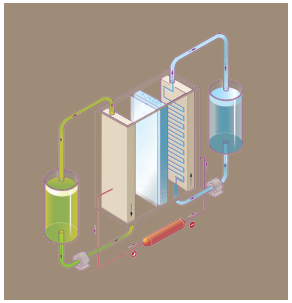

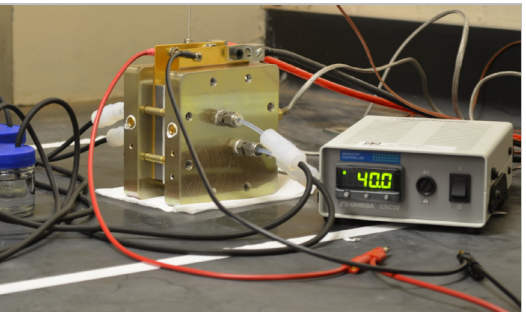

# Thermoelectrochemical Energy Storage

27 September 2012


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Sandia National Laboratories


Sandia National Laboratories

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# Thermoelectrochemical Energy Storage

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- **Problem**: **Flow batteries** exhibit **inefficiencies** that are affected by operating temperature.

- **Opportunity**: Power plants produce **waste heat** that can be recovered and applied to other processes.
  - We can use the heat to increase the temperature of all or part of a flow battery system.

- **Approach**: Demonstrate the advantage of **non-isothermal** operation of a flow battery.
  - Charge at higher temperature and discharge at lower temperature
  - **Energy efficiency at least 5% higher** than isothermal operation

# Battery Efficiency & Temperature

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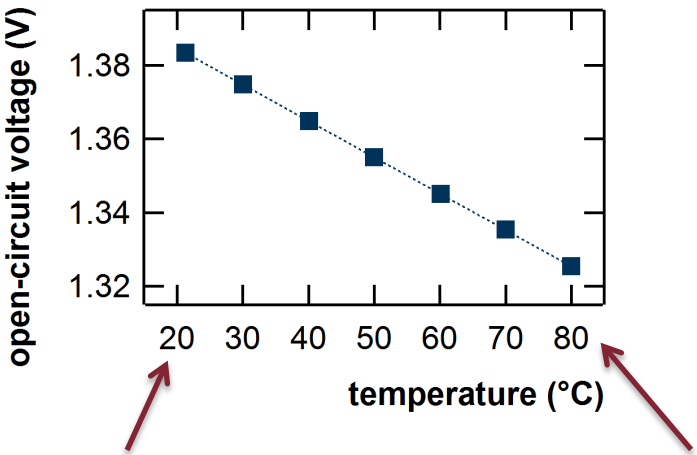
## All-Vanadium Flow Battery

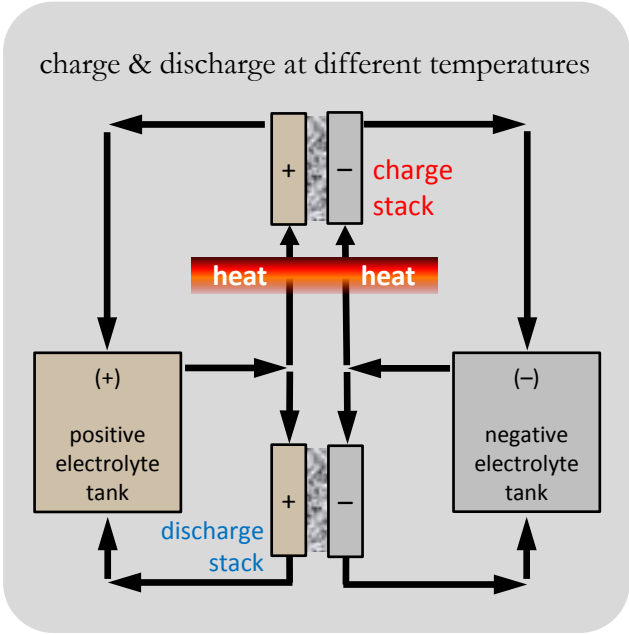



- Electrochemical cells (including flow batteries) have an equilibrium (open-circuit) voltage that is dependent on temperature
- Voltage vs. temperature data is rarely collected for flow battery chemistries
- Voltage is a major component of the energy efficiency of a system

maximize

voltage efficiency | coulombic efficiency

$$\text{“round trip” energy efficiency} = \left(\frac{\text{discharge voltage}}{\text{charge voltage}}\right) \times \left(\frac{\text{discharge electrons}}{\text{charge electrons}}\right)$$



# FY12 Milestones & Accomplishments

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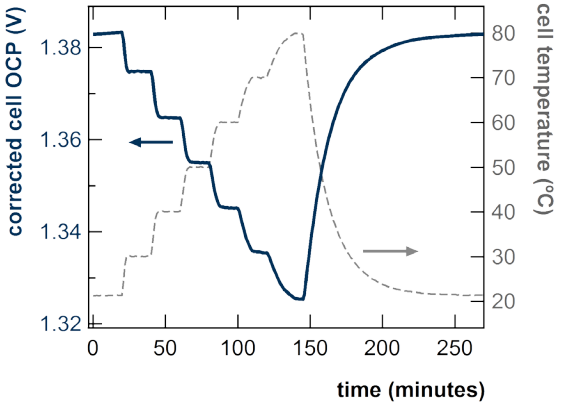
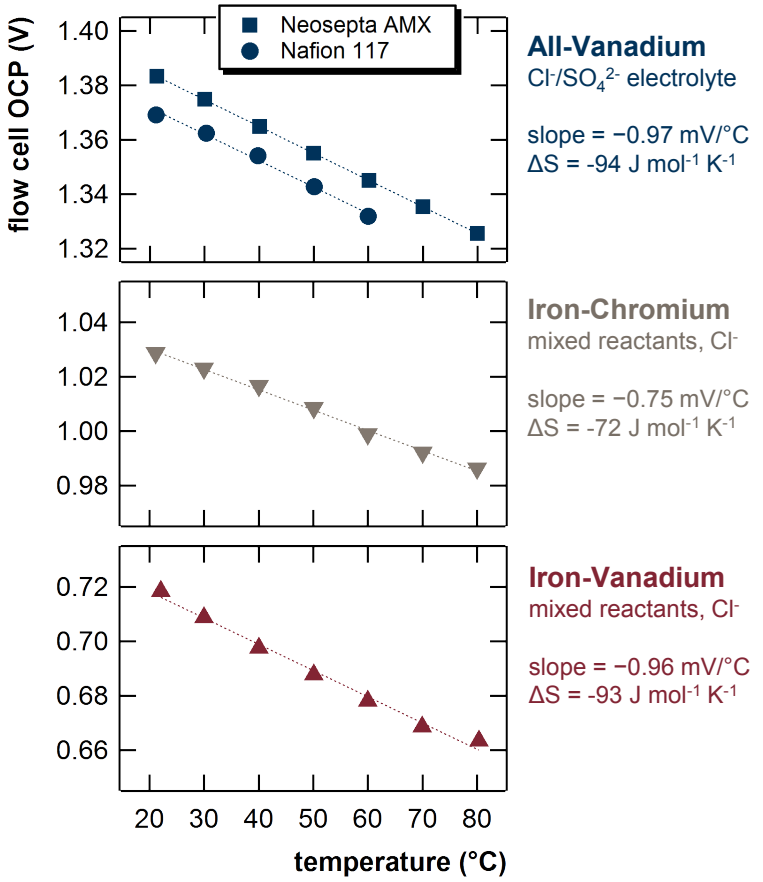
- Literature review and identification of cell chemistries of interest
- Experimental set-up for “half-cells” and full flow cells
  - High-precision voltage vs. temperature measurement
  - LabVIEW program developed: integration for automated measurement
- Half-cell (voltage vs. reference vs. temperature) testing of $Fe^{2+/3+}$ redox couple with various electrolyte compositions
- Flow cell testing (voltage vs. temperature) of typical chemistries
  - all-vanadium with mixed $Cl^-/SO_4^-$ electrolyte
  - iron-chromium chloride (mixed and unmixed reactants)
  - iron-vanadium with $Cl^-$ electrolyte
- Preliminary demonstration and prediction of **increase in voltage efficiency** from operating in non-isothermal mode
- Presentation at International Flow Battery Forum in Munich (June 2012)

# Voltage-Temperature Data

## Flow Cell Open-Circuit Voltage




**All-Vanadium**
$Cl^-/SO_4^{2-}$ electrolyte

slope = −0.97 mV/°C
$\Delta S$ = -94 J mol$^{-1}$ K$^{-1}$

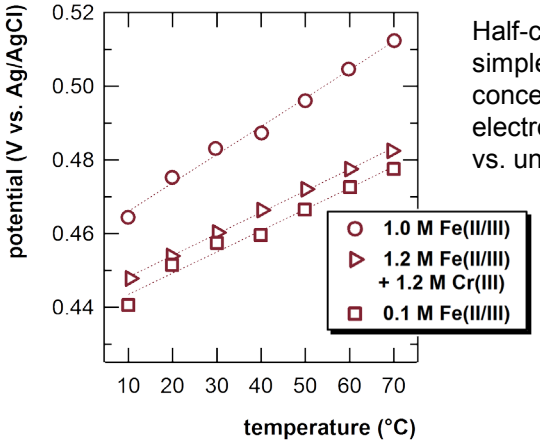
**Iron-Chromium**
mixed reactants, $Cl^-$

slope = −0.75 mV/°C
$\Delta S$ = -72 J mol$^{-1}$ K$^{-1}$

**Iron-Vanadium**
mixed reactants, $Cl^-$

slope = −0.96 mV/°C
$\Delta S$ = -93 J mol$^{-1}$ K$^{-1}$

## $Fe^{2+/3+}$ Half-Cells (vs. reference electrode)

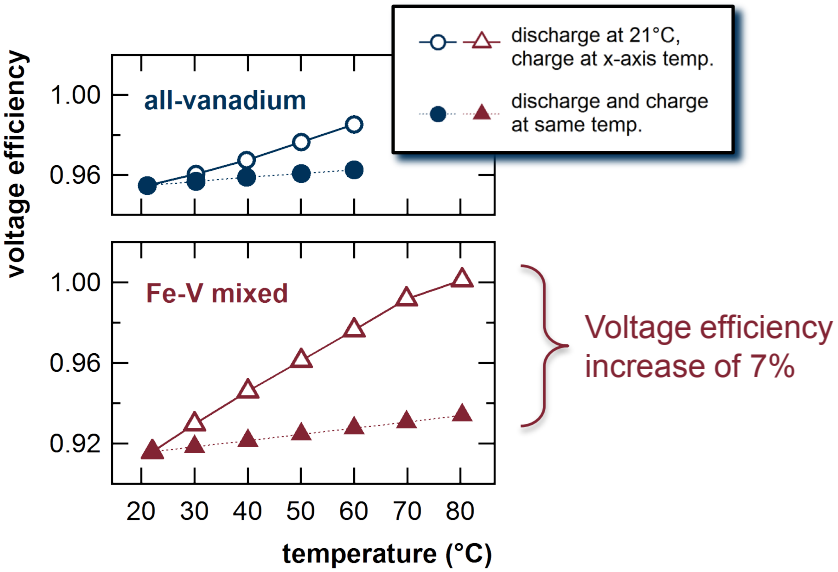



Half-cell measurements allow the simple variation of redox active concentration, supporting electrolyte concentration, mixed vs. unmixed reactants.

Flow cells are at 50% state-of-charge for the voltage-temperature measurement. Flow rate is 0.1 ml/min on positive and negative electrodes.

# Efficiency Improvement

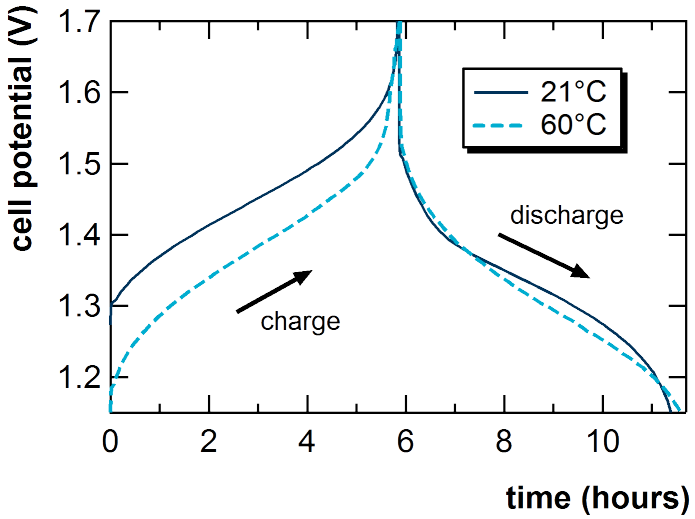
## Predicted




Voltage-temperature data from previous slide used to estimate the voltage efficiency at 50 mA $cm^{-2}$. Major assumption is that all cell polarization is from the ohmic resistance of a Nafion 117 membrane. Nafion conductivity values from: C. H. Lee et al, *Ind. Eng. Chem. Res.* **44**: 7617 (2005)

## Measured

All-vanadium flow cell at 10 mA/$cm^2$




### Voltage Efficiency

isothermal (60°C): 93.2%
non-isothermal (60-21°C): 95.2%

Increase of 2%

# Summary

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- Non-isothermal operation of flow batteries
  - Charge at higher temperature, discharge at lower temperature
  - Possible increase in round-trip efficiency > 5%
  - Voltage-temperature data needed to evaluate feasibility
  - Voltage-temperature data also useful for thermal models, fundamental studies
- Experimental set-up developed for voltage-temperature measurements of half-cells and full flow cells
- Half-cell and flow cell data was acquired for iron, chromium, and vanadium chemistries
  - All-vanadium and iron-vanadium flow cells show most promise for benefitting from non-isothermal temperature scheme
- Based on acquired data, iron-vanadium flow cell predicted to benefit from an **efficiency increase of 7%** by using a non-isothermal configuration
- Observed **increase in voltage efficiency of 2%** in all-vanadium flow cell

# Future Tasks

- Repeat all measurements to obtain error estimates and make data publication-ready
- Additional variation of electrolyte composition in half-cells to determine effect of concentration and supporting electrolyte
- Short-term and long-term cycling of cells under different temperature regimes to **measure efficiency advantage of non-isothermal configurations**
- Submission of manuscript(s) to peer-reviewed publications

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