

Abstract

Thermally regenerative electrochemical cycles (TREC) are batteries with half-cells specially chosen, allowing **direct conversion of "low quality" thermal energy into "high quality" electrical current**. TREC batteries can be discharged in the "forward" direction, then heated, then discharged again, but in the "reverse" direction. Upon cooling, the TREC battery can again be discharged. In principle, this cycle can be repeated many times.

We identified an **aqueous iron/silver electrochemical cell as a candidate TREC cell, monitoring potential versus temperature (forward reaction spontaneous at the positive potential, reverse reaction at negative)**. Nitrate- and ammonium-containing iron salts were replaced with the corresponding sulfates to eliminate reactions with counter anions. Additionally, improvements were made to reduce solvent evaporation upon heating.

Motivation

- Our ultimate objective is to develop a battery composed of a TREC cell that can make use of thermal cycling.
- The most popular commercially available battery, the alkaline manganese oxide/ zinc cell is a onetime-use cell.
- A feasible TREC-based battery could reduce waste and convert otherwise unused thermal heat into useful electricity.

Background – Electrochemistry

- Electrochemistry is the study of chemical species that can transfer electrons to electrode surfaces or accept electrons from those surfaces, undergoing oxidation or reduction, respectively.
- An electrochemical cell consists of two half cells. In one half cell, **the anode, oxidation** of one of the electroactive chemical species takes place. In the other half cell, **the cathode, reduction** of the other electroactive species takes place. **See the diagram in the next section.**
- In a galvanic cell, the electrons transferred to the anode by the chemical species undergoing oxidation make their way through the external circuit to the cathode. At the cathode surface, the electrons are transferred to the chemical species undergoing reduction. The circuit is completed by the flow of ions, both positive and negative, inside the cell, through the salt bridge.
- This study uses potentiometry, the measurement of cell potential (voltage). The voltage of a cell (E in the equation below) is the difference between the potential of the right half-cell and the left half-cell and is related to the Gibbs Free Energy (ΔG) change for the cell reaction.

$$\Delta G = -nFE = -nF(E_{right} - E_{left})$$

- If a half-cell process is given by the chemical reaction



then concentrations of electroactive species in the half cells can also be taken into account using the Nernst Equation.

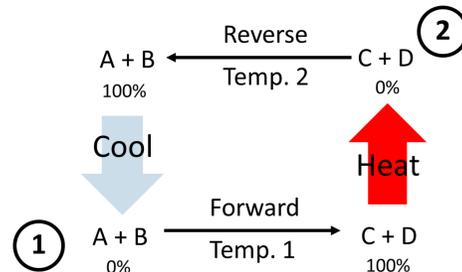
$$E_{right} = E^o - \left(\frac{RT}{nF}\right) \ln \left(\frac{[\text{Reduced Form}]^x}{[\text{Oxidized Form}]^y}\right)$$

- Here, E^o is the standard state electrode potential (concentrations at 1 M), R is the molar gas constant (you never thought you'd see it again), T is the temperature in Kelvins, n is the number of electrons transferred for the particular electrode process, and F is the Faraday Constant, 96,485 Coulombs per mole of electrons.

Basic Idea Behind TREC

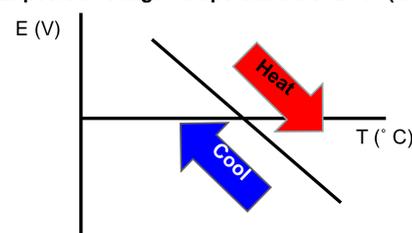
- The basic idea behind TREC is to run an electrochemical cell in its forward and spontaneous direction. See 1 in the figure below. The two half cells are chosen so that, upon heating to a sufficiently high enough temperature, the reverse cell reaction becomes spontaneous. See 2 below. Once the cell is discharged in the reverse direction, it is cooled and is ready to undergo the forward direction again.

Schematic Representation of a TREC Cycle



- A positive voltage indicates that the forward reaction is spontaneous. A negative voltage means that the reverse reaction is spontaneous. Therefore, initial experiments will simply concentrate on building cells for potentiometry and demonstrating, for a chosen cell, that the voltage changes from positive to negative upon heating to a higher temperature.

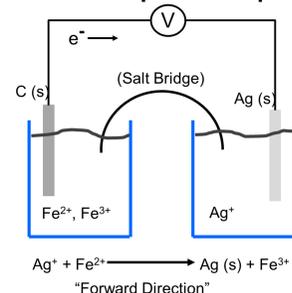
Expected Voltage-Temperature Behavior (Ideal Case)



Experimental Section

- All the experiments described involve setting up similar electrochemical cells. Using "line notation," the cell is
- [C(s)|0.05 M Fe²⁺, 0.05 M Fe³⁺|| 0.1 M AgNO₃ | Ag(s)]**

Basic cell setup for all experiments



Setup - Experiment 1

Anode

- 150 mL Beaker
- 20 mL 0.1 M Fe(NH₄)₂(SO₄)₂ + 20 mL 0.1 M Fe(NO₃)₃
- Solid carbon electrode (#2 Pencil).

Cathode

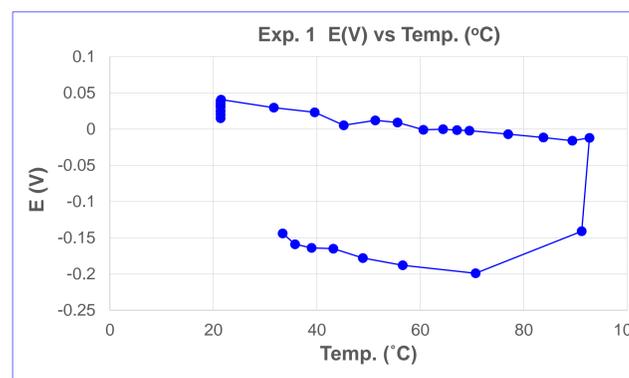
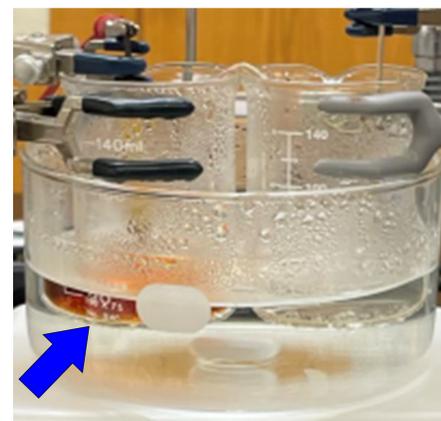
- 150 mL Beaker
- 40 mL 0.1 M AgNO₃
- Electrode (92% Ag, 8% Cu).

Salt Bridge

- String soaked in 0.1 M KNO₃

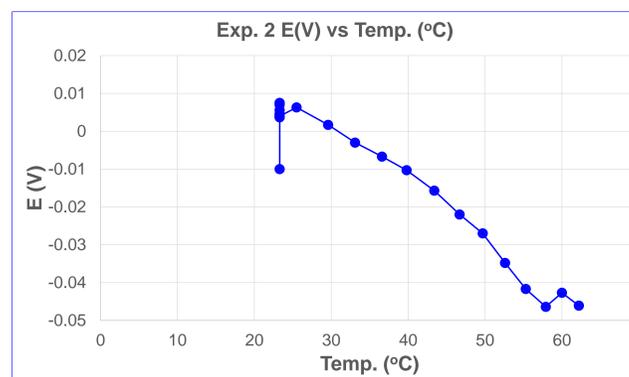
Results – Experiment 1

- A negative voltage was obtained. However, voltage does not come back into the positive range upon cooling.
- Noticeable darkening, seen in photo below, of the Iron half-cell (Left), leading us to believe an unwanted reaction is occurring in the iron solution



Results - Experiment 2

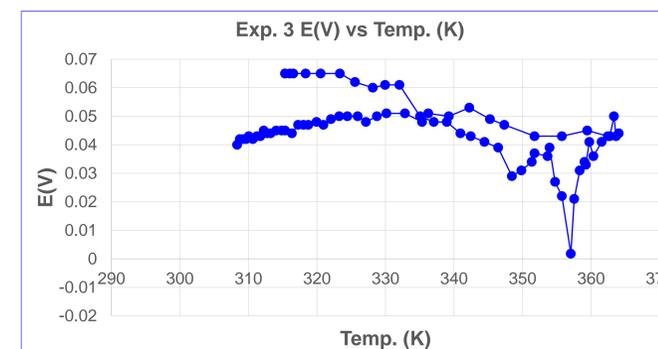
- The same set up as Experiment 1 was used, except 150 mL Erlenmeyer flasks were used.
- The flasks were stoppered to prevent water (solvent) from evaporating during heating
- Holes were drilled in the stoppers for electrodes and a notch cut out for the string for the salt bridge.
- Less evaporation occurred in the half-cells.
- The iron solution still turns color.



Results - Experiment 3

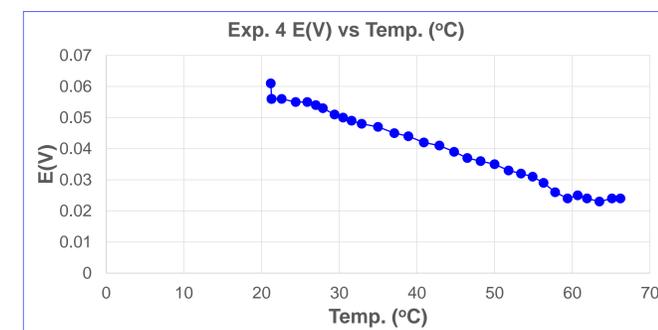
- The same set up as Experiment 2 was used, except 150 mL Erlenmeyer flasks with sidearm flasks were used for each half cell. The side arm flasks were joined with rubber tubing and the string for the salt bridge threaded through both side-arms. This protected the string from drying out during the experiment.

- The nitrate-containing iron salts used in Expt's 1 and 2 were replaced with the corresponding sulfates. This was done to avoid the possible oxidation reaction of Fe²⁺ by NO₃⁻ in the iron half-cell.
- Less evaporation occurred in the half-cells.
- Unable to obtain a negative voltage.
- Slight return in voltage after heating



Results - Experiment 4

- Experimental setup the same as Experiment 3 except Ferric Sulfate (Hydrous) was replaced with anhydrous Ferric Sulfate.
- Less evaporation occurred in the half-cells.
- Unable to obtain a negative voltage.
- No color change in iron half-cell



Next Steps

- Improve upon current cell to obtain a negative voltage.
- Develop a TREC battery based on the improved iron/silver cell.
- Explore other cell chemistries.

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