Sandia National Laboratories

Al-Fe Based Molten Salts for Long Duration Energy Storage

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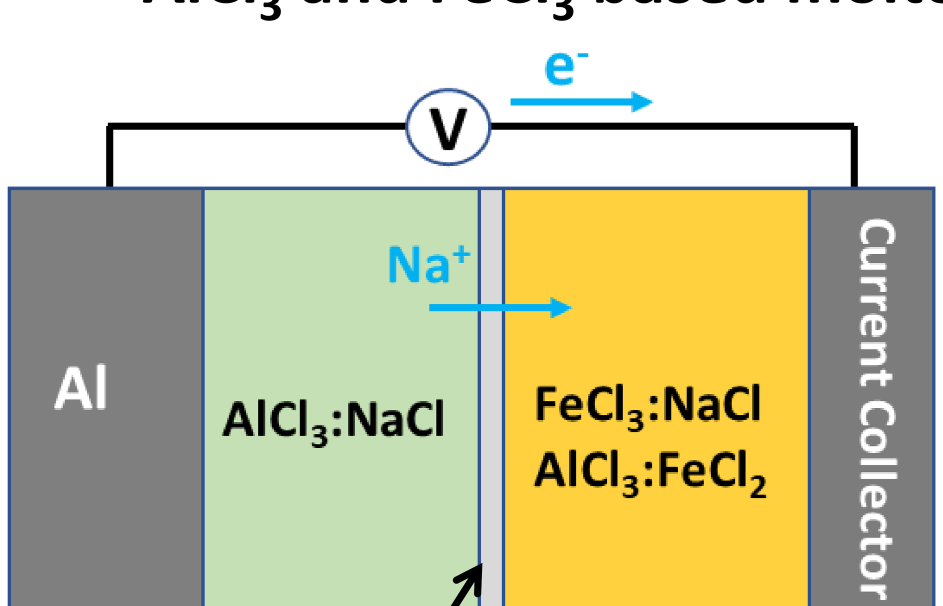
Motivation & Objective

- ***There is a need for high energy density long duration energy storage that utilizes earth abundant elements, such as Al and Fe. Ternary molten salt compositions of $AlCl_3$-$FeCl_3$-NaCl and $AlCl_3$-$FeCl_2$-NaCl were evaluated for their phase behavior at intermediate temperatures (~160 - 210 °C).***
- ***Objective: Find and explore properties of a new molten salt system which utilizes Al and Fe components and can be operated as an electrochemically active medium for long duration energy storage.***
- ***Compositions of $AlCl_3$-$FeCl_3$-NaCl identified that were fully or nearly fully molten at 160 °C. The electrochemistry of these salts was probed and found that the Al is reducible and the Fe species will cycle between the Fe^{3+}/Fe^{2+} oxidation states (as $FeCl_3/FeCl_2$) and remain dissolved in the melt at more elevated temperatures. Also found that $AlCl_3$ was needed in the melt to facilitate the $FeCl_2$ dissolution.***

1. Al-Fe Battery Overview

- **Battery composed of metallic Aluminum and utilizing $AlCl_3$ and $FeCl_3$ based molten salts as electrolytes**



NaSICON
(ceramic separator)

Anode:
$Al + 3Cl^- \rightarrow AlCl_3 + 3e^-$

Cathode:
$FeCl_3 + e^- \rightarrow FeCl_2 + Cl^-$

Predicted Cell Potential	E_{cell} = 2.43 V
$Al \rightarrow Al^{3+} + 3e^-$	E_{red} = -1.66 V
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	E_{red} = +0.77 V

- **Upon discharge:**
  - **Oxidize Al metal to $AlCl_3$ in a $AlCl_3$:NaCl molten salt**
  - **Reduce $FeCl_3$ to $FeCl_2$ in a $FeCl_3$:$AlCl_3$:NaCl molten salt**
  - **Na^+ transports through NaSICON separator**
  - **NaSICON prevents potentially unwanted reactions between Al metal and $FeCl_3$/$FeCl_2$ species**

2. Active Materials Cost Analysis

Goal is for costs to be <$16/kWh for system

Assumptions made:
- **Fe^{3+}/Fe^{2+} cycle**
- **Excess NaCl to account for $AlCl_3$ composition change**
- **100% efficiency**

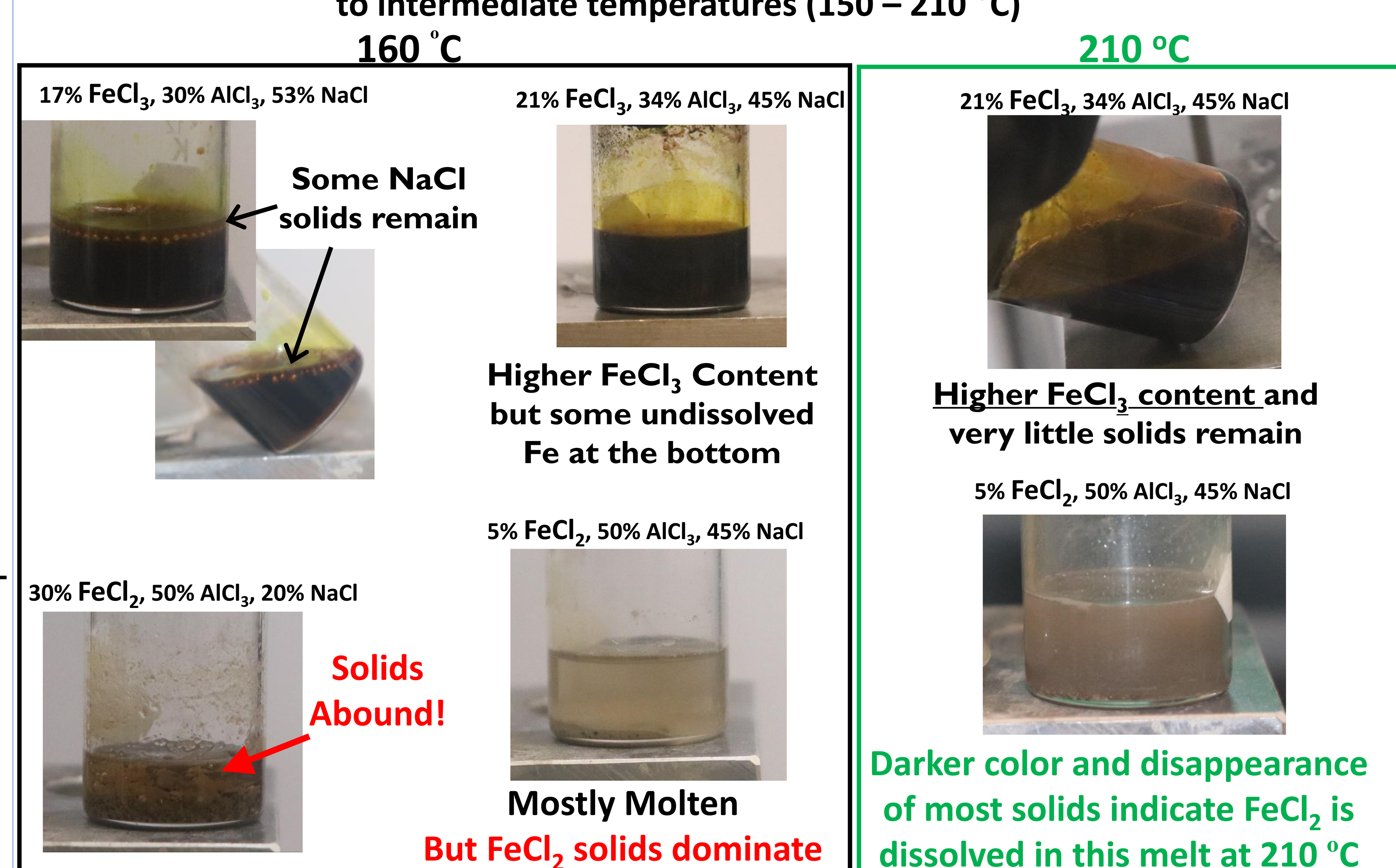
Material	Cost ($/kg)
Al	1.146
Fe	0.184
$AlCl_3$	1.5
$FeCl_3$	1
NaCl	0.05
Li metal	>100
Na metal	>50

All materials are relatively cheap - compared to Na and Li

Estimated active materials costs for 1 kWh = $8.53

3. Phase Behavior of $AlCl_3$-$FeCL_3$-NaCl Melt

Compositions of $FeCl_3$:$AlCl_3$:NaCl and $FeCl_2$:$AlCl_3$:NaCl evaluated at various low to intermediate temperatures (150 – 210 °C)

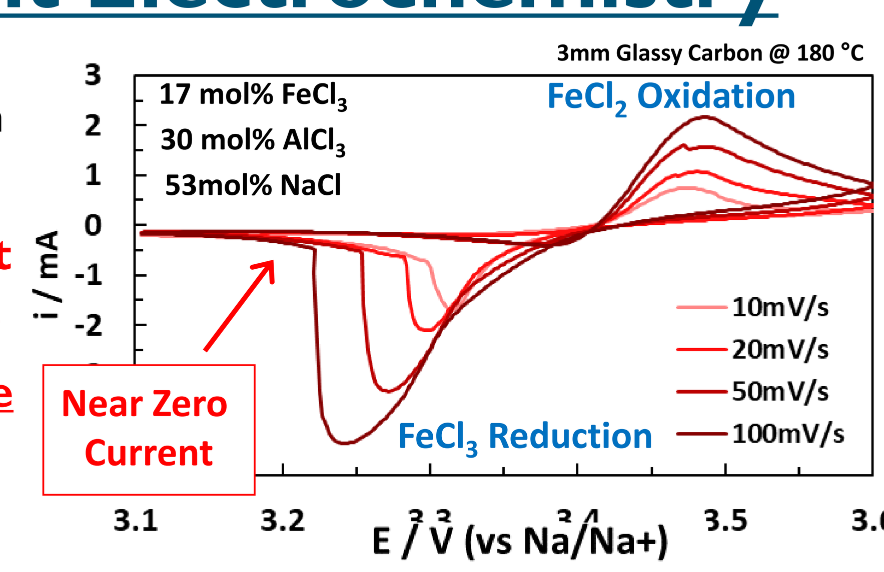


4. Temperature Dependent Electrochemistry

Large $FeCl_3$ reduction and similar $FeCl_2$ oxidation currents observed in $FeCl_3$:$AlCl_3$:NaCl melts.

Current observed to drop to near zero currents at the 180 °C test condition, even for fast scan rates.

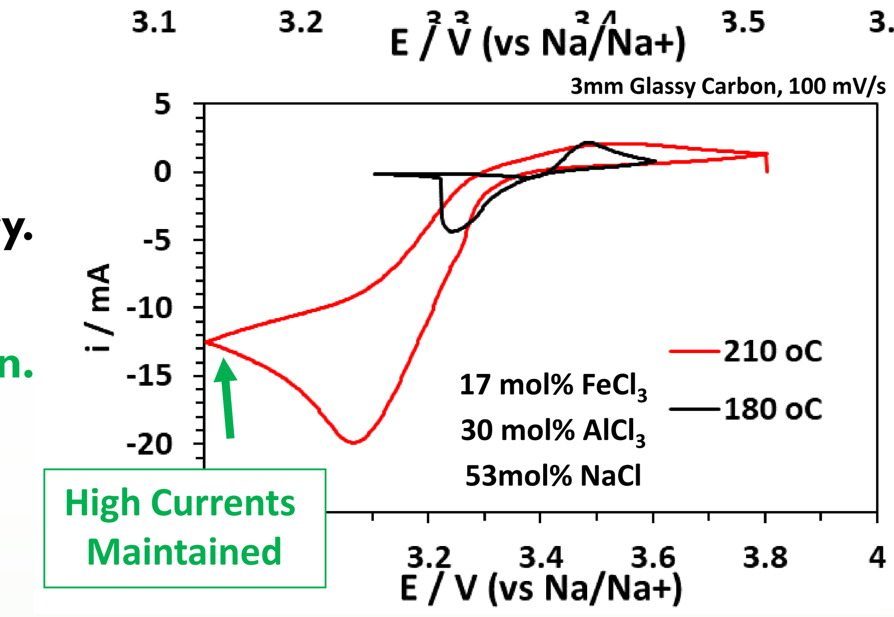
$FeCl_2$ produced at electrode is not soluble at these temperatures and blocks the electrode!



Increasing the temperature of the melt had a significant effect on the observed electrochemistry.

At 210 °C the $FeCl_3$ reduction current does not drop to zero as is observed in the 180 °C condition.

The produced $FeCl_2$ is able to dissolve into the melt and allows the current to remain high!



Summary

- **New molten salts comprised of Al and Fe halides were evaluated for their composition and temperature dependent phase behavior. Compositions identified where salts are nearly fully molten at low to intermediate temperatures. Temperature dependent electrochemical behavior observed where $FeCl_2$ produced at the electrode surface (from $FeCl_3$ reduction) is insoluble in the melt at lower temperatures. By increasing the test temperatures, the produced $FeCl_2$ dissolves into the melt allowing the un-blocked electrode to sustain large reduction currents.**
- **Future work will investigate ways to increase $FeCl_2$ concentration in the melt and to facilitate its oxidation (perhaps using different electrode materials or higher surface area carbon felts) in order to optimize the molten salt catholyte electrochemical behavior in a working battery and demonstrate it in a working battery.**

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