

Thermoelectrochemical Energy Storage

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Nick Hudak

Advanced Power Sources R&D

Sandia National Laboratories



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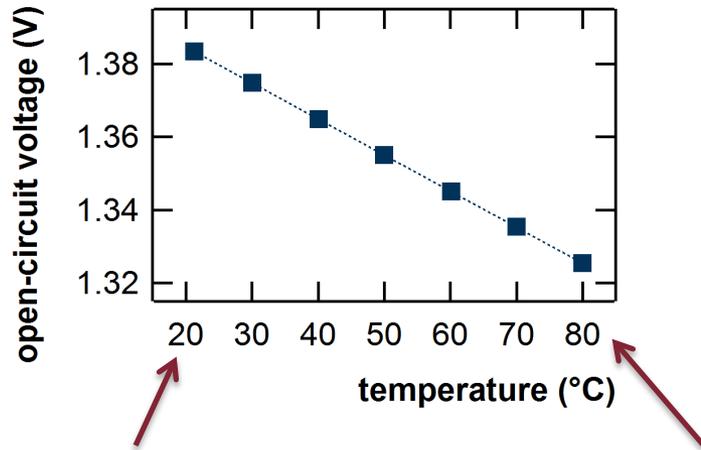
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Thermoelectrochemical Energy Storage

- **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

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

discharge at this temperature (higher V)

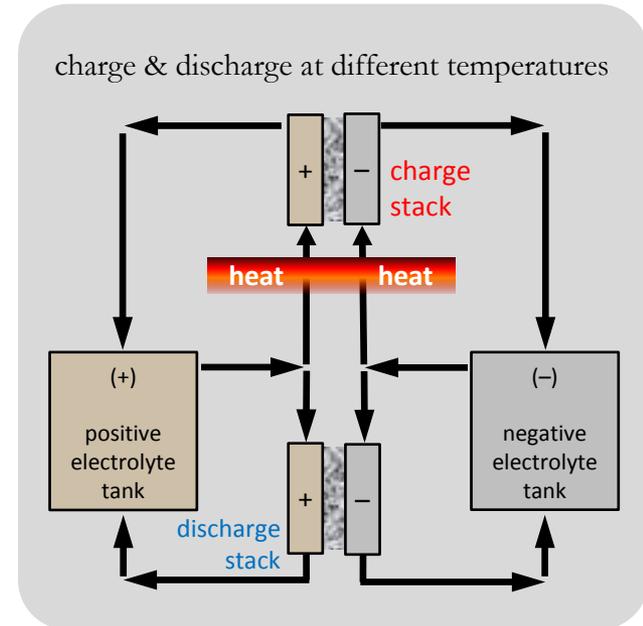
charge at this temperature (lower V)

maximize

voltage efficiency

coulombic efficiency

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

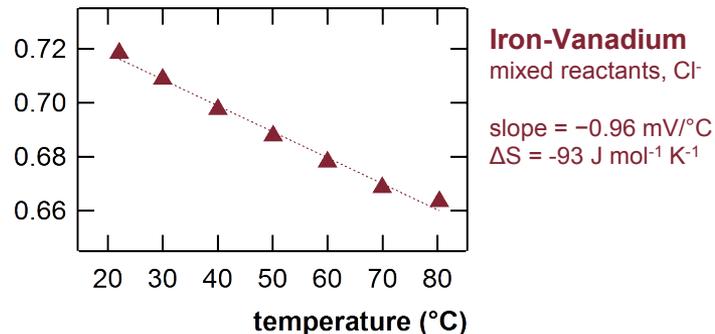
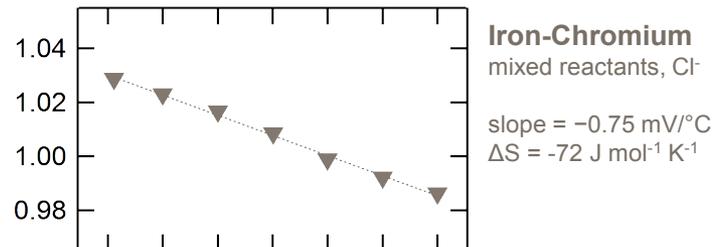
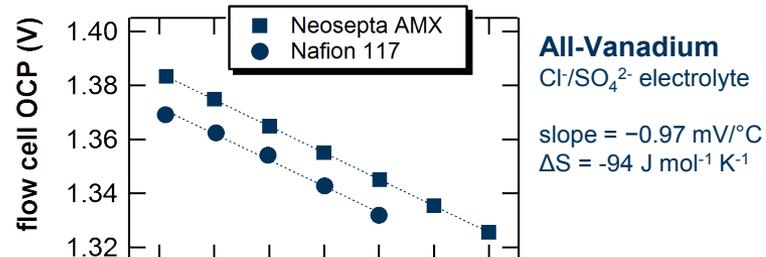
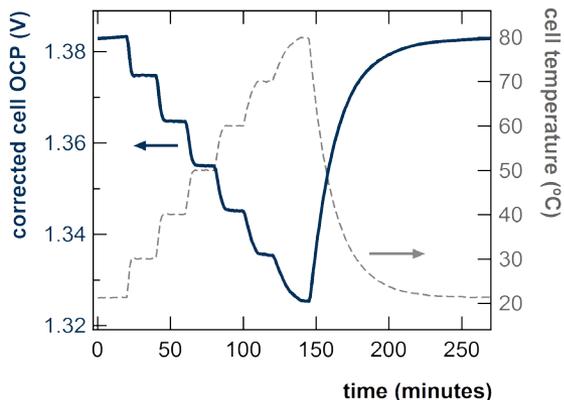


FY12 Milestones & Accomplishments

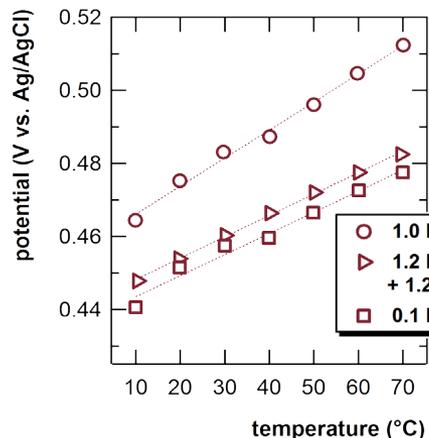
- Literature review and identification of cell chemistries of interest
- Experimental set-up for “half-cells” and full flow cells
 - High-precision voltage vs. temperature measurement
 - LabVIEW program developed: integration for automated measurement
- Half-cell (voltage vs. reference vs. temperature) testing of $\text{Fe}^{2+/3+}$ redox couple with various electrolyte compositions
- Flow cell testing (voltage vs. temperature) of typical chemistries
 - all-vanadium with mixed $\text{Cl}^-/\text{SO}_4^-$ 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



Fe²⁺/³⁺ Half-Cells (vs. reference electrode)

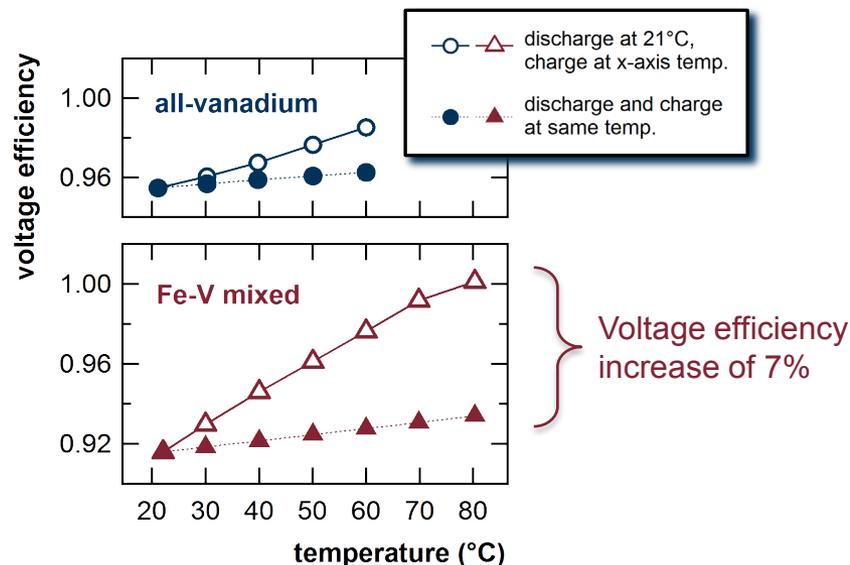


Half-cell measurements allow the simple variation of redox active concentration, supporting electrolyte concentration, mixed vs. unmixed reactants.

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

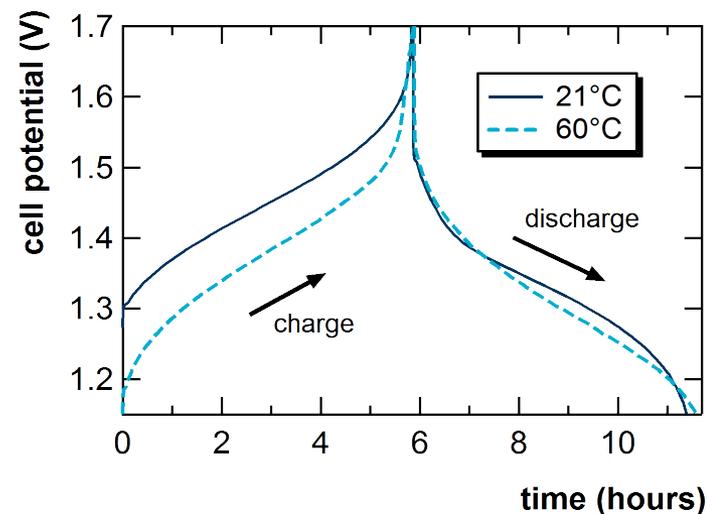
Predicted



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/cm²



Voltage Efficiency

isothermal (60°C): 93.2%
 non-isothermal (60-21°C): 95.2% } Increase of 2%

Summary

- 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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For more information, please contact:

Nick Hudak

nhudak@sandia.gov

+1 505 844 2171