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Electrochemical Simulations of Molten Salt Catholytes Reveal Speciation can Surpass Kinetics for Iodide Oxidation Rates

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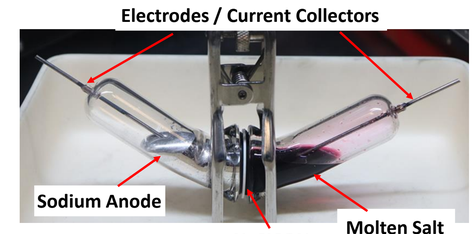
Motivation & Objective

- ***Molten sodium batteries offer great promise as a safe, low cost and scalable solution to grid scale energy storage. Newly developed low temperature catholytes promise to lower the operational range near the melting point of sodium metal (97.8 °C). These catholytes are composed of NaI with a corresponding Lewis acid compound (MX_3 = $AlCl_3$, $AlBr_3$ or $GaCl_3$). The effect the corresponding Lewis acid has on the electrochemical kinetics and speciation is not well known. Hard Soft Acid Base (HSAB) theory can be used to make some predictions, but understanding is limited. To better understand these systems, electrochemical simulations are performed with a model that accounts for both the chemical speciation and the iodide oxidation kinetics.***
- ***Objective: Probe effect of different Lewis acids on the electrochemical kinetics and chemical speciation of the resulting catholyte.***
- ***Modeling and simulations of electrochemical behavior enables detailed understanding of fundamental differences between different Lewis acid base compositions.*** *[Percival, S. J.; Lee, R.Y.; Small, L. J., J. Electrochem. Soc.* **2021**, *168*, 126511]

Molten Sodium Battery Test Cell



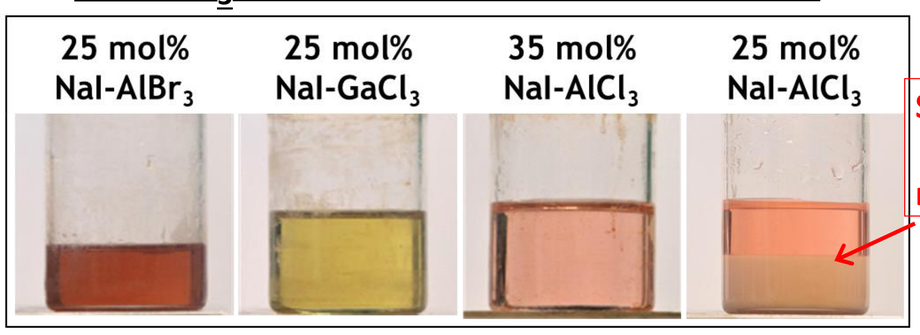
Reversible battery reactions:
Anode: $Na^+ + e^- \rightarrow Na$
Cathode: $3I^- \rightarrow I_3^- + 2e^-$

Small, et al. *J. Power Sources,* **2017**, *360*, 569-574.
Percival, et al. *J. Electrochem. Soc.,* **2018**, *165*, A3531.

1. Concentrations Affected by Melt Behavior

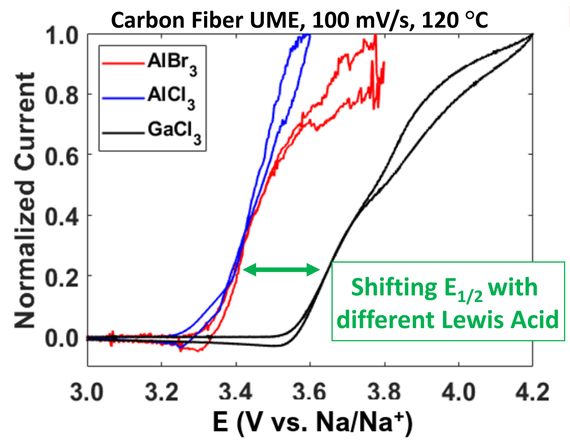
- **Fully liquid salt needed to know actual concentrations of species.**

NaI-MX_3 Lewis Acid-Base Salts at 120 °C



- **25mol% NaI-$AlBr_3$ and 25mol% NaI-$GaCl_3$ are fully molten at 120 °C**
- **The 25mol% NaI-$AlCl_3$ melt had large amounts of solids present at 120 °C – 35mol% NaI-$AlCl_3$ was fully molten**

2. Carbon Fiber Ultramicroelectrode CVs Reveal:

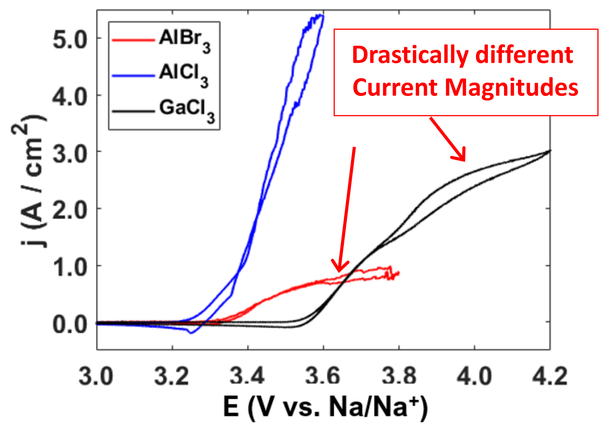


$E_{1/2}$ shift matches HSAB theory - $GaCl_3$ is a softer Lewis Acid (closest to I^-) - forming a stronger bond that is harder to oxidize

Ideal for energy storage – leads to higher energy density

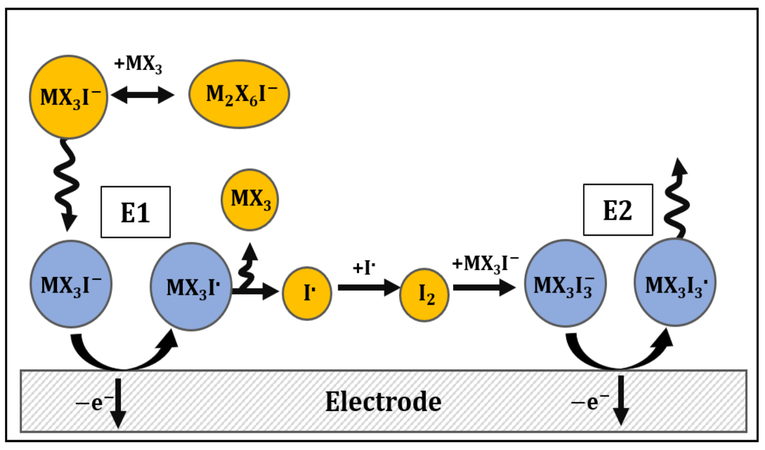
Large limiting current differences in melts with the same reactant concentration (MX_3I^-)
Some reactant is inaccessible at these potentials

Dimer speciation ($M_2X_6I^-$) is impeding e-chem, ultimately hindering battery performance



3. Simulation Chem/Electrochem Model

Modeling is a powerful technique that can be used to extract both rate constants and chemical equilibrium constants from electrochemical data.



[C1] $2MX_3I^- \longleftrightarrow M_2X_6I^- + I^-$
[C2] $2MX_3 \longleftrightarrow M_2X_6$
[C3] $MX_3I^- + MX_3 \longleftrightarrow M_2X_6I^-$
[E1] $MX_3I^- \longleftrightarrow MX_3I^{\cdot} + e^-$
[C4] $MX_3I^{\cdot} \longleftrightarrow MX_3 + I^{\cdot}$
[C5] $I^{\cdot} + I^{\cdot} \longleftrightarrow I_2$
[C6] $MX_3I^- + I_2 \longleftrightarrow MX_3I_3^-$
[E2] $MX_3I_3^- \longleftrightarrow MX_3I_3^{\cdot} + e^-$
[C7] $MX_3I_3^{\cdot} \longleftrightarrow MX_3I^{\cdot} + I_2^+$

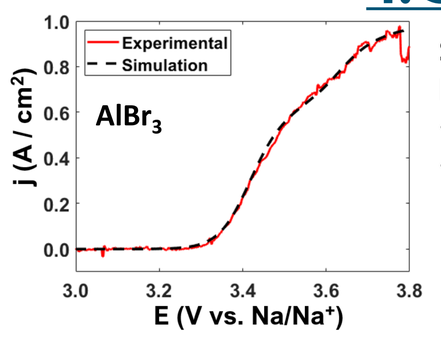
Chemical equation number corresponds to equilibrium constants

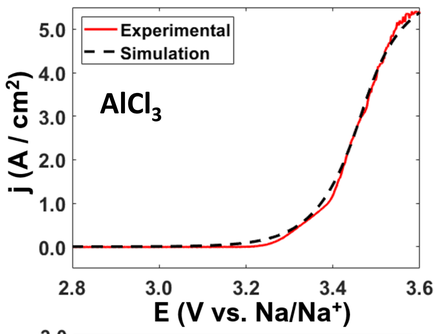
- Model consists of multiple chemical steps and two electrochemical steps (shown in blue)
- Accounts for multiple species: radical intermediates, the electrochemically active "monomers" (MX_3I^- and $MX_3I_3^-$) and the "dimer" ($M_2X_6I^-$)
  - $M_2X_6I^-$ - not considered active at these potentials - effectively lowers available reactant concentration

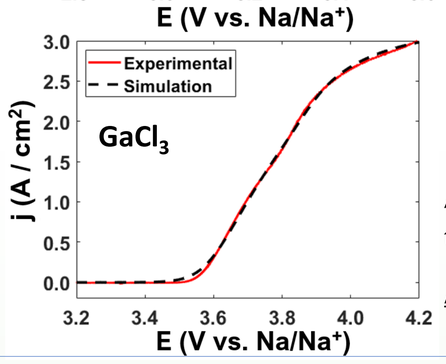
Various constants used in model were largely kept constant between Lewis acids

	C2		C3		C4		C5		C6		C7	
	K_{eq}	k_f	K_{eq}	k_f	K_{eq}	k_f	K_{eq}	k_f	K_{eq}	k_f	K_{eq}	k_f
$AlBr_3$	2.8×10^7	1.0×10^7	4600	1.0×10^4	—	1.0×10^{10}	—	1.0×10^{14}	500	1.0×10^4	—	1.0×10^{10}
$AlCl_3$	2.8×10^7	1.0×10^7	900	1.0×10^4	—	1.0×10^{10}	—	1.0×10^{14}	500	1.0×10^4	—	1.0×10^{10}
$GaCl_3$	2.8×10^7	1.0×10^7	1300	1.0×10^4	—	1.0×10^{10}	—	1.0×10^{14}	500	1.0×10^4	—	1.0×10^{10}

4. Speciation vs. Kinetics







Simulated CVs using our model match experimental CVs
Electron Transfer (ET) kinetics determined including:

- The standard heterogeneous electron transfer rate constant (k_o)
- The charge transfer coefficient (α)

	E1			E2		
	E^o (V)	k^o (cm s^{-1})	α	E^o (V)	k^o (cm s^{-1})	α
$AlBr_3$	3.79	0.80	0.64	3.93	0.70	0.61
$AlCl_3$	3.49	0.014	0.49	3.69	0.30	0.50
$GaCl_3$	4.00	0.26	0.63	4.17	0.09	0.77

$AlBr_3$ had the highest ET kinetics despite having the lowest currents and predictions to be the lowest of the three

	MX_3I^- Concentration		
	Initial (mol l^{-1})	Equilibrium (mol l^{-1})	Reactant available (%)
$AlBr_3$	3.10	1.37	44.2
$AlCl_3$	6.09	4.91	80.6
$GaCl_3$	3.42	2.41	70.5

LOW CONC.

$AlBr_3$ (despite the highest ET kinetics) shows a speciation profile that favors the dimer ($M_2X_6I^-$) and thus decreases available reactant

An ideal system would have a very fast ET kinetics and high reactant concentration to optimize battery performance

Summary

- **Using a model that accounts for the electrochemical steps and various chemical equilibria between species, electrochemical simulations were performed to match observed electrochemical behavior of different Lewis acid-base molten salts.**
- **Revealed: positive *shift in $E_{1/2}$ with softer Lewis acid ($GaCl_3$), $AlBr_3$ system had the highest ET kinetics but lowest available reactant and ultimately, speciation can matter more to an applied electrochemical system than fast kinetics alone.***
- **Future work will investigate how changing compositions will effect the speciation and kinetics with the goal to optimize the molten salt catholyte electrochemical behavior in a working battery.**

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