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Electrochemical Assessment of Molten NaI-$AlCl_3$ Catholytes for Sodium Batteries

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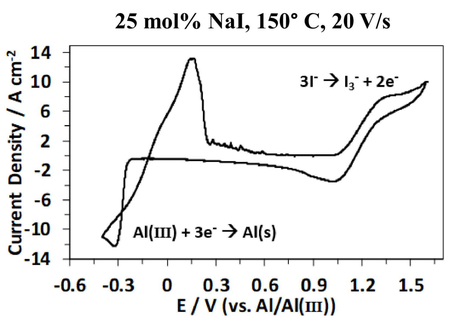
- ***Molten sodium batteries offer great promise as a safe, low cost and scalable solution to grid scale energy storage, but high operating temperatures (>275 °C) limit their usefulness and application.***
  - ***Lower operating temperature will reduce cost while increasing safety and battery lifetime.***
- ***Challenge: How can the operating temperature be lowered towards the melting point of sodium metal (97.7 °C)?***
- ***Identifying and using new lower melting point catholytes.***
  - ***New NaI-$AlCl_3$ molten salt catholytes were electrochemically characterized at various temperatures and compositions to understand the physical limitations, thus enabling increased catholyte performance at lower temperatures and prevention of phase separations upon charging/discharging.***

Schematic of a NaI Battery

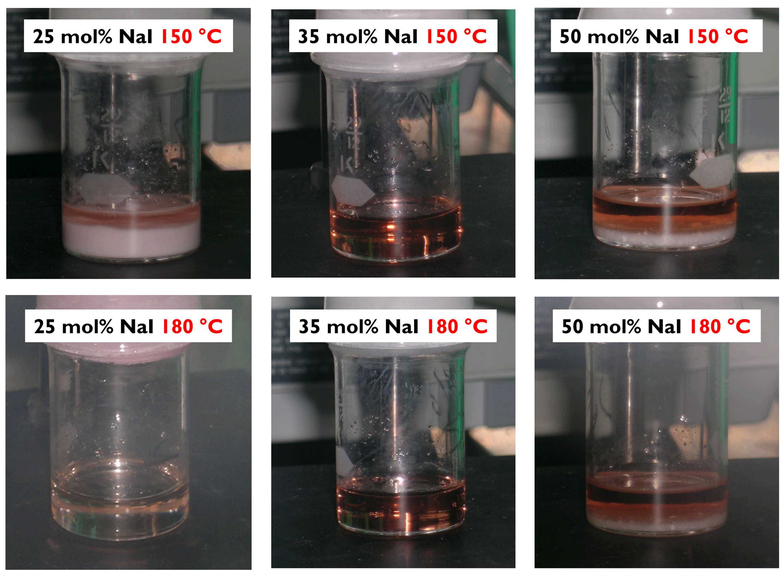
Carbon UME Molten Salt Electrochemistry



- Molten salts probed using carbon Ultramicroelectrodes (UME).
- Allows detailed investigation of properties macro electrodes are unable to easily analyze.

Reversible battery reactions:
Anode: $Na^+ + e^- \rightarrow Na$
Cathode: $3I^- \rightarrow I_3^- + 2e^-$
As the battery is charged, Na+ concentration decreases in the catholyte.

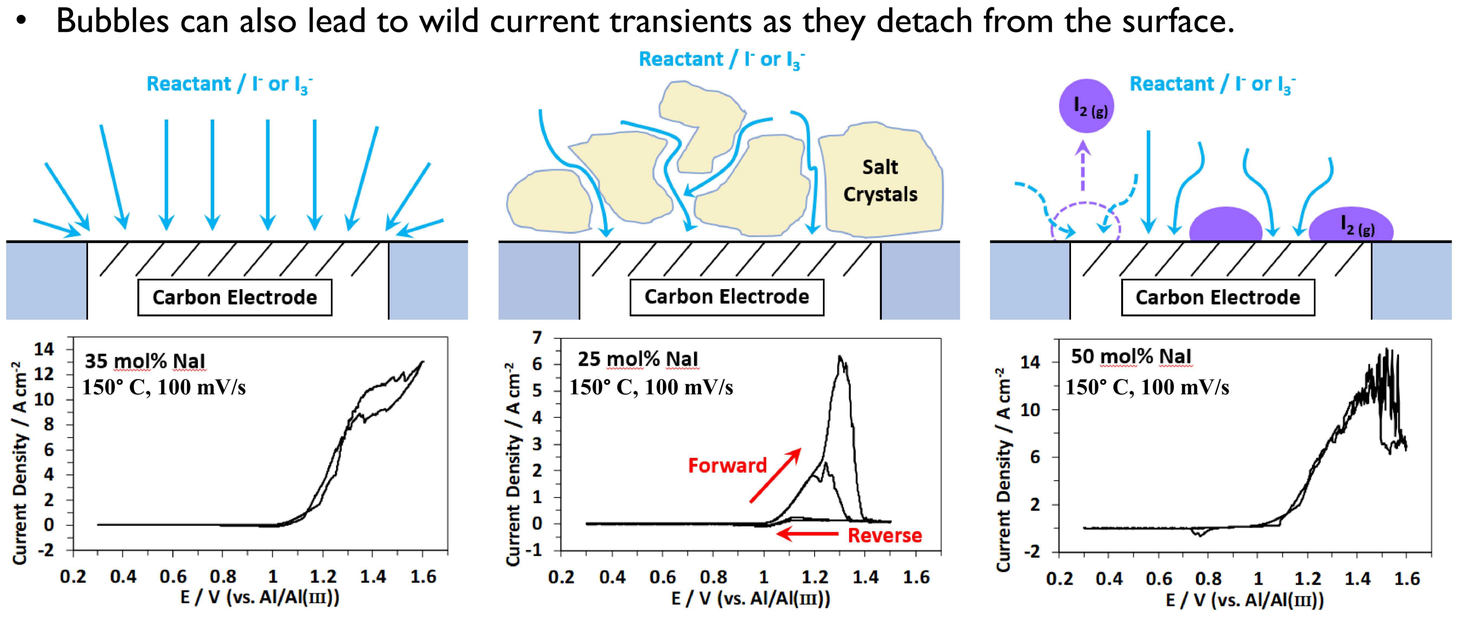
Molten Salt Phases



- Compositions identified that are fully molten at the lower 150 °C temperature.
- Multiple phases observed in some compositions with some fully melting with increased temperature.

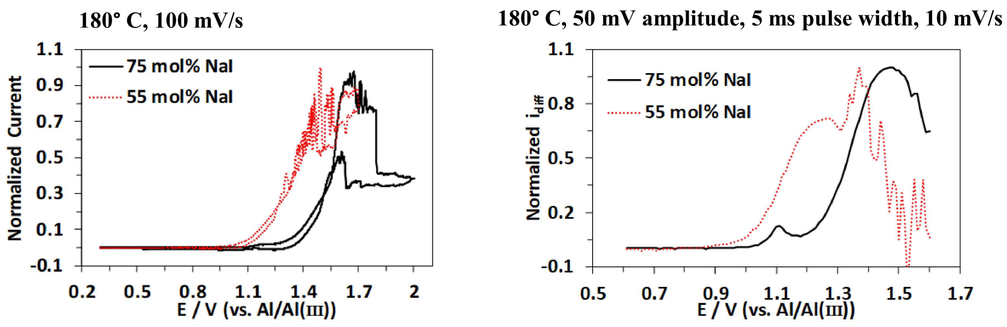
Diffusion Profiles

- Diffusion profiles of the reactant (I^- or I_3^-) affected by different phases, hindering mass transport.
- Solids or immiscible "bubbles" present at the electrode surface will block diffusion.
- Bubbles can also lead to wild current transients as they detach from the surface.



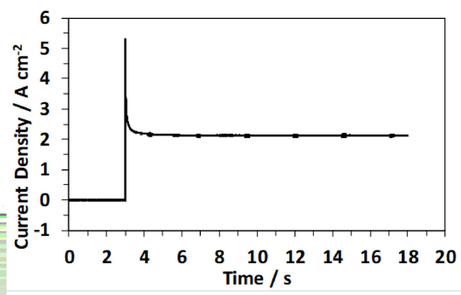
Anodic Potential Shift

- Unexpected anodic shift observed for the I^- oxidation potential in very high NaI mol% (75 mol% NaI).
- Differential Pulse Voltammetry shows small peak near expected potential (1150 mV) with a large peak 300 mV more anodic.

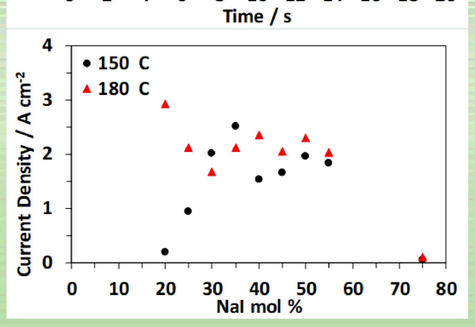


Chronoamperometry

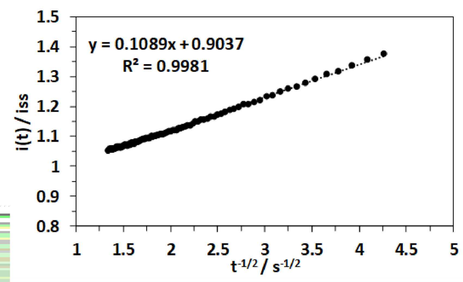
Chronoamperometric response at carbon UME used to determine electrochemical and physical properties of the molten salt compositions.



- Current densities generally increased for higher operating temperature.



- Increased current density not significant enough to warrant higher operating temperatures in the mid range NaI compositions.



- Chronoamperometric response combined with the UME steady state current relationship produces a straight line vs $t^{1/2}$.
- Slope of the line used to determine diffusion coefficients of the I^- in the melt.

Salt Composition / mol% NaI	Diff. Coef. @ 150 °C / 10^{-6} cm^2 s^{-1}	Diff. Coef. @ 180 °C / 10^{-6} cm^2 s^{-1}
20	N/A	2.2
25	5.7	5.1
30	7.8	3.8
35	5.2	7.2
40	5.7	6.2
45	3.5	5.2
50	1.9	2.9
55	1.6	2.1
75	2.9	5.3

New low temperature molten salt catholyte offers a promising route to efficient, long lifetime molten sodium batteries for grid scale energy storage.

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