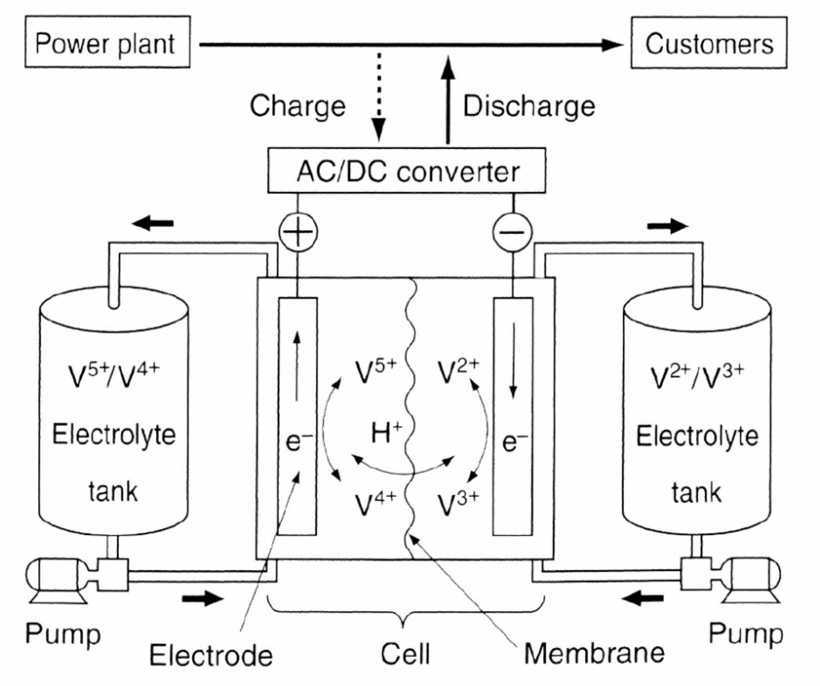
- At the cathode (charging to the right):

$$V0^{2+} + H_2O \rightleftharpoons VO_2^+ + 2H^+ + e^-$$

- Anode half-cell standard potential
  - $E_{0a} = -0.26\ V$
- Cathode half-cell standard potential
  - $E_{0c} = 0.99\ V$
- Cell standard potential
  - $E_0 = 1.25\ V$
- Cell potential given by the ***Nernst equation***
  - Nominal value often considered $1.4\ V$

Proton-Exchange Membrane

- Half-cells separated by a ***proton-exchange membrane*** (PEM)
- Allows protons to flow
  - From catholyte to anolyte during charging
  - From anolyte to catholyte during discharging



Source: EPRI

Electrochemical Model

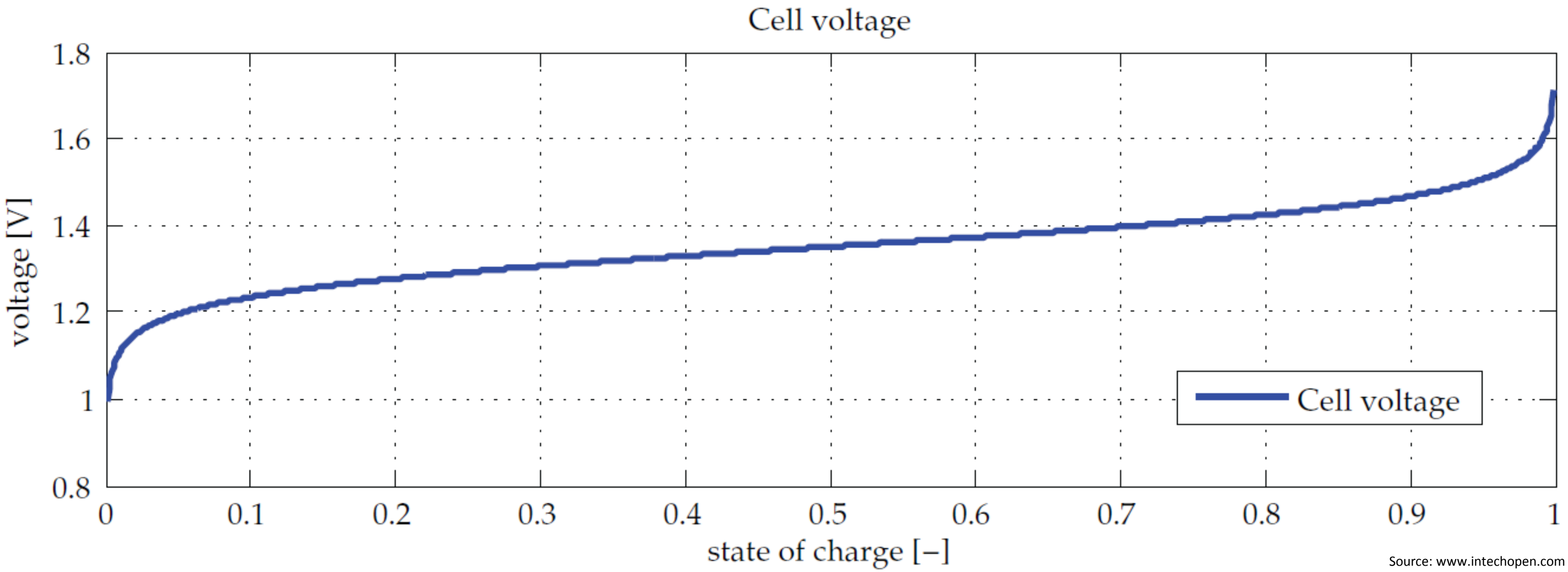
Electrochemical Model

- As is the case for most batteries, a complete ***electrochemical model*** for a VRB is very complex

- Electrochemical model describes the relationship between cell voltage and
  - State of charge (SOC)
  - Operating conditions
    - Current
    - Electrolyte flow rate
    - Temperature
  - Internal losses
  - Electrolyte concentrations

Open-Circuit Voltage

- The open-circuit voltage as a function of SOC :

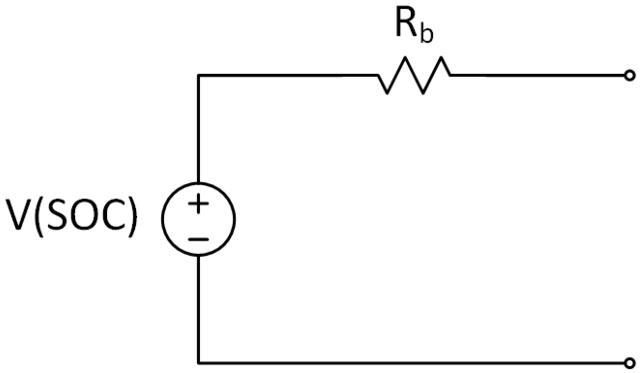


Source: www.intechopen.com

Equivalent Circuit Model

- Simple RFB equivalent circuit model
  - Thévenin equivalent circuit
  - State-of-charge-dependent open-circuit voltage source

- The resistance models losses in the battery
  - ***Voltaic*** losses
    - Ohmic and ionic losses in the electrodes, electrolytes, and membrane
  - ***Coulombic*** (***Faradaic***) losses
    - Losses due to chemical side reactions



Mechanical Model

RFB Fluid Model

- The equivalent circuit model accounts for electrical and electrochemical behavior of the flow battery
    - Models electrical and electrochemical losses that affect efficiency

- Flow batteries require electrolyte to be ***pumped*** through the cell stack
    - Pumps require power
    - Pump power affects efficiency

- Need a ***fluid model*** for the battery in order to understand how ***mechanical losses*** affect efficiency

RFB Fluid Model

- Power required to pump electrolyte through cell stack
- Pumping power is proportional to
  - Density of the fluid
  - Head loss through the system
  - Flow rate

$$P_{pump} = \rho g h Q = \Delta p Q \tag{1}$$

- Total power required by the pump is determined by the pump efficiency

$$P_{pump,in} = \frac{P_{pump}}{\eta_{pump}} \tag{2}$$

RFB Fluid Model

- ***Pressure drop through the system*** includes pressure drops through both the piping and the cell stack

$$\Delta p = \Delta p_{pipe} + \Delta p_{stack} \tag{3}$$

- ***Pressure drop along the piping*** is the sum of frictional losses and minor losses

$$\Delta p_{pipe} = -\gamma\left(\Delta z + h_f + h_m\right) \tag{4}$$

where

γ: specific weight of the fluid ($\gamma = \rho g$)
Δz: height differential along the pipe
h_f: frictional losses
h_m: minor losses

RFB Fluid Model

- The ***frictional losses*** and ***minor losses*** are the sum of the losses along each section of pipe or from each fitting, valve, bend, etc.
  - Given by the ***Darcy-Weisbach equation***

$$h_{f,i} = f_i \frac{L_i}{D_i} \frac{V_i^2}{2g} \qquad (5)$$

and

$$h_{m,i} = k_{L,i} \frac{V_i^2}{2g} \qquad (6)$$

where

f_i: Darcy friction factor – dependent on roughness, diameter, and Reynolds number

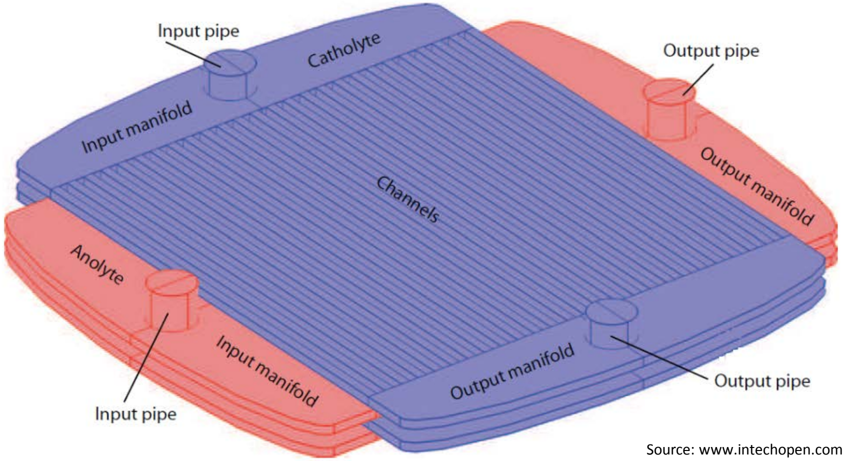
$k_{L,i}$: loss coefficient associated with each lossy feature (e.g. inlet, outlet, valves, bends, etc.)

L_i: length of section

D_i: diameter of section

RFB Fluid Model

- Calculating pressure drop across the cell stack becomes much more complicated
  - Analytically intractable
  - Evaluate using computational fluid dynamics (CFD) simulation



Source: www.intechopen.com

- CFD used for cell stack design to ensure
  - Uniform electrolyte flow across electrodes
  - Minimal pressure drop through stack

Efficiency

Flow Battery Efficiency

- We would like to derive an expression for the ***round-trip efficiency*** of the flow battery
  - Ratio of the ***energy delivered from*** the battery to the ***energy delivered to*** the battery

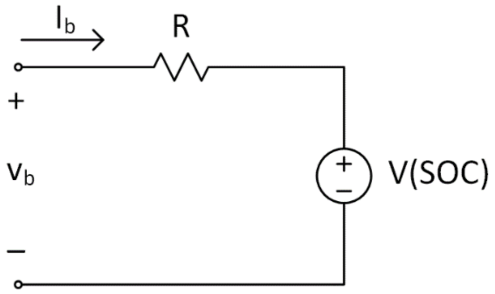
$$\boxed{\eta_{rt} = \frac{E_{out}}{E_{in}} \cdot 100\%} \tag{7}$$

- The input energy, E_{in}, is the electrical energy delivered to the battery terminals plus the energy delivered to the pumps

$$E_{in} = E_{in,b} + E_{pump,in} \tag{8}$$

Flow Battery Efficiency

- The energy quantities in (8) are given by the integrals of the respective powers
  - For the battery



$$E_{in,b} = \int_0^{t_c} P_b(t)\, dt$$

$$E_{in,b} = \int_0^{t_c} i_b(t) v_b(t)\, dt \qquad (9)$$

where t_c is the charging time

  - The pump runs and requires power during both charge and discharge, so,

$$E_{pump,in} = \int_0^{t_c+t_d} P_{pump,in}(t)\, dt \qquad (10)$$

where $P_{pump,in}$ is given by (2)

Flow Battery Efficiency

- Substituting (10) and (9) into (8), we have

$$E_{in} = \int_0^{t_c} i_b(t) v_b(t)\, dt + \int_0^{t_c+t_d} P_{pump,in}(t)\, dt \qquad (11)$$

- Note that not all of $E_{in,b}$ is stored
  - Some energy is lost in R_b
- Stored energy is

$$E_{stored} = E_{in,b} - E_{R_{b,in}}$$

$$E_{stored} = \int_0^{t_c} i_b(t) v_b(t)\, dt - \int_0^{t_c} i_b^2(t) R_b\, dt \qquad (12)$$

- The energy output from the battery is equal to the stored energy minus losses in R_b as energy flows out of the battery

$$E_{out} = E_{stored} - E_{R_{b,out}} = E_{in,b} - E_{R_{b,in}} - E_{R_{b,out}}$$

$$E_{out} = \int_0^{t_c} i_b(t) v_b(t)\, dt - \int_0^{t_c+t_d} i_b^2(t) R_b\, dt \qquad (13)$$

Flow Battery Efficiency

- Substituting (11) and (13) into (7), gives the round-trip efficiency:

$$\boxed{\eta_{rt}=\frac{\int_0^{t_c} i_b(t)v_b(t)\,dt-\int_0^{t_c+t_d} i_b^2(t)R_b\,dt}{\int_0^{t_c} i_b(t)v_b(t)\,dt+\int_0^{t_c+t_d} P_{pump,in}(t)\,dt}} \qquad (14)$$

- This is round-trip efficiency at the terminals of the battery
  - DC-DC efficiency
  - Typical values: 70% … 85%

Flow Battery Efficiency

- More meaningful is AC-AC round-trip efficiency
  - Accounts for power conversion system
  - May include transformer losses as well

$$\boxed{\eta_{rt,AC} = \eta_{rt,DC} \cdot \eta_{pcs}^{2} \cdot \eta_{tf}^{2}}$$

  - $\eta_{rt,DC}$ is given by (14)
  - Transformer loss typically ~1%
  - Typical values: 65% … 75%

Electrolyte Flow Rate

- Efficiency is determined, in part, by the amount of power consumed by the pumps
    - Pumping power dependent on ***flow rate***:

$$P_{pump} = \Delta p \cdot Q$$

- ***Minimum required flow rate*** is a function of:
    - Battery input/output power
        - Higher power requires higher flow rate
    - State of charge
        - Higher flow rate for:
            - Charging at high SOC
            - Discharging at low SOC

Flow Rate

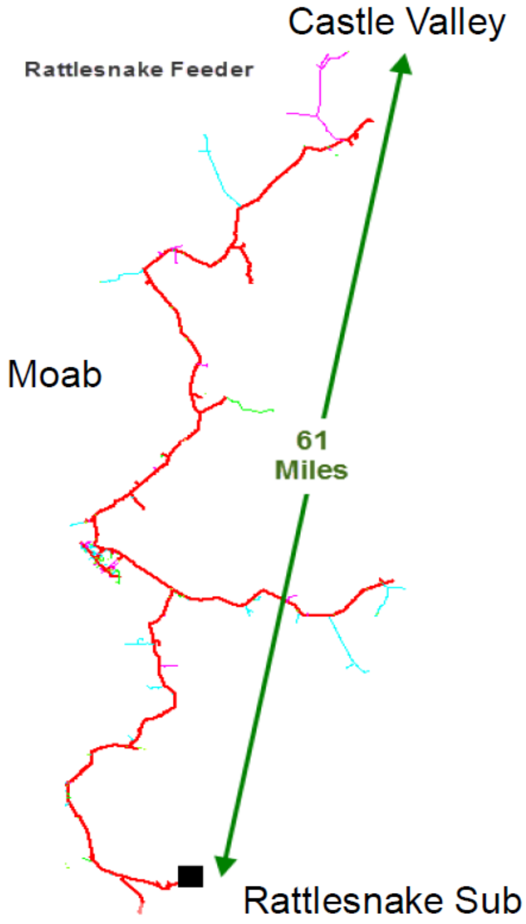
- One approach to setting flow rate for a given power charge/discharge:
  - Set flow rate to the maximum value required during the charge/discharge cycle

- Better yet, adjust flow rate to optimize efficiency
  - Dynamically adjust flow rate to the minimum required value for the current operating point
  - Variable flow rate will be a function of
    - SOC
    - Battery current
  - Necessary to account for non-equilibrium (transient) concentration effects within the cell

Notable Flow Battery Projects

Castle Valley, UT

- PacifiCorp (Utah Power) service area
- Rattlesnake #22 feeder
  - 85 miles long
  - 25 kV
  - 10,957 kVA connected distribution transformers
  - Serves Moab and Castle Valley
  - At or over capacity during hot summer months
  - Customer complaints of poor power quality
- Environmentally, geologically pristine, sensitive area



Source: VRB Power Systems

Castle Valley, UT – VRB

- ***Vanadium redox flow battery***
  - VRB Power Systems, Inc.
  - Installed between the two load centers on the long distribution feeder
  - **Power**: 250 kW *and* 250 kvar
  - **Energy storage**: 2 MWh
  - **Discharge time**: 8 hours
  - 3800 sq. ft.
  - HVAC system maintains temperature at 5 °C … 40 °C
- Purpose of the battery: ***asset deferral***
  - Alternative would be to upgrade the feeder

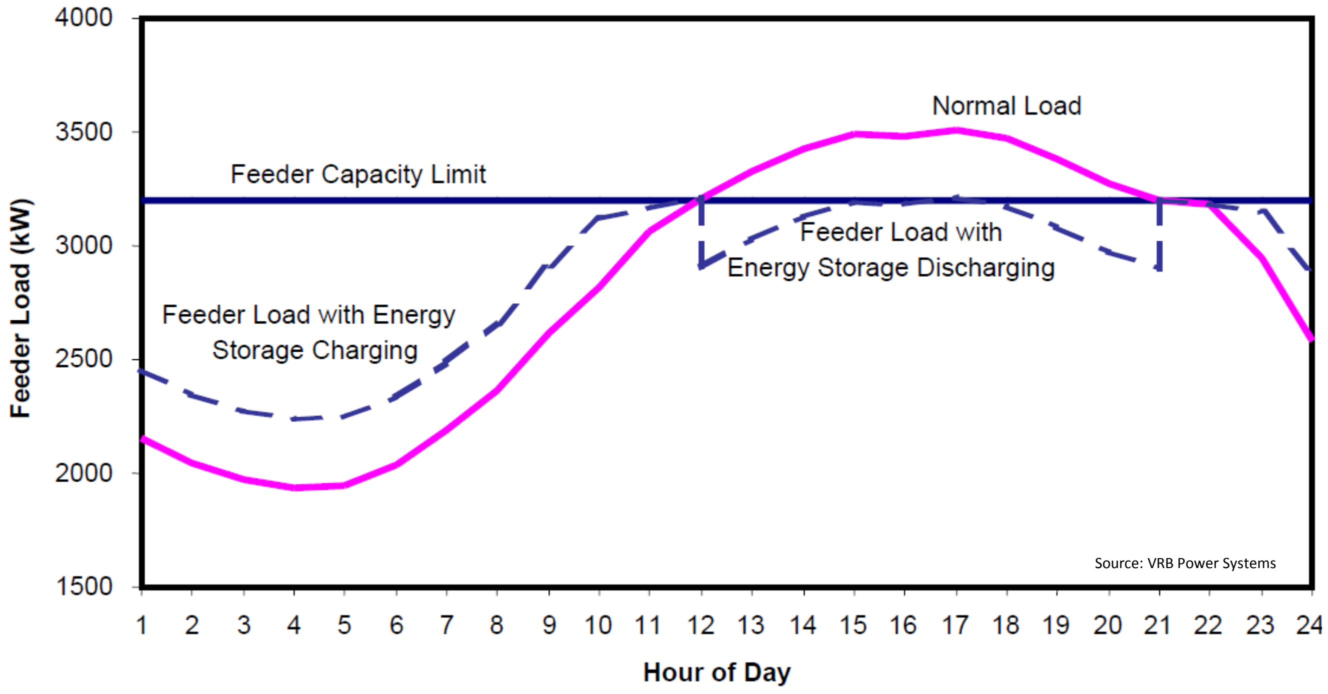
Source: VRB Power Systems

Castle Valley, UT – VRB

Source: VRB Power Systems

Castle Valley, UT – VRB

- Battery provides:
  - Peak shaving
  - Voltage regulation



Source: VRB Power Systems

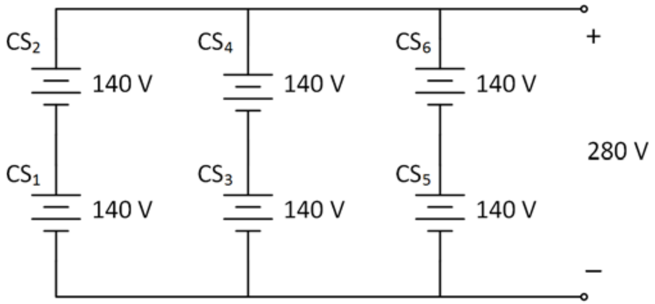
Castle Valley, UT – Electrolyte Tanks

- Electrolyte storage tanks
  - Only two
    - Other systems use many
  - Fiberglass
  - 43’ long × 9.5’ diameter
  - 70,000 liters

Source: VRB Power Systems

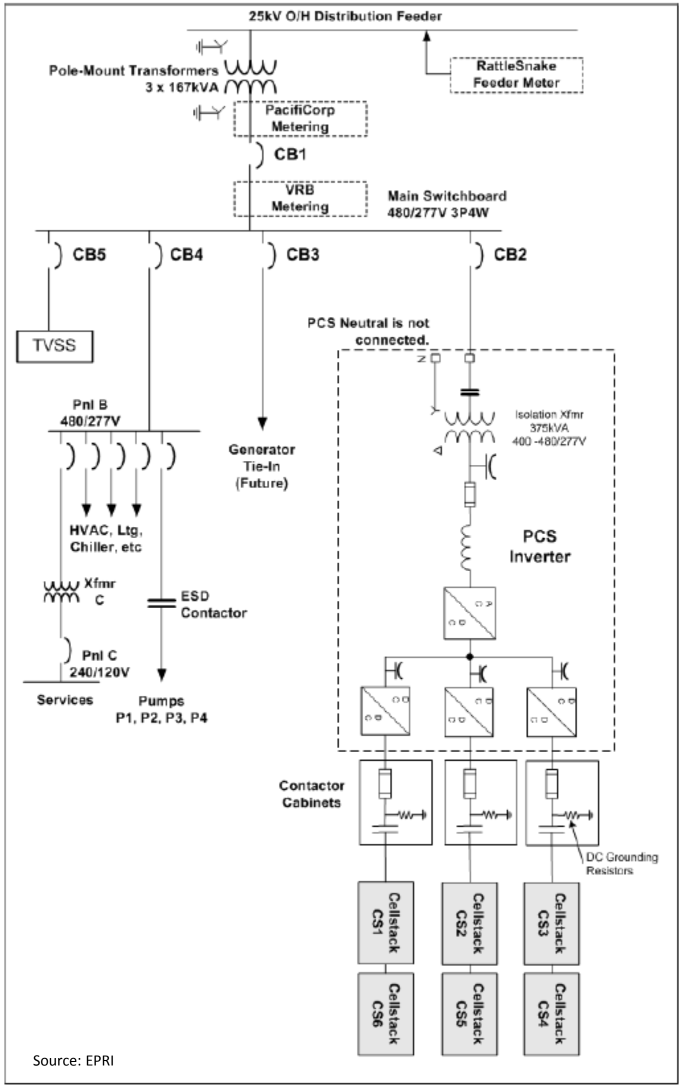
Castle Valley, UT – Stacks

- Six cell stacks
  - Three two-stack series combinations connected in parallel
- 100 cells per stack
  - Nominal stack voltage: 140 V
- Stack dimensions: 1.0 m × 1.1 m × 1.3 m
- Each stack can provide 42 kW continuously
  - Brief bursts of 150 kW possible
- Nominal DC battery voltage: 280 V



Castle Valley, UT – Power Conversion System

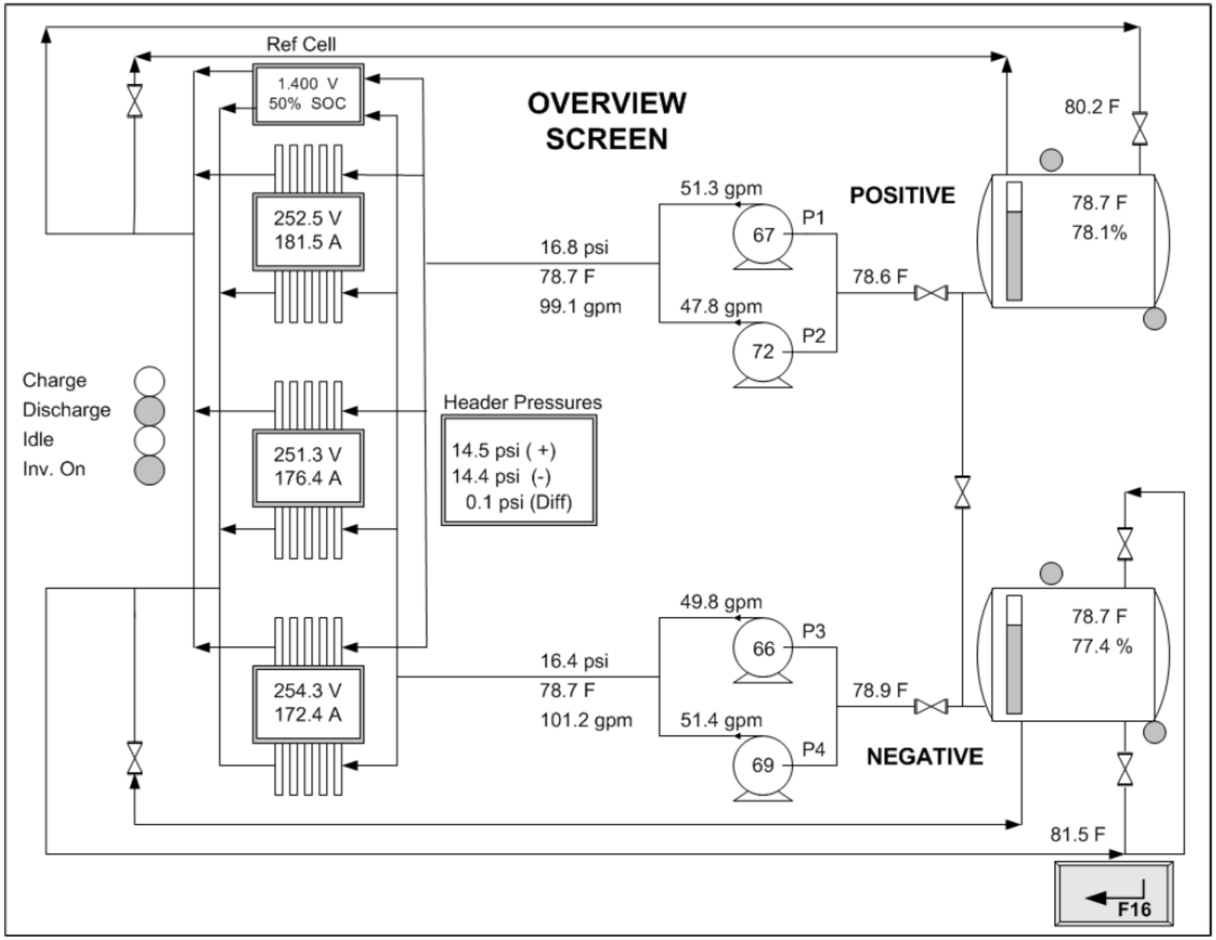
- ☐ 375 kVA transformer connects to 3-ϕ, 480 V bus
- ☐ Inverter includes AC-DC and DC-DC inverters
- ☐ 353 kVA
- ☐ 94% efficiency
- ☐ Power output: 250 kW and 250 kvar
  - ◘ Leading or lagging power factor



Source: EPRI

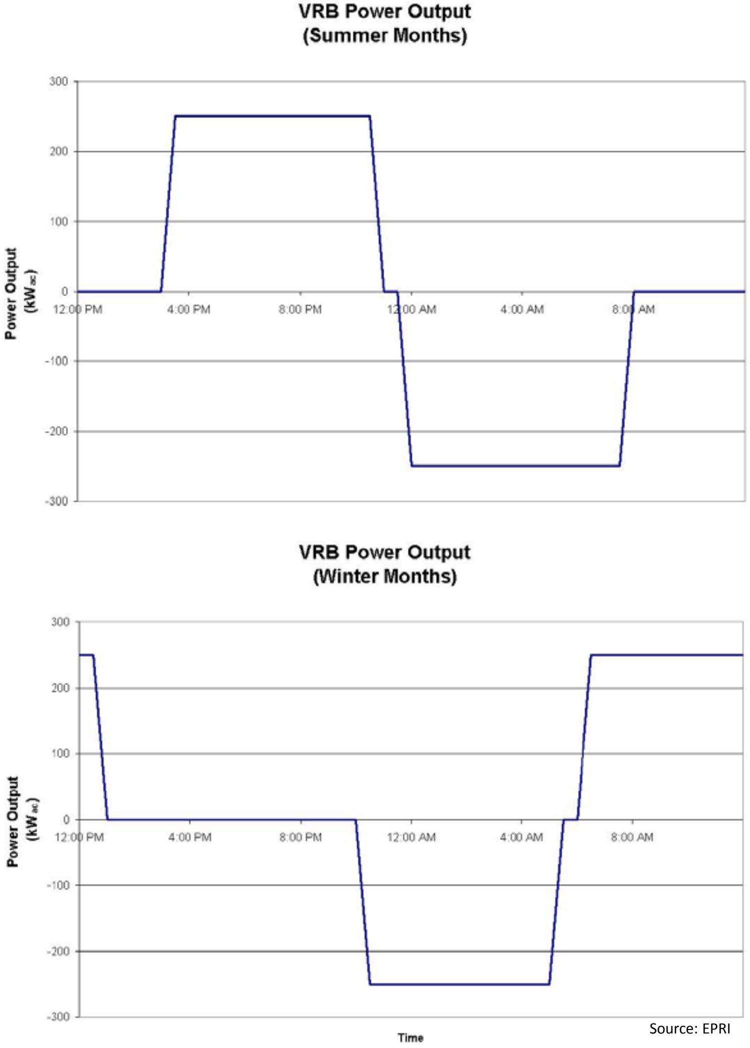
Castle Valley, UT – HMI

- Human-machine interface:



Castle Valley, UT – Battery Operation

- Predetermined daily baseline charge/discharge profiles
  - Summer and Winter profiles
- Variable real/reactive power provided on top of baseline power for voltage regulation
- DC-DC efficiency: 78%
- AC-AC efficiency: 69%



Source: EPRI

Turlock, CA – Fe/Cr Flow Battery

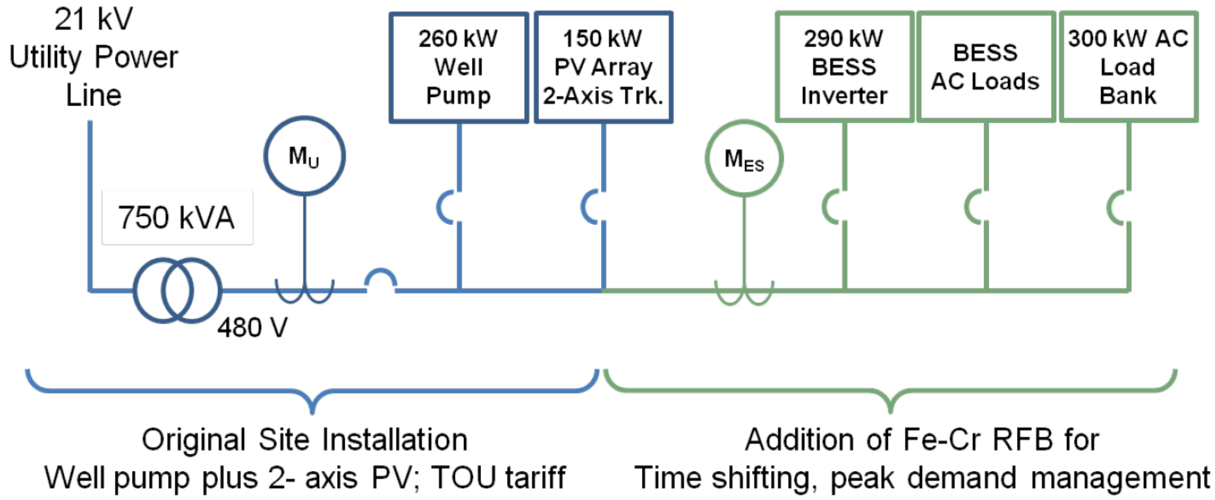
- Battery purpose
  - Integration of renewables
  - Load shifting
- Fe/Cr flow battery
  - 250 kW charge/ discharge
  - 1 MWh
  - 4 hours of charge/ discharge
  - EnerVault Corporation

Source: EnerVault

Turlock, CA – Fe/Cr Flow Battery

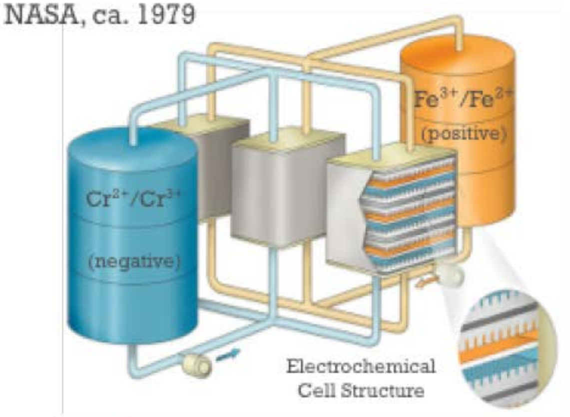
- Almond orchard
  - 150 kW solar PV array
  - 260 kW well pump for irrigation
- Nine 120-cell stacks
  - 30 kW each

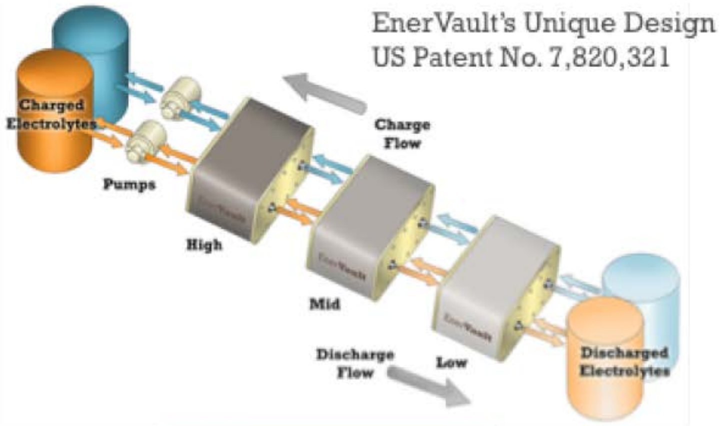
Source: EnerVault

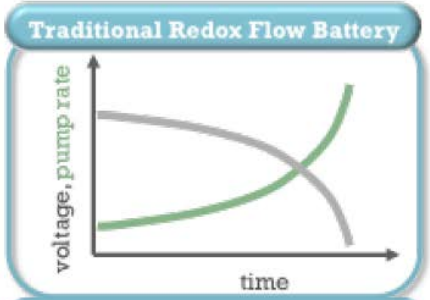


Turlock, CA – Fe/Cr Flow Battery

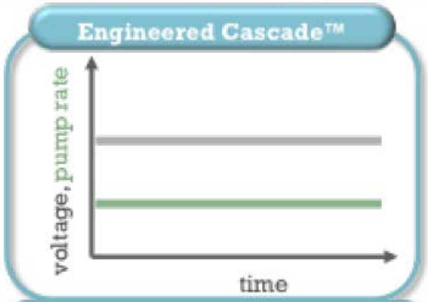
- Unlike most flow batteries, EnerVault connects cell stacks in series







- Fast response to power change
- Narrow state of charge range
- Lower Efficiency



- Long duration steady power
- Wide state of charge range
- Higher Efficiency

Source: EnerVault

Pullman, WA – VRB

- Washington State University, Pullman, WA
  - Vanadium redox flow battery
  - Largest flow battery in North America or EU
  - 1 MW
  - 4 MWh
  - UniEnergy Technologies
- Battery used for
  - Frequency regulation
  - Voltage regulation

Pullman, WA – VRB

- UET battery modules
  - 600 kW
  - 2.2 MWh
  - Five 20’ shipping containers
  - 20 MW per acre
  - 40 MW per acre if double-stacked
  - ~$700/kWh
  - 65% … 70% AC efficiency