Sandia National Laboratories

Earth Abundant Al-Fe Based Molten Salts for Energy Storage

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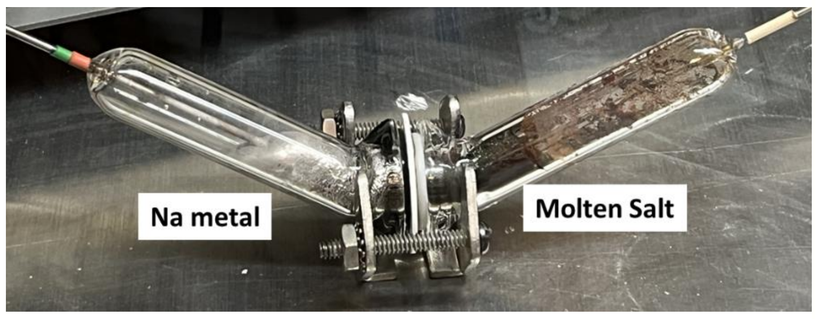
Motivation & Objective

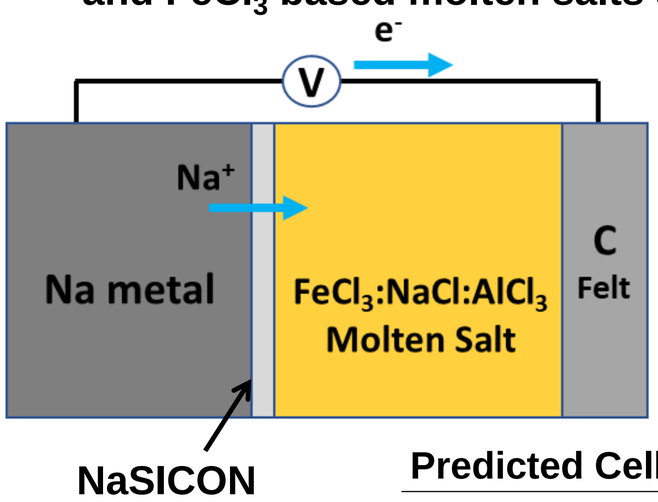
- ***There is a need for high energy density long duration energy storage that utilizes earth abundant elements, such as Al and Fe. New catholyte molten salts consisting of ternary compositions of $AlCl_3$-$FeCl_3$-NaCl could help advance low to intermediate temperature molten salt energy storage.***
- ***Objective: Explore phase melting and electrochemical properties of new molten salt systems utilizing Al and Fe components and evaluate battery cycling behavior of these salts***



- ***Compositions of $AlCl_3$-$FeCl_3$-NaCl that were fully or nearly fully molten at 160 °C were identified and electrochemistry showed 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. Full battery cell constructed with these salts and a Na anode, showed a much higher operating voltage than expected with cycling behavior displaying high energy efficiencies and stability.***

1. Al-Fe Battery Overview

- **Battery composed of a molten Na anode and $AlCl_3$ and $FeCl_3$ based molten salts as the catholyte**



Anode:
$$Na + Cl^- \rightarrow NaCl + e^-$$

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

Predicted Cell Potential $E_{cell} = 3.48$ V

$Na \rightarrow Na^+ + e^-$ $\quad E_0 = -2.71$ V

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ $\quad E_0 = +0.77$ V

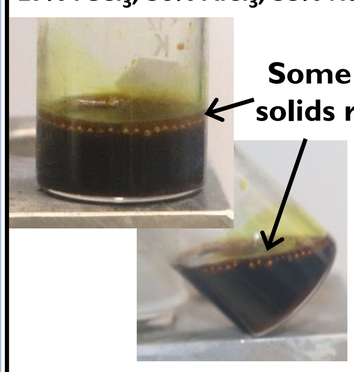
- **Upon discharge:**
  - **Oxidize Na metal to Na^+ and Na^+ transports through NaSICON separator**
  - **Reduce $FeCl_3$ to $FeCl_2$ in a $FeCl_3$:$AlCl_3$:NaCl molten salt**

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

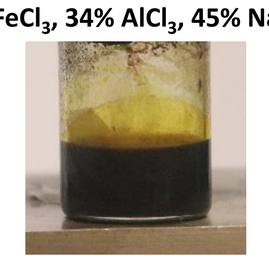
Compositions of $FeCl_3$:$AlCl_3$:NaCl and $FeCl_2$:$AlCl_3$:NaCl

160 °C

17% $FeCl_3$, 30% $AlCl_3$, 53% NaCl

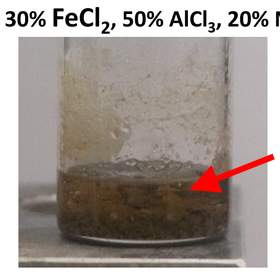


21% $FeCl_3$, 34% $AlCl_3$, 45% NaCl

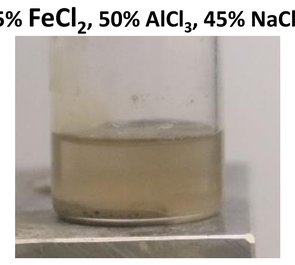


Higher $FeCl_3$ Content but some undissolved Fe at the bottom

30% $FeCl_2$, 50% $AlCl_3$, 20% NaCl



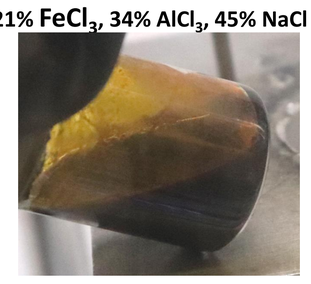
5% $FeCl_2$, 50% $AlCl_3$, 45% NaCl



Mostly Molten
But $FeCl_2$ solids dominate

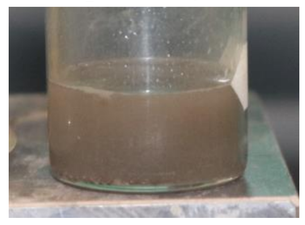
210 °C

21% $FeCl_3$, 34% $AlCl_3$, 45% NaCl



Higher $FeCl_3$ content and very little solids remain

5% $FeCl_2$, 50% $AlCl_3$, 45% NaCl



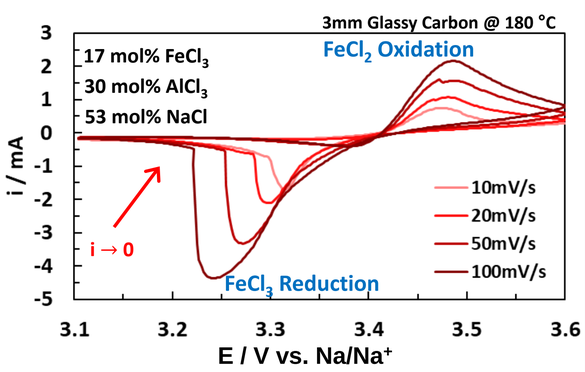
Darker color and disappearance of most solids indicate $FeCl_2$ is dissolved in this melt at 210 °C

3. Temperature Effect on Electrochemistry

Redox activity for $FeCl_3/FeCl_2$ redox pair observed in $FeCl_3$:$AlCl_3$:NaCl melts.

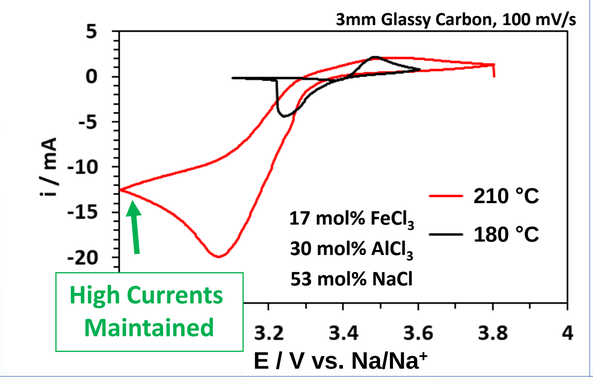
Currents drop to near zero at the 180 °C test condition, even for fast scan rates.

Produced $FeCl_2$ is not highly soluble at these temperatures and precipitates, blocking the electrode!



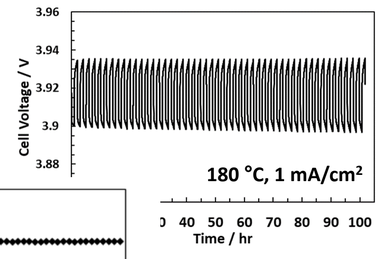
Increasing melt temperature had a significant effect on the electrochemistry.

At 210 °C the produced $FeCl_2$ is able to dissolve into the melt and allows the current to remain high!

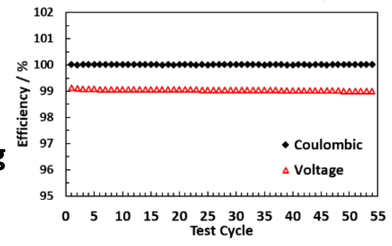


4. Battery Cell Cycling Evaluation

Battery cycling at 180 °C proved very stable with a low depth of discharge for 50 cycles (>99% VE)

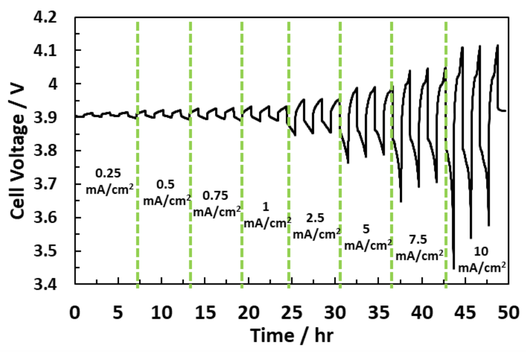


Electrode blocking effect reduced due to large surface area carbon felt current collector

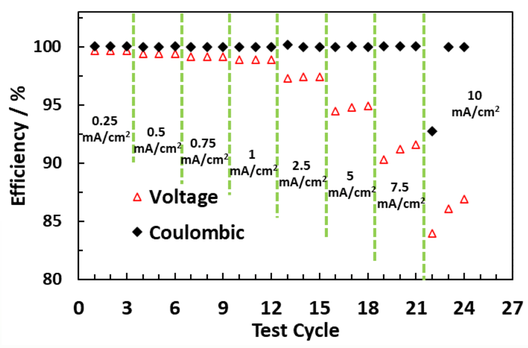


20mol% $FeCl_3$
35mol% $AlCl_3$
45mol% NaCl

Efficiencies noticed to be improving with cycling



Rate test also showed high efficiencies (>80%) up to 10 mA/cm²



Even better cycling efficiencies expected at higher 210 °C temperatures!

Summary

- **New ternary molten salts comprised of Al and Fe halides were evaluated for their phase behavior at different temperatures with some compositions identified to be nearly fully molten. Electrochemical behavior observed from the $FeCl_3/FeCl_2$ redox pair with largely insoluble $FeCl_2$ blocking the electrode at lower temperatures but not at higher temperatures, where the $FeCl_2$ dissolves into the melt allowing large reduction currents.**
- **Full cell battery cycling tests of the ternary $AlCl_3$-$FeCl_3$-NaCl melts with a Na anode showed a higher than expected voltage but good battery cycling stability and efficiencies over 50 cycles at low DoD. Rate testing showed cycling efficiencies still >80% at the highest charge/discharge currents of 10 mA/cm².**
- ***Improved cycling efficiencies expected at higher temperatures according to the preliminary electrochemistry and higher DoD tests underway.***
- **1 patent application, 1 SNL Technical Advance (TA) and 1 paper to be submitted**

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