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OFFICE OF ELECTRICITY DELIVERY & ENERGY RELIABILITY

Sandia National Laboratories

THERMOELECTROCHEMICAL ENERGY STORAGE

Using Waste Heat to Increase the Efficiency of Flow Batteries

New Start Project, August 2011

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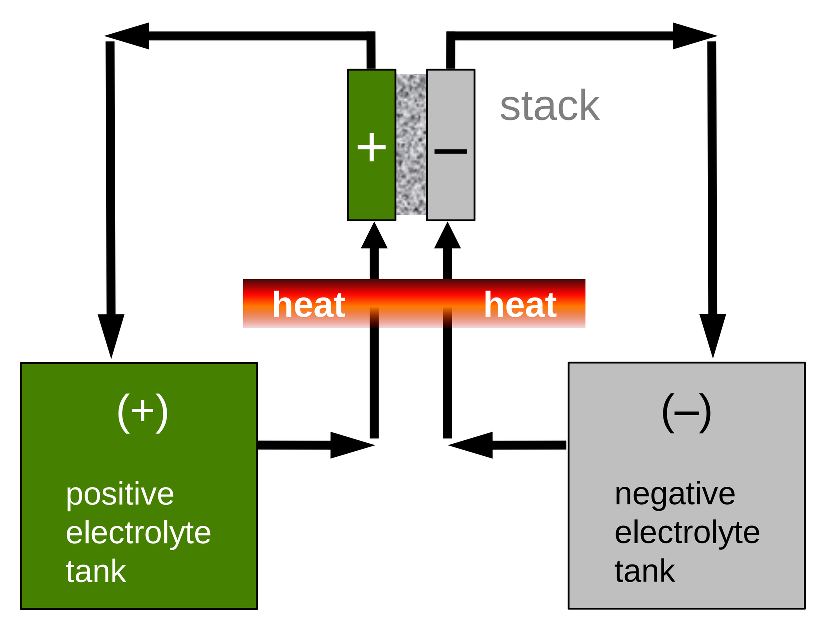
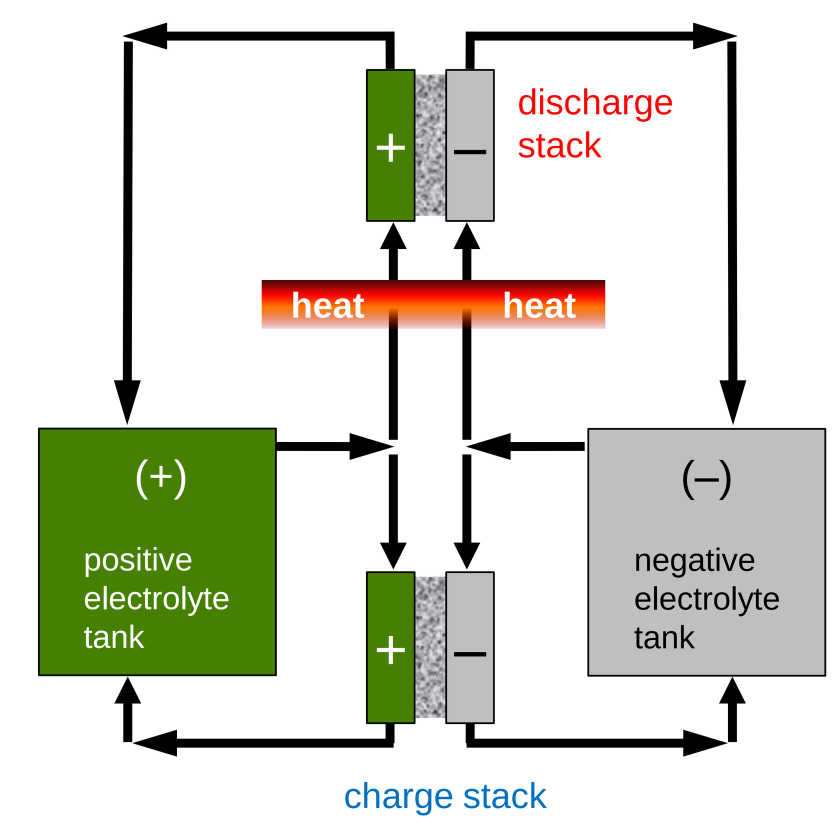
Purpose

- Demonstrate how low-grade waste heat from internal losses or external processes can be used to increase the voltage efficiency of flow batteries (by possibly ~10%)
- Quantify the voltage dependence on temperature for typical flow battery reactions
- Assess the feasibility of operating the battery charge and discharge at different temperatures

Conventional Flow Battery with Heated Reactant Flow



Proposed Flow Battery with Charge and Discharge at Different Temperatures



Battery Efficiency

$$\eta = \eta_{charge} \cdot \eta_{voltage}$$

energy efficiency (neglects the energy required for pumping and thermal management)

$$\eta_{charge} = \frac{Q_{discharge}}{Q_{charge}}$$

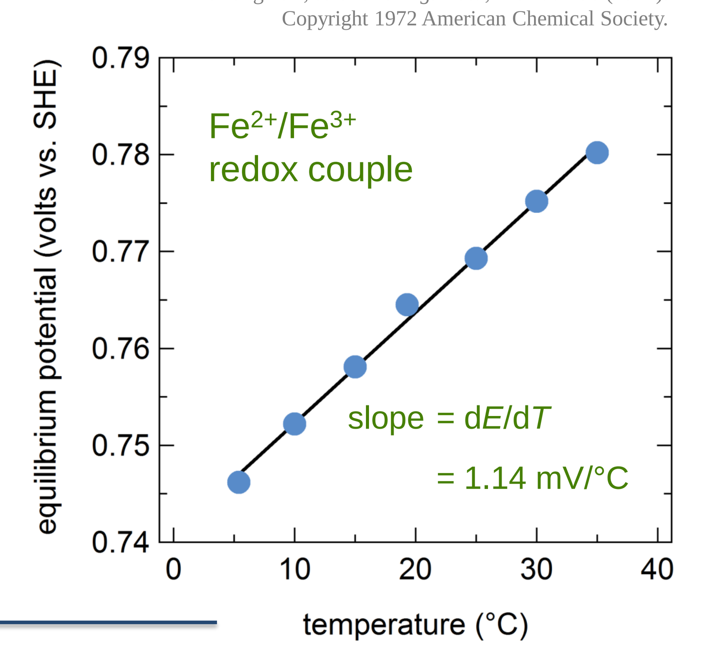
charge efficiency
AKA coulombic efficiency
(also influenced by temperature)

$$\eta_{voltage} = \frac{V_{discharge}}{V_{charge}}$$

voltage efficiency
(equal to power efficiency for galvanostatic cycling)

Voltage and Temperature

Adapted with permission from D. O. Whittemore & D. Langmuir, *J. Chem. Eng. Data*, 17: 288-290 (1972). Copyright 1972 American Chemical Society.



Changes in temperature cause changes in V_{charge} and $V_{discharge}$

Concept

Temperature affects the voltage of a battery in two ways:

- *Overpotential*: Losses from kinetic, ohmic, and mass transport effects decrease with increasing temperature (usually considered).
- *Equilibrium potential (see inset)*: Open-circuit voltage increases or decreases with temperature and is dependent on cell chemistry (usually ignored).

Goal: operate the charge and discharge portions of the cycle at different temperatures to maximize discharge voltage and minimize charge voltage

Electrochemical Thermodynamics

$$-nFE^{\circ} = \Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

equilibrium (open-circuit) potential

$$\left.\frac{\partial E^{\circ}}{\partial T}\right|_{P} = \frac{1}{nF}\Delta S^{\circ}$$

entropy of reaction

temperature coefficient (mV/°C)

Temperature Dependence of Common Flow Battery Reactions

System	Discharge Reaction	V vs. SHE (at 25°C)	*dE/dT* (mV/°C)	cell *dE/dT* (mV/°C)
All-Vanadium	$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.001	-0.90 or -0.22	-0.62 – -2.4 ?
	$V^{2+} \rightarrow V^{3+} + e^-$	-0.255	(1.5) or 0.4	
H_2-Chlorine gas	$Cl_{2\,(gas)} + 2e^- \rightarrow 2Cl^-_{(aq)}$	1.361	-1.248	-1.25
	$H_{2\,(gas)} \rightarrow 2H^+_{(aq)} + 2e^-$	0.000	0.000	
Zinc-Bromine gas	$Br_{2\,(gas)} + 2e^- \rightarrow 2Br^-_{(aq)}$	1.094	-1.094	-1.21
	$Zn^{\circ}_{(s)} \rightarrow Zn^{2+} + 2e^-$	-0.762	0.119	
Zinc-Bromine solution	$Br_{2\,(aq)} + 2e^- \rightarrow 2Br^-$	1.098	-0.499	-0.62
	$Zn^{\circ}_{(s)} \rightarrow Zn^{2+} + 2e^-$	-0.762	0.119	
Iron-Chromium	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.771	1.175	+0.22 ?
	$Cr^{2+} \rightarrow Cr^{3+} + e^-$	-0.42	(1.4)	

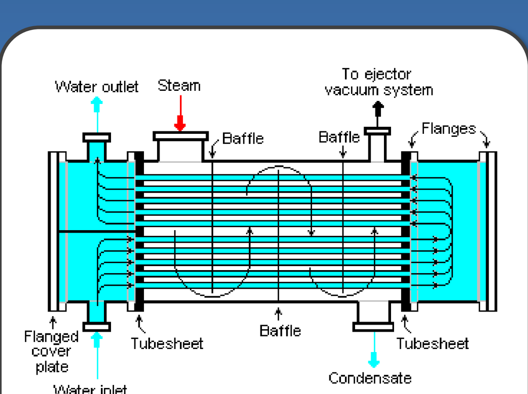
- Available data are limited to near-room-temperature.
- How does d*E*/d*T* change at higher temperatures (near 100°C)?
- d*E*/d*T* for many redox couples has not been tested or show varied results among different publications (especially the vanadium couples).

Compiled from:
- S.G. Bratsch, *J. Phys. Chem. Ref. Data* **18**(1): 1 (1989)
- G. Milazzo and S. Caroli, *Tables of Standard Electrode Potentials*, Wiley (1978)
- *Lange's Handbook of Chemistry*, 11th edition, Editor John A. Dean, McGraw-Hill (1974)

Values in parentheses are estimated.

Impact on DOE/OE Energy Storage Mission

- Even small increases in power plant efficiency will translate to significant cost and energy savings
- Can be applied in conventional power plants or renewable energy power plants
- Flow battery can make use of excess thermal energy from other plant processes (e.g. steam from conventional or co-generation power plants, flue gas from gas turbines, molten salt in solar thermal plants).



Example: Route the redox battery flow stream through surface condenser (or other heat exchanger) to increase its temperature.

FY12 Plan

- Experimentally determine d*E*/d*T* of vanadium and Fe-Cr systems. Are they competitive with theoretical values for gas-phase systems (Br_2 or Cl_2)?
- Demonstrate effect of placing charge and discharge at different temperatures using simplified flow battery. What are the effects on voltage *and* charge efficiencies?
- Feasibility study to determine if any beneficial effects will scale up to plant level

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