

# Thermodynamics of Flow Battery Electrode Reactions

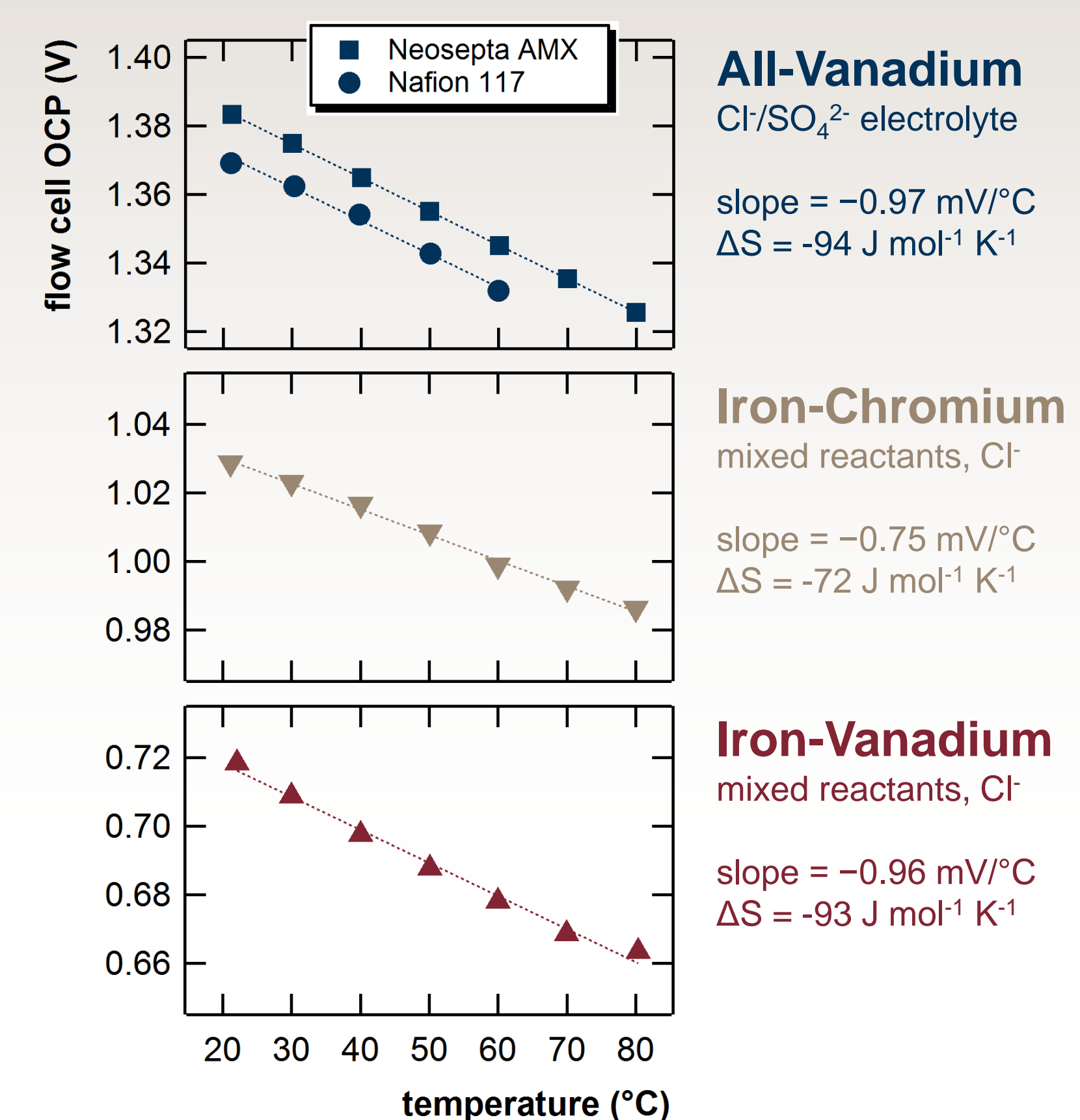
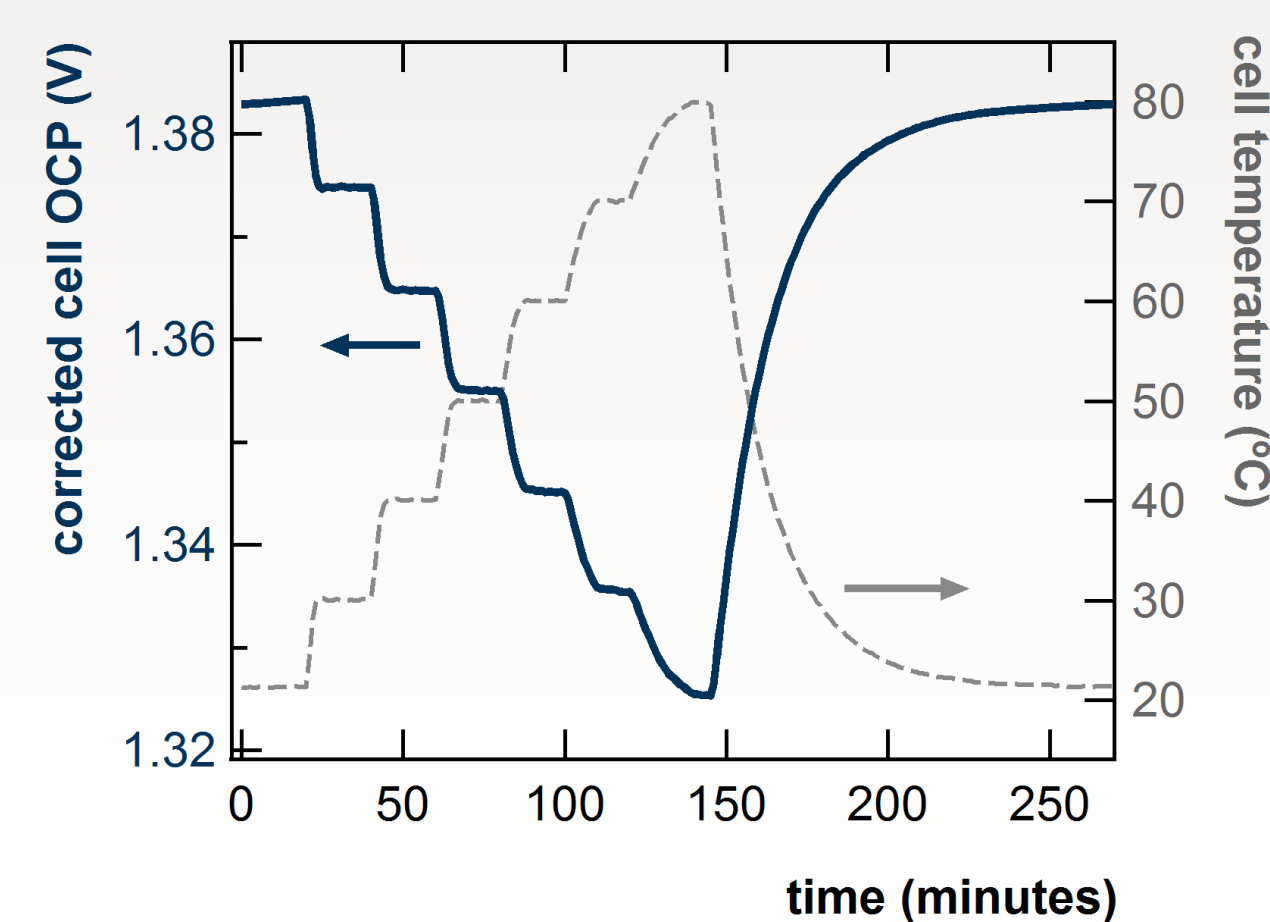
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Sandia National Laboratories, Albuquerque, New Mexico, U.S.A.

## Motivation

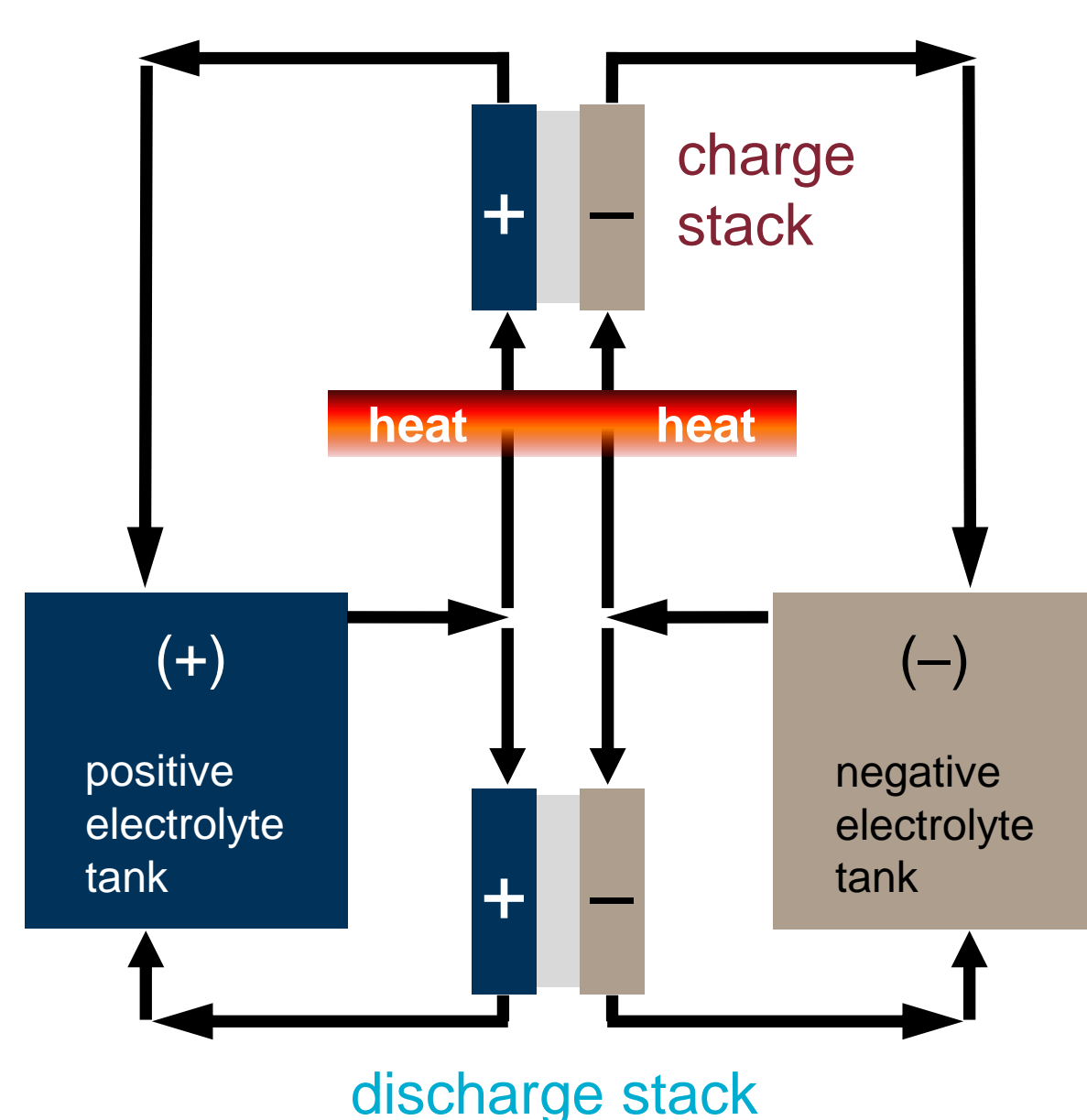
- Dependence of open-circuit potential (OCP) on temperature for flow battery chemistries is largely unknown
- $dE/dT$ , ratio of voltage change to temperature change, is proportional to the **partial molar entropy** of the electrochemical reaction
  - This thermodynamic quantity is a component of the heat consumption or output during battery charge or discharge and is necessary for an accurate thermal model of a flow battery system
- Potential-temperature relationship is also necessary for appropriate selection of operating temperature(s)
  - Operation of **charge and discharge at different temperatures** may result in increased efficiency
  - Goal is to charge the cell at a temperature with lower voltage and discharge at a temperature with higher voltage

## Voltage-Temperature Relationship in Flow Cells

In a flow cell or battery, a change in temperature corresponds to a change in open-circuit potential (OCP). This is shown below for an all-vanadium flow cell at 50% state-of-charge. Voltage values are corrected for a slightly drifting baseline.



## Proposed Flow Battery with Charge and Discharge at Different Temperatures



Excess thermal energy from external processes (e.g. from steam in a coal-fired power plant) can be used to raise the temperature of the charge or discharge process.

This can result in higher voltage efficiency compared to an isothermal system.

## Electrochemical Thermodynamics

- Gibbs free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ), and entropy ( $\Delta S$ ) of electrochemical reaction obtained by measuring open-circuit potential of the cell at different temperatures

$$-nFE = \Delta G = \Delta H - T\Delta S$$

equilibrium (open-circuit) potential

$$\left. \frac{\partial E}{\partial T} \right|_p = \frac{1}{nF} \Delta S$$

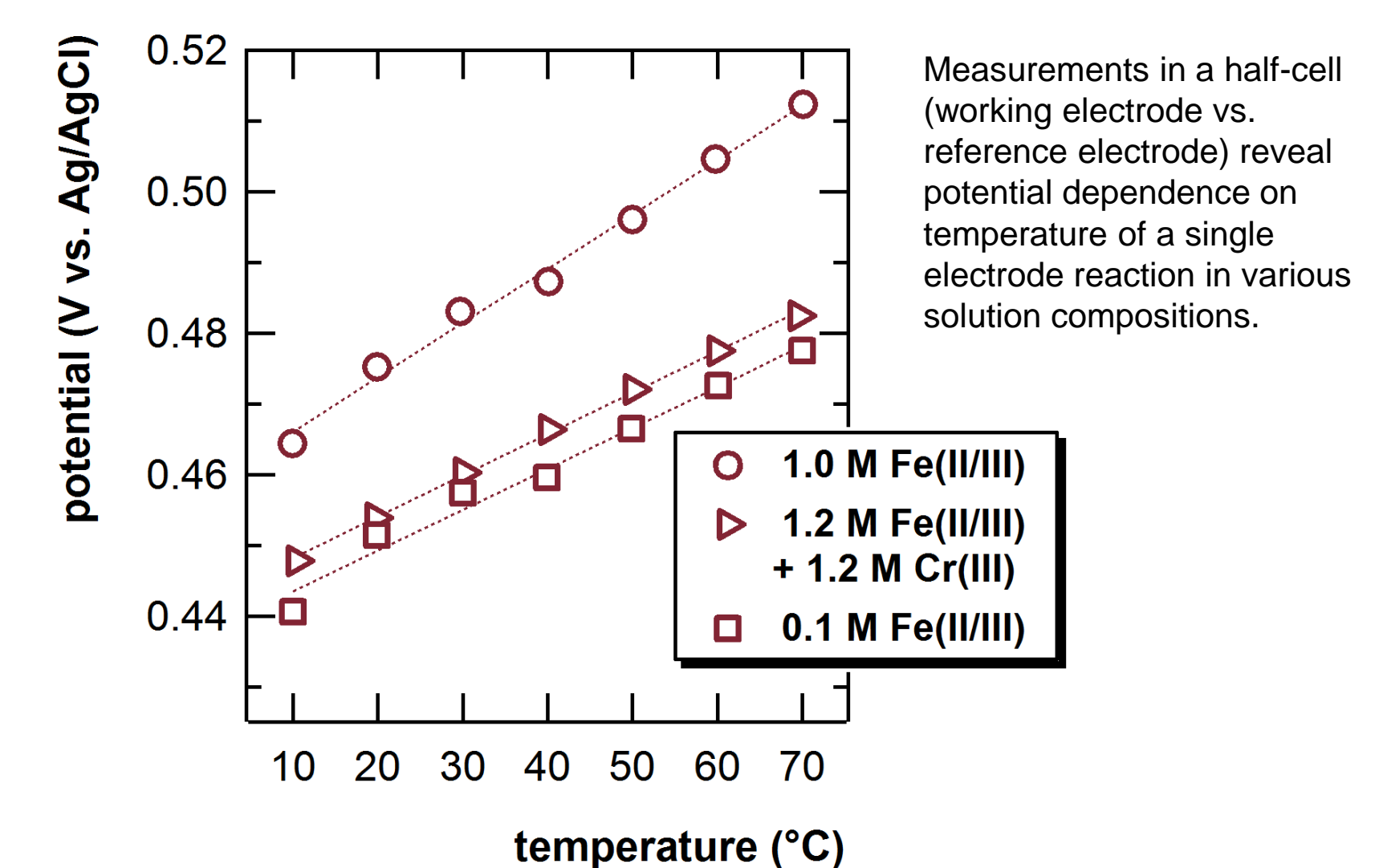
partial molar entropy of the electrochemical reaction

temperature coefficient (slope of plots to the right)

- $-T\Delta S$  is the molar amount of heat released when cell is discharged under reversible conditions
  - i.e. minimum amount of heat released independent of cell current
  - reaction-specific and necessary for thermal modeling of cells, systems, or stacks
  - Heat from irreversible losses is dependent on current, contributes to the total heat output

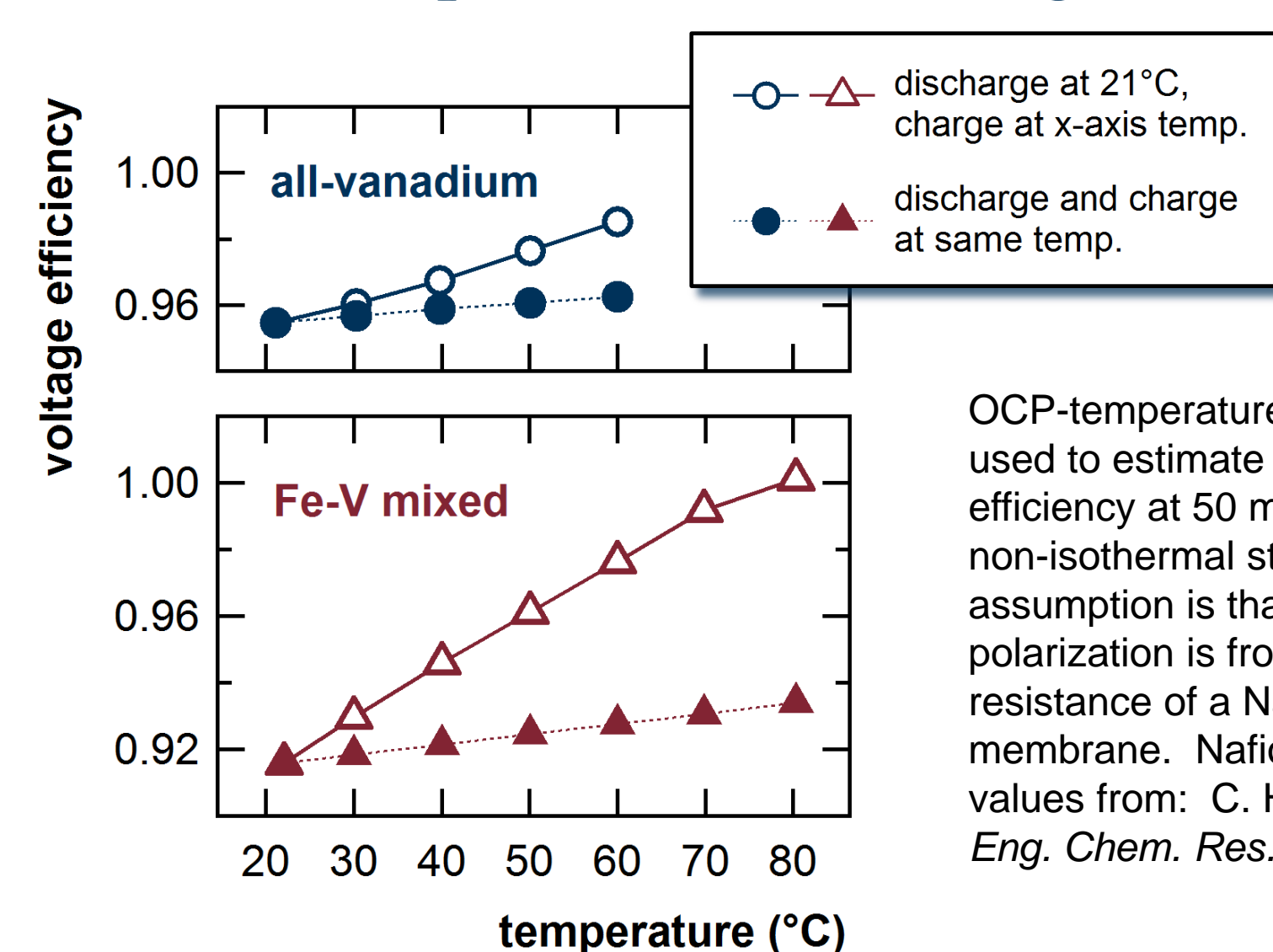
## Electrode Potential vs. Temperature

Fe<sup>2+/3+</sup> redox couple with HCl electrolyte



Measurements in a half-cell (working electrode vs. reference electrode) reveal potential dependence on temperature of a single electrode reaction in various solution compositions.

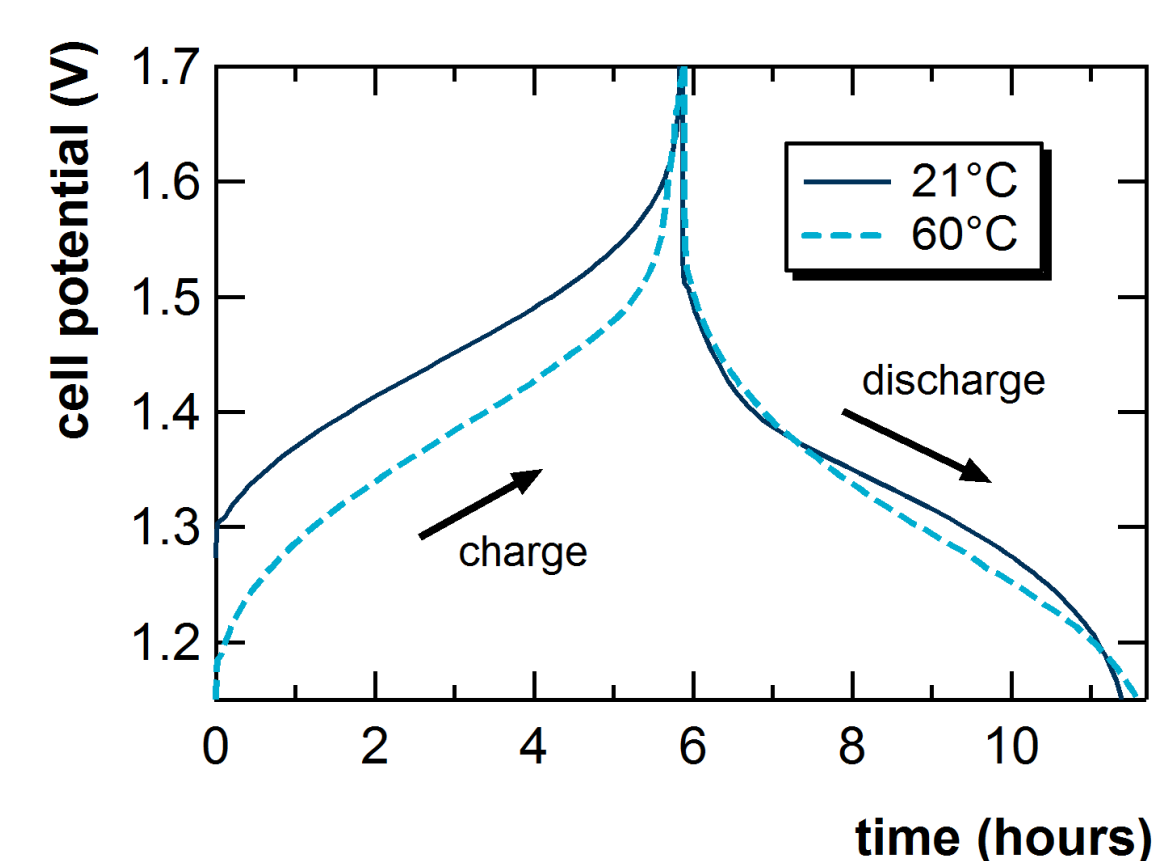
## Predicted Improvement in Voltage Efficiency



OCP-temperature data from above used to estimate the voltage efficiency at 50 mA cm<sup>-2</sup> using the non-isothermal strategy. 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)

## All-Vanadium Redox Flow Cell at 10 mA/cm<sup>2</sup>

Voltage efficiency improvement of 2% demonstrated using the non-isothermal charge-discharge strategy



## Conclusions

- Voltage-temperature relationship and partial molar entropy determined for all-vanadium, Fe-Cr, and Fe-V flow cells, linear relationship over 20-80°C range
- Fe<sup>2+/3+</sup> redox couple potential also shows linear dependence on temperature vs. Ag/AgCl reference
- Data used to show that increase in voltage efficiency (as high as 7%) can be achieved by operating charge and discharge at different temperatures

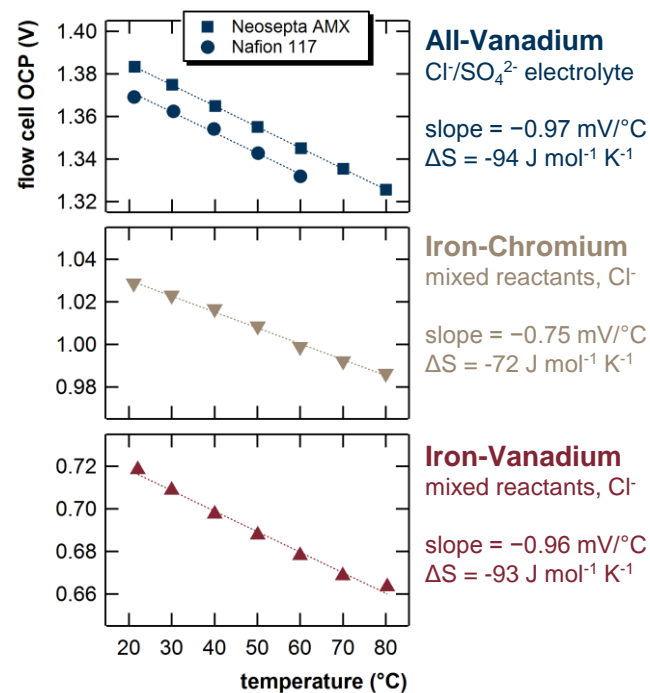
# Thermodynamics of Flow Battery Electrode Reactions

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# Thermodynamics of FB Electrode Reactions

## Motivation

- Dependence of open-circuit potential (OCP) on temperature for flow battery chemistries is largely unknown
- **Partial molar entropy** of the electrochemical reaction
  - component of the heat consumption or output during battery cycling
  - necessary for an accurate thermal model of a flow battery system
- Potential-temperature relationship is also necessary for appropriate selection of operating temperature(s)
  - Operation of **charge and discharge at different temperatures** may result in increased efficiency relative to an isothermal system
  - Goal is to charge the cell at a temperature with lower voltage and discharge at a temperature with higher voltage

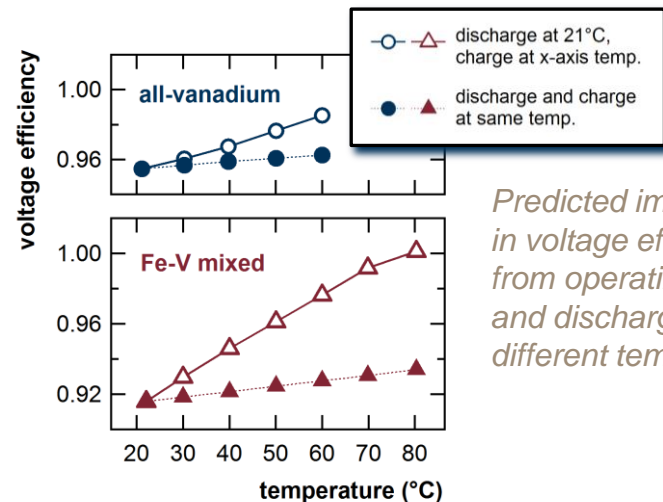
Gibbs free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ), and entropy ( $\Delta S$ ) of an electrochemical reaction obtained by measuring open-circuit potential of the cell at different temperatures.

$$-nFE = \Delta G = \Delta H - T\Delta S$$

equilibrium (open-circuit) potential

$$\left. \frac{\partial E}{\partial T} \right|_P = \frac{1}{nF} \Delta S$$

slope of OCP vs. temperature plot



*Predicted improvement in voltage efficiency from operating charge and discharge at different temperatures.*