Next Generation Redox Flow Battery Prototype Development

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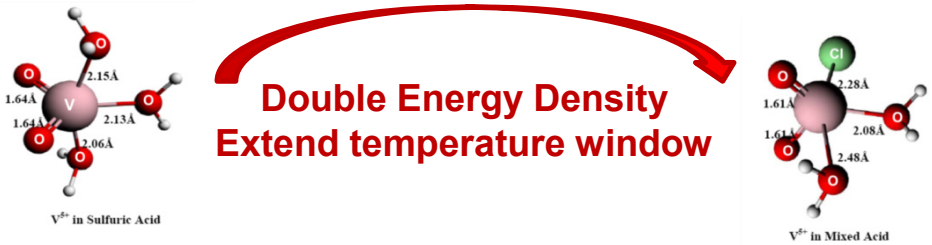
1 UniEnergy Technology

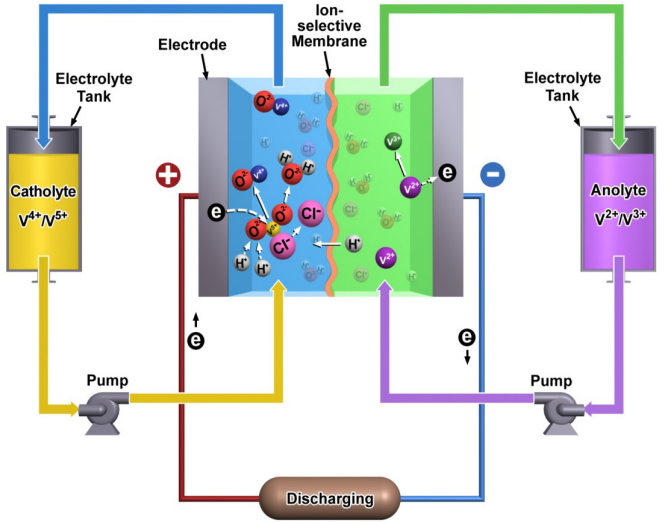
Objective

Validate new mixed acid electrolyte chemistry in larger scale 1 kW /1 kWh stack to identify potential issues and challenges with scale-up.

Outline

- Shunt current model
- CFD and pressure drop
- 1 kW construction
- 1kW stack demonstration





Catholyte: $VO^{2+} + Cl^- + H_2O - e \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} VO_2Cl + 2H^+$ ε_{co}=1.0 V

Anolyte: $V^{3+} + e \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} V^{2+}$ ε_{ao}=-0.25

Overall: $VO^{2+} + Cl^- + H_2O + V^{3+} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} VO_2Cl + 2H^+ + V^{2+}$ E_o=1.25 V

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Scale-up challenges for 1kW system

- Shunt current through fluid path due to ionically conductive electrolyte
  - *Want high electrolyte resistance along flow path to reduce shunt current*
- Minimize pressure drop to reduce pumping energy loss
  - *Uniform flow distribution in every cell and a single cell is required*
- Trade-off design between flow and shunt current

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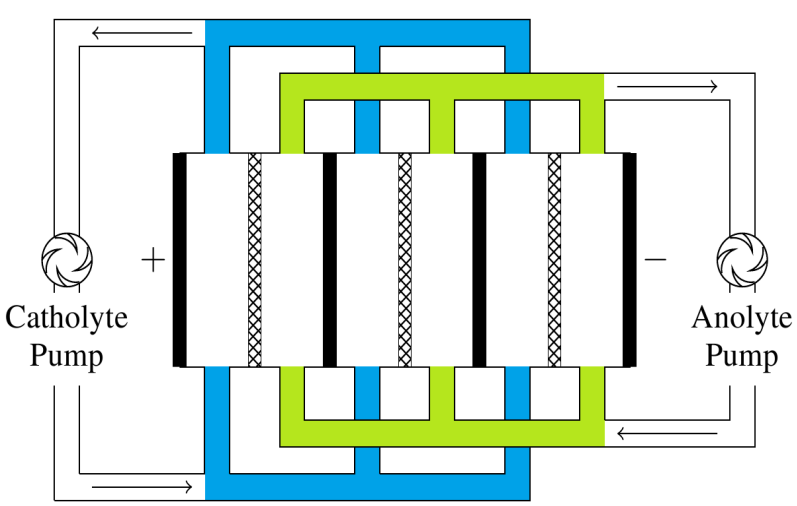
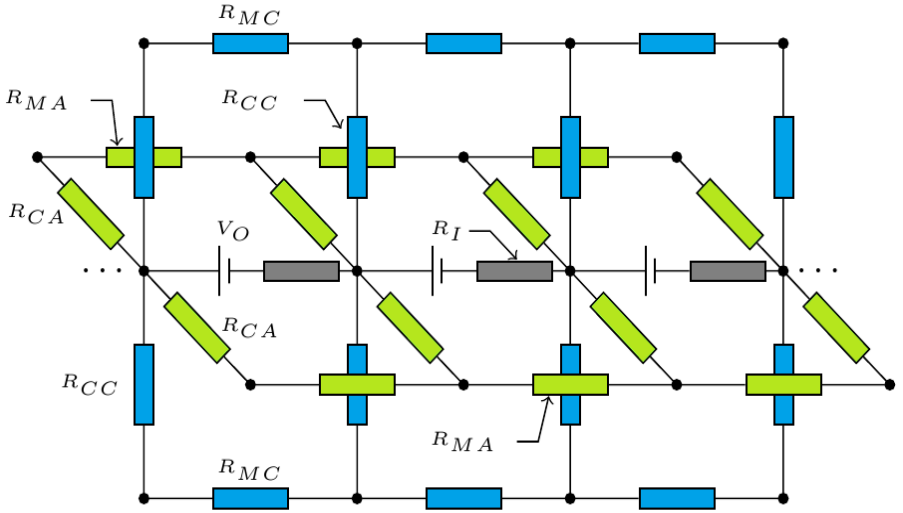
Shunt Current Model.



(a)



(b)

Schematic of a) redox flow cell stack assembly, and (b) equivalent electric circuit model

1. Dimensionless channel resistance

$$r = \sqrt{\frac{R_c}{4R_i + R_m}} \approx \sqrt{\frac{R_c}{R_m}}$$

2. Characteristic shunt current

$$I_K = \frac{V_{oc} - I_L R_i}{4R_i + R_m} \approx \frac{V_{cell}}{R_m}$$

3. Number of cell: n

$$\frac{r}{n} < \frac{1}{2e}$$ ⇒ **High shunt loss**

Design Guidelines (< 1%)

$$\frac{i_{avg}}{I_K} < 0.3 \Rightarrow \frac{r}{n} > 1$$

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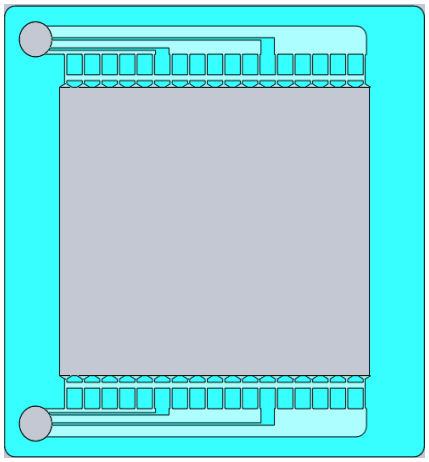
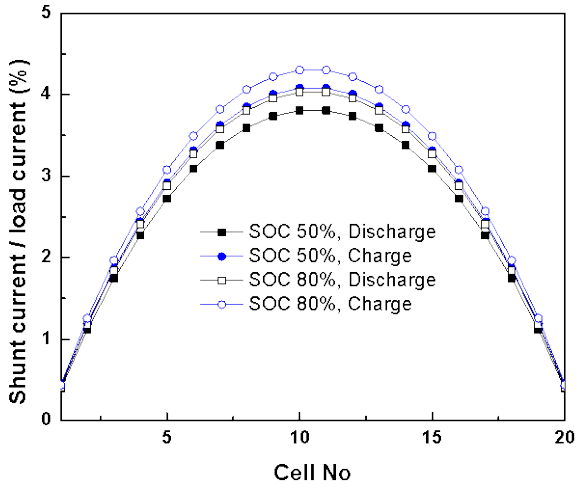
Evolution of Stack Design

Gen 1.1



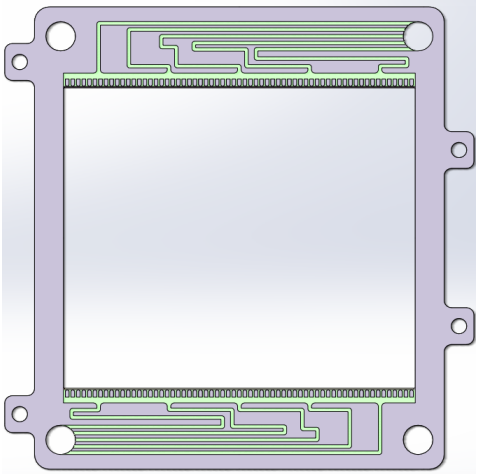


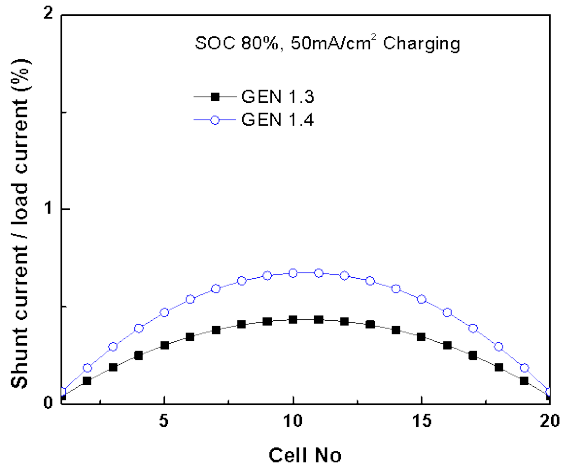
$$R_c / R_m = 86$$

$$\frac{r}{n} = 0.46$$

Shunt loss: ~ 3 %

Gen 1.4





$$R_c / R_m = 1200$$

$$\frac{r}{n} = 1.73$$

Shunt loss: < 1 %

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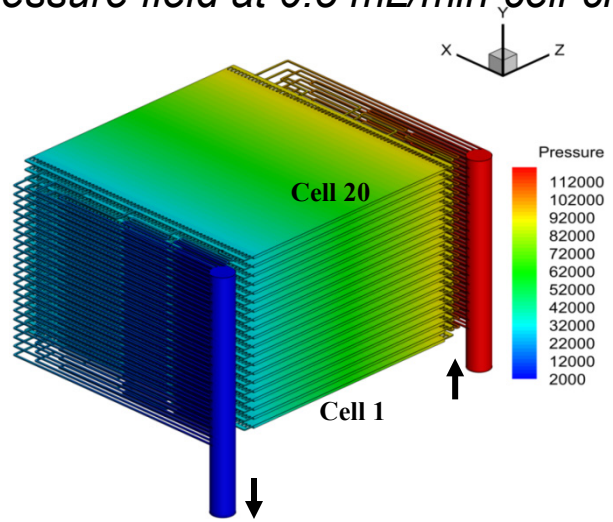
Fluid Flow Model (CFD, Star CD)

Determined material properties for 1.7 M V + 5 M S electrolyte at 25°C

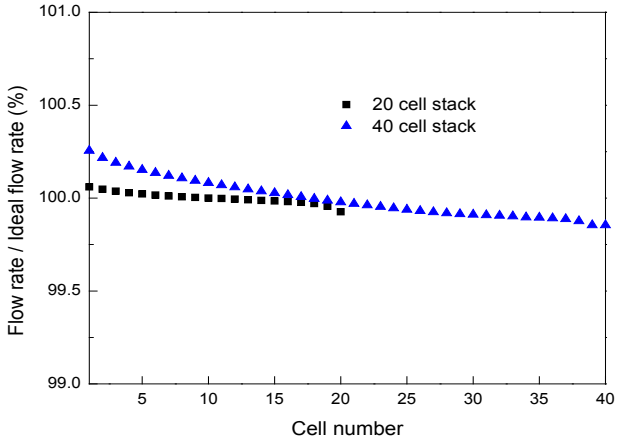
- *density (ρ= 1400 kg / m^3),*
- *viscosity (μ= 6 cP)*
- *and determined permeability (k=1.685 x 10^{-10} m^2) of electrode felt from* $-\frac{\mu}{k}v = \nabla p$

Stack CFD

Pressure field at 0.5 mL/min-cell-cm^2



flow rate distribution in the stack



Combined CFD and shunt current analyses confirmed that Gen 1.4 design should enable 1 kW prototype stack with:

- < 1% shunt current loss
- < 1% deviation in flow across all cells

Key parameters for 1 kW / 1 kWh prototype system

Current Density	80 mA/cm^2
SOC Range	15-85
Electrolyte Concentration	2M V, 2M S, 5 M Cl
Electrolyte Volume (liters)	30/30
Stack Dimension (cm)	31 (W) × 44 (H) × 40 (L)
Active area (cm^2)	780
Number of cells	15
Electrode	Graphite felt (SGL GFD4.6) SIGRACET® expanded Graphite (TF6)
Flow frame	PVC (polyvinyl chloride)
Membrane	Nafion® 115

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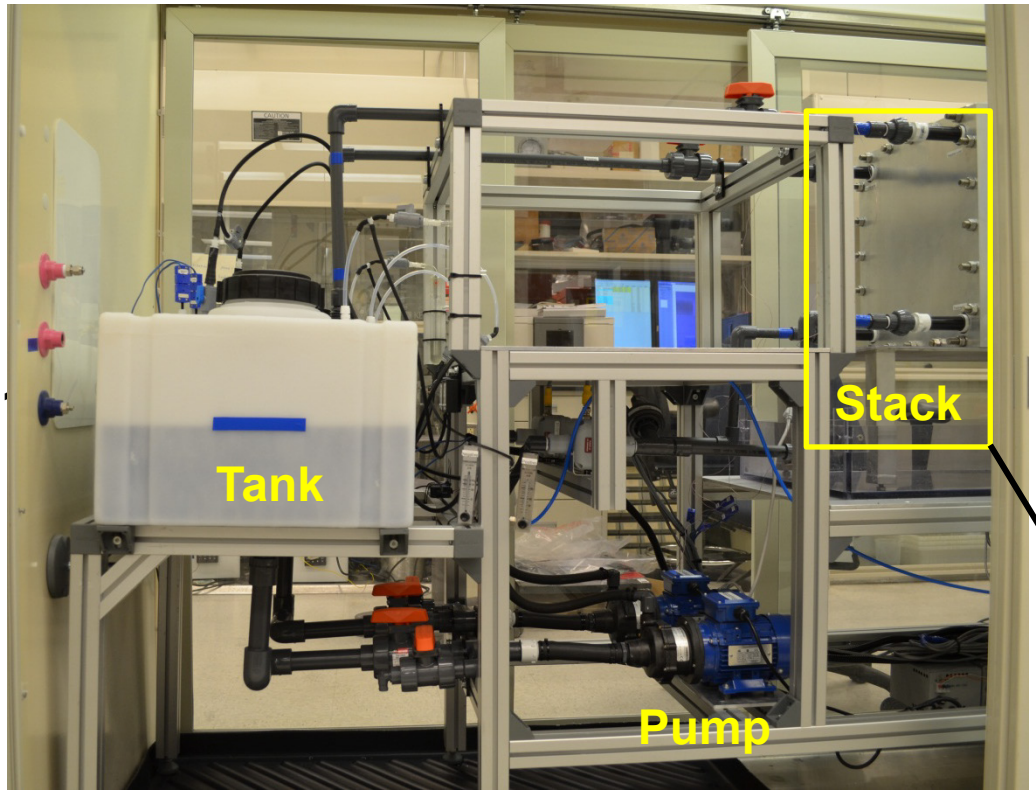
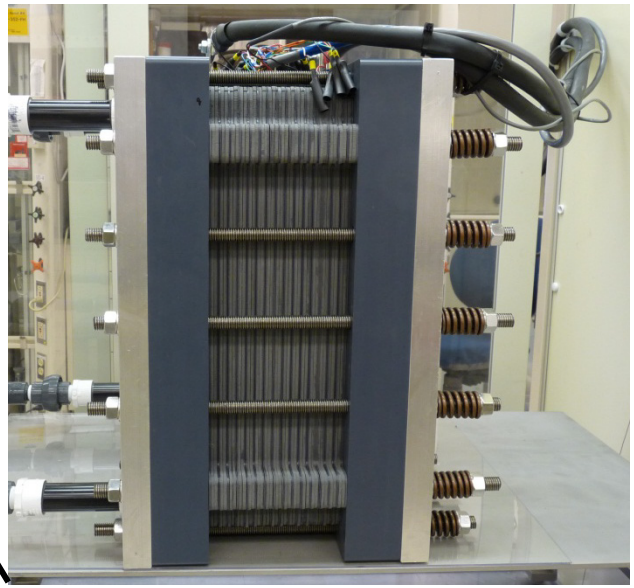
1 kW/ 1 kWh mixed acid system



1kW / 1kWh VRFB System



1kW Stack

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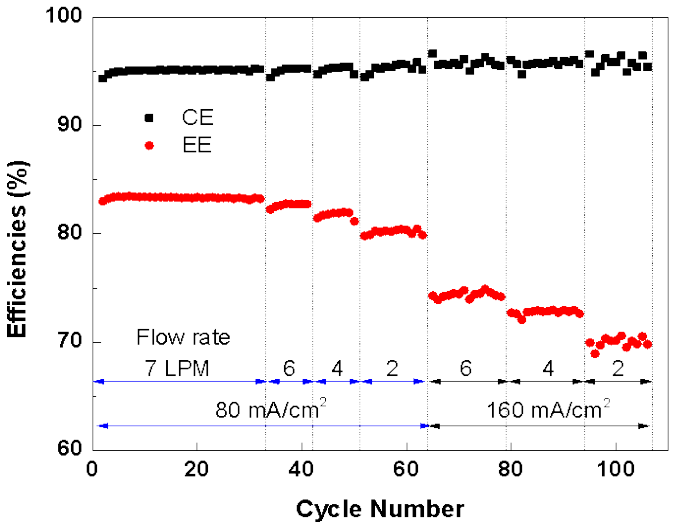
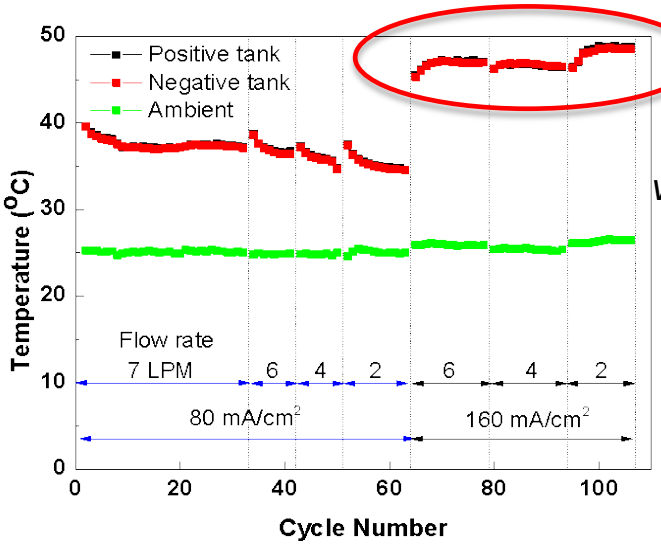
1 kW stack performance

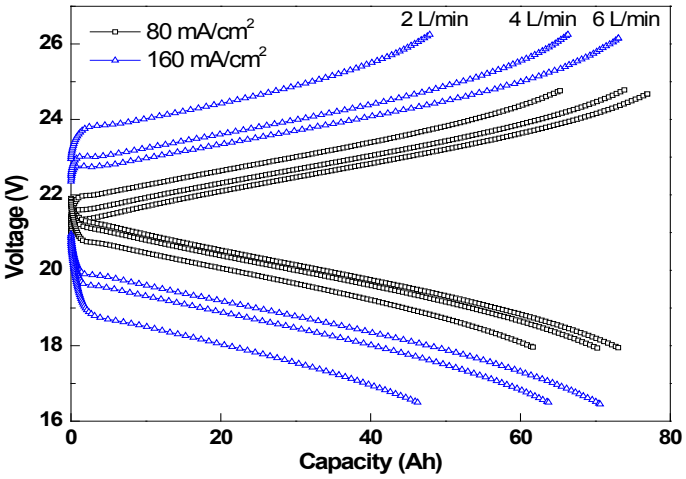
Test Conditions

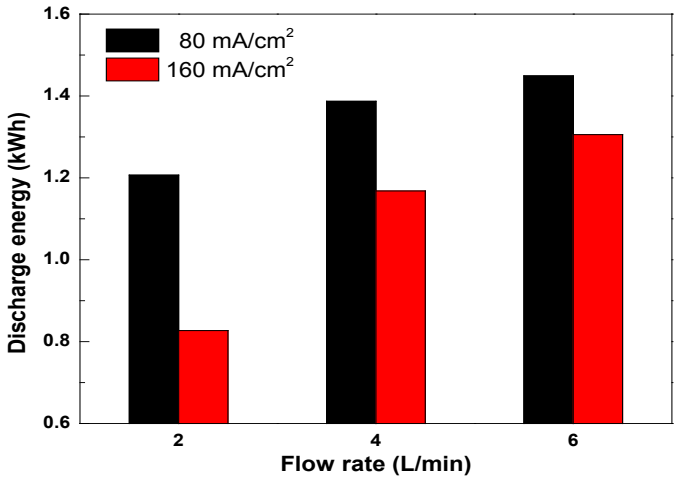
- *Flow rates 2, 4, 6, and 7 slpm*
- *15-85 SOC @ 80 mA/cm²*





Temperature exceeds stability of conventional vanadium electrolyte





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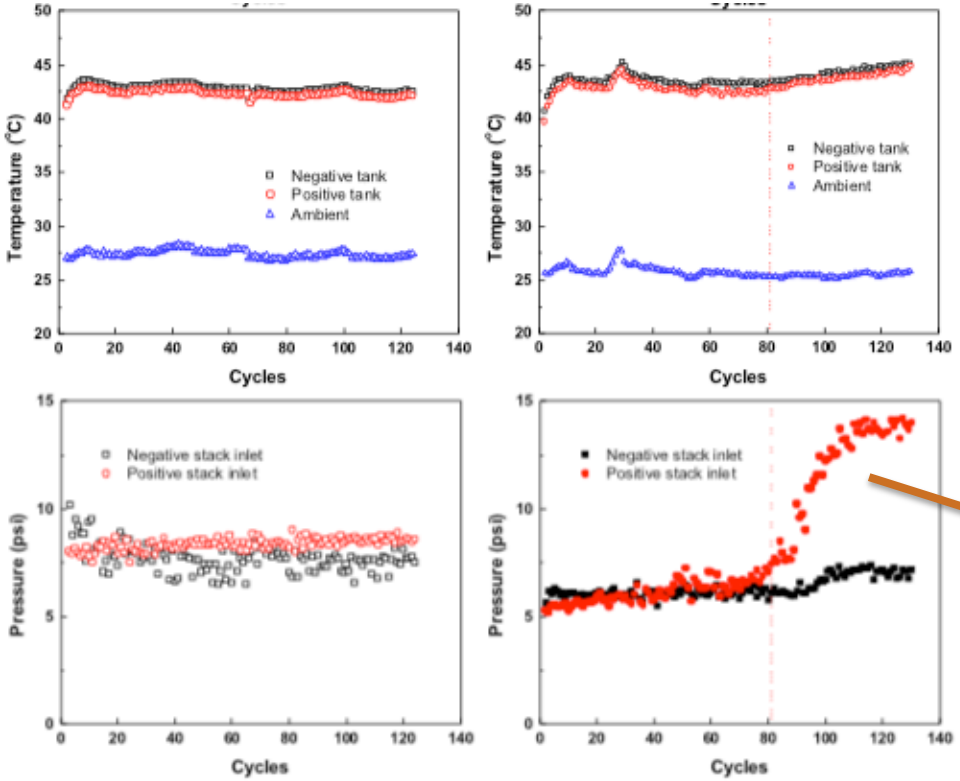
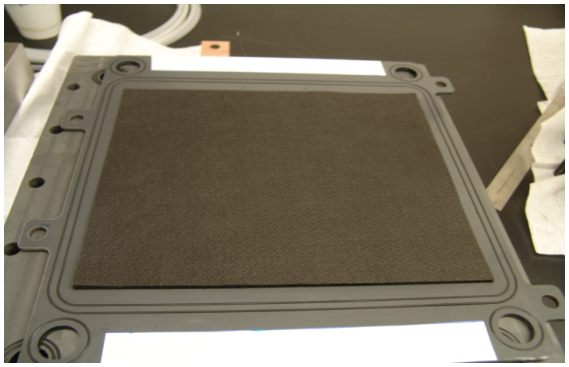
Comparison of Conventional and Mixed Acid Electrolyte under high temperature operation

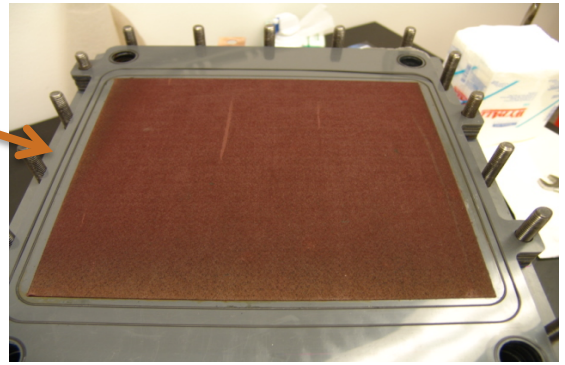
2.0 M
Mixed acid electrolyte

1.5 M
Conventional electrolyte



Negative electrode after 130 cycle with conventional electrolyte:





Positive electrode after 130 cycle with conventional electrolyte showing precipitation.

- Increase in pressure resulting from precipitation of V^{5+} with conventional electrolyte.
- No precipitation observed with mixed acid electrolyte with 50% increased concentration

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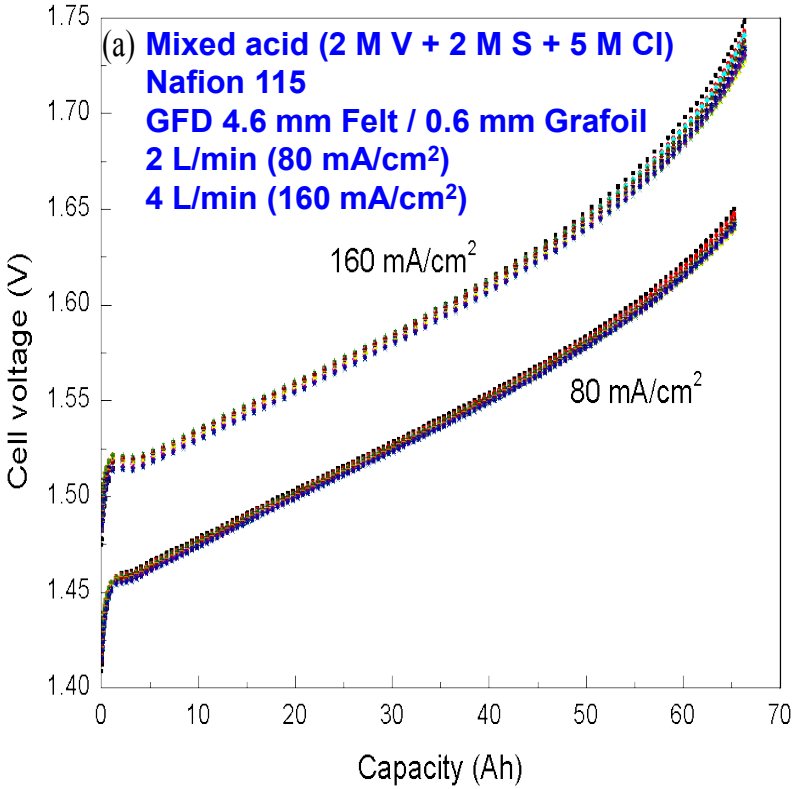
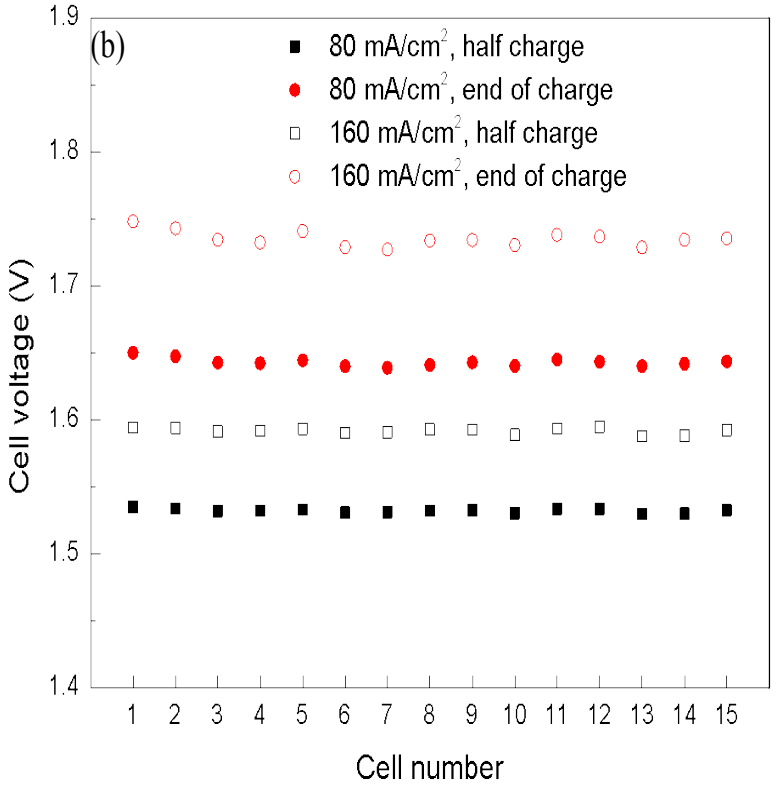
1 kW Stack cell-to-cell uniformity.



Current vs. capacity for all 15 cells in the stack



Cell voltage vs. cell number at 50% and 100% SOC

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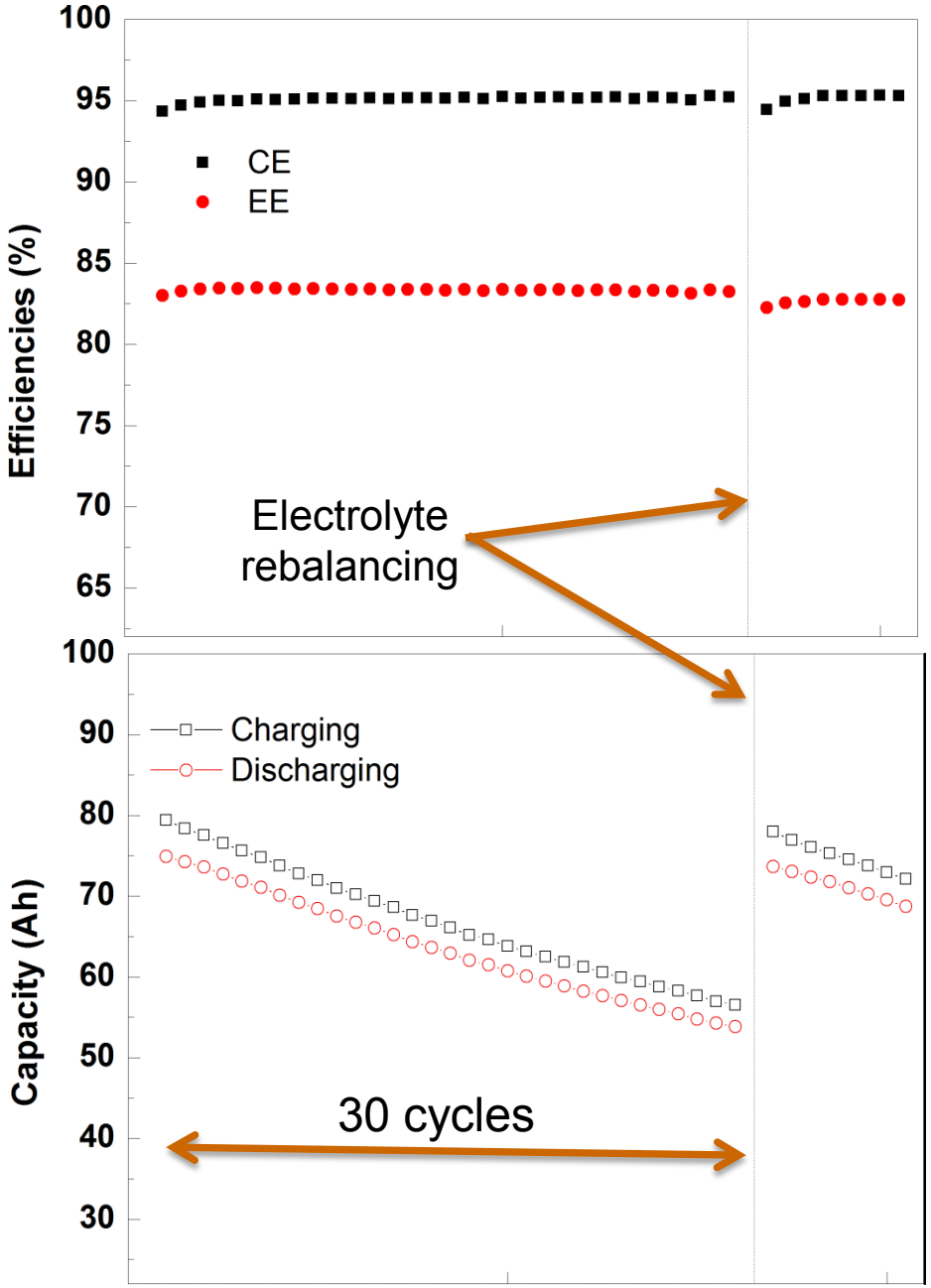
1 kw System Capacity Fade.



- *2M V, 2M S, 5M Cl mixed acid electrolyte*
- *80 mA/cm²*
- *15-85% SOC*
- *Nafion 115 membrane*
- *T_{tank} ~ 38 ℃*

- *Current efforts are focused on mitigating capacity fade in single cell component tests which will be incorporated into the stack in FY13.*

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Summary

- *Able to demonstrate mixed acid operating > 1.1 kW at 80 mA/cm^2 with a round trip energy efficiency of 82% for the stack and an energy content of 1.4 kWh.*

Future Work

- *Improve EE at higher current density.*
- *Incorporate lower cost membrane*
- *Improve capacity fade*
- *V/Fe chemistry demonstration with microporous separator*

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