

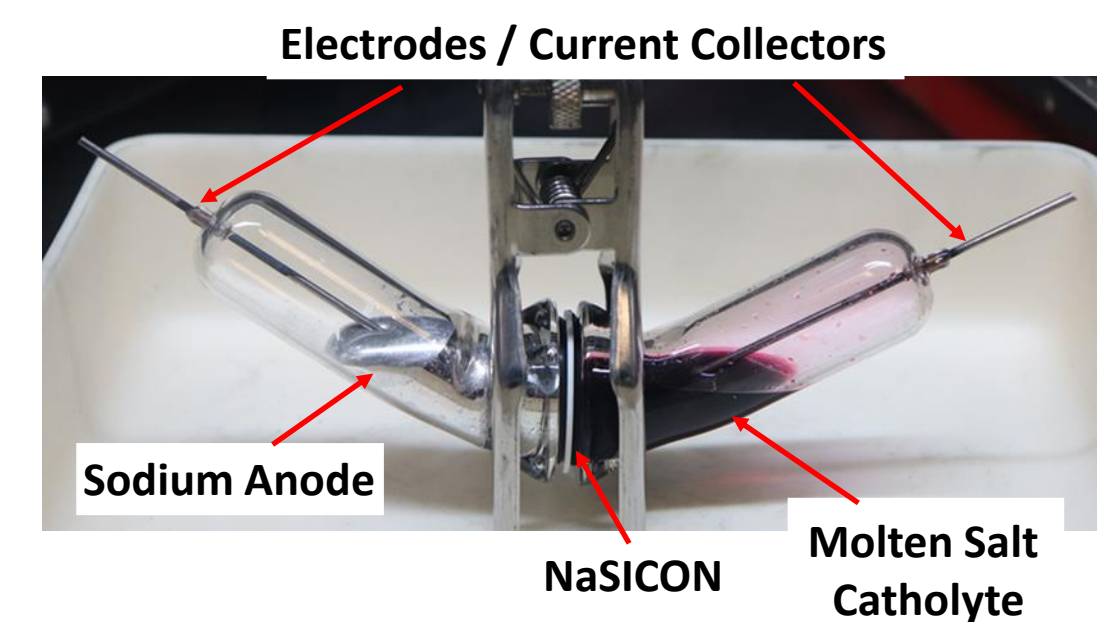
# Molten Salt Speciation Affects Electrochemistry and Battery Cycling: Raman Spectroscopy and Modeling Analysis

Stephen J. Percival, Adam Maraschky, William Delmas, Stephen Meserole, William Bachman, Amanda Peretti, Erik D. Spoerke and Leo J. Small (PI)  
Sandia National Laboratories, Albuquerque, NM, USA  
sperciv@sandia.gov, ljsmall@sandia.gov

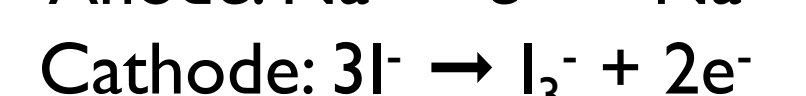
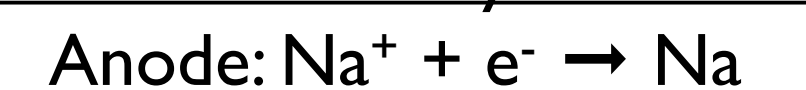
## Motivation & Objective

- Molten sodium batteries offer great promise as a safe, low cost and scalable solution to grid scale energy storage. Newly developed low temperature catholytes consisting of ratios of Lewis acid ( $MX_3$ ) and Lewis base (NaI) are promising, but display different electrochemical behaviors based on the identity of the corresponding Lewis acid ( $MX_3 = AlCl_3, AlBr_3$  or  $GaCl_3$ ). Additionally, composition (acidic vs basic melts) also show dramatic differences in battery cycling behavior and interfacial resistances. To better understand these systems, Raman spectroscopy and electrochemical simulation are used to understand how molecular speciation affects the observed electrochemical behavior.
- Objective:** Probe effect that molten salt composition (acidic vs basic) and corresponding Lewis acid has on the electrochemical behavior and battery cycling efficiency.
- Raman spectroscopy and electrochemical modeling/simulations enables detailed understanding of fundamental differences between different Lewis acid base compositions through evaluation of monomer ( $MX_3I^-$ ) and dimer ( $M_2X_6I^-$ ) concentration, which affects the basic electrochemistry and battery interfacial resistances of the NaSICON catholyte interface in different ways.

## Molten Sodium Battery Test Cell



Reversible battery reactions:

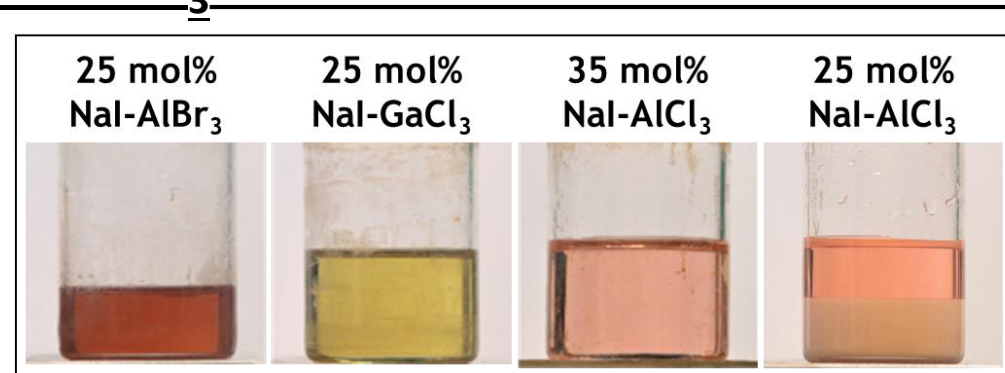


Small, et al. *J. Power Sources*, 2017, 360, 569-574.

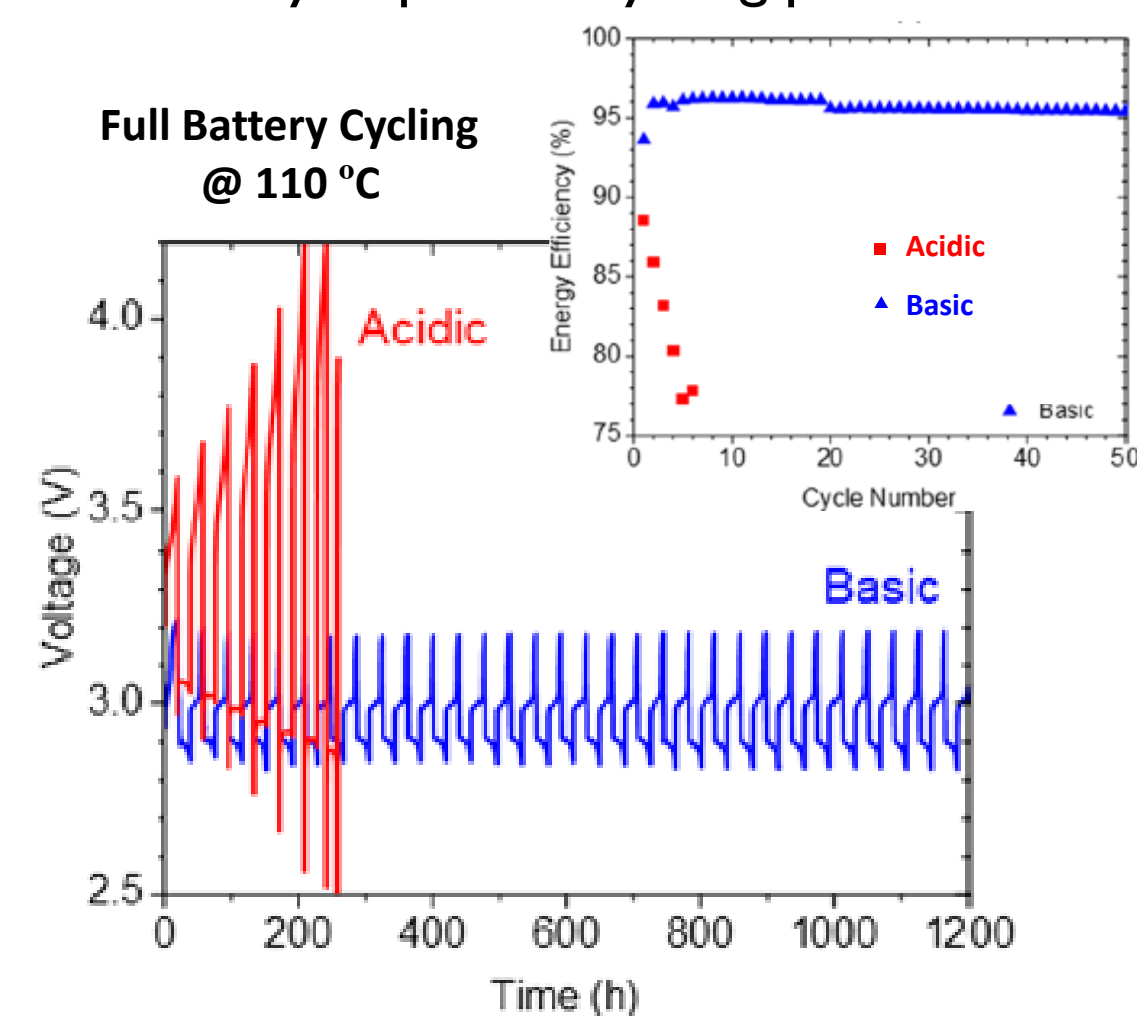
Percival, et al. *J. Electrochem. Soc.*, 2018, 165, A3531.

## 1. Speciation Affects – CVs + Battery Cycling

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



In full battery tests, acidic melts ( $AlCl_3$  rich) had poor cycling behavior while basic melts (NaI rich) had drastically improved cycling performance



NaSICON interface showed increasing interfacial resistance as battery cycling continued in acidic melts – Why?

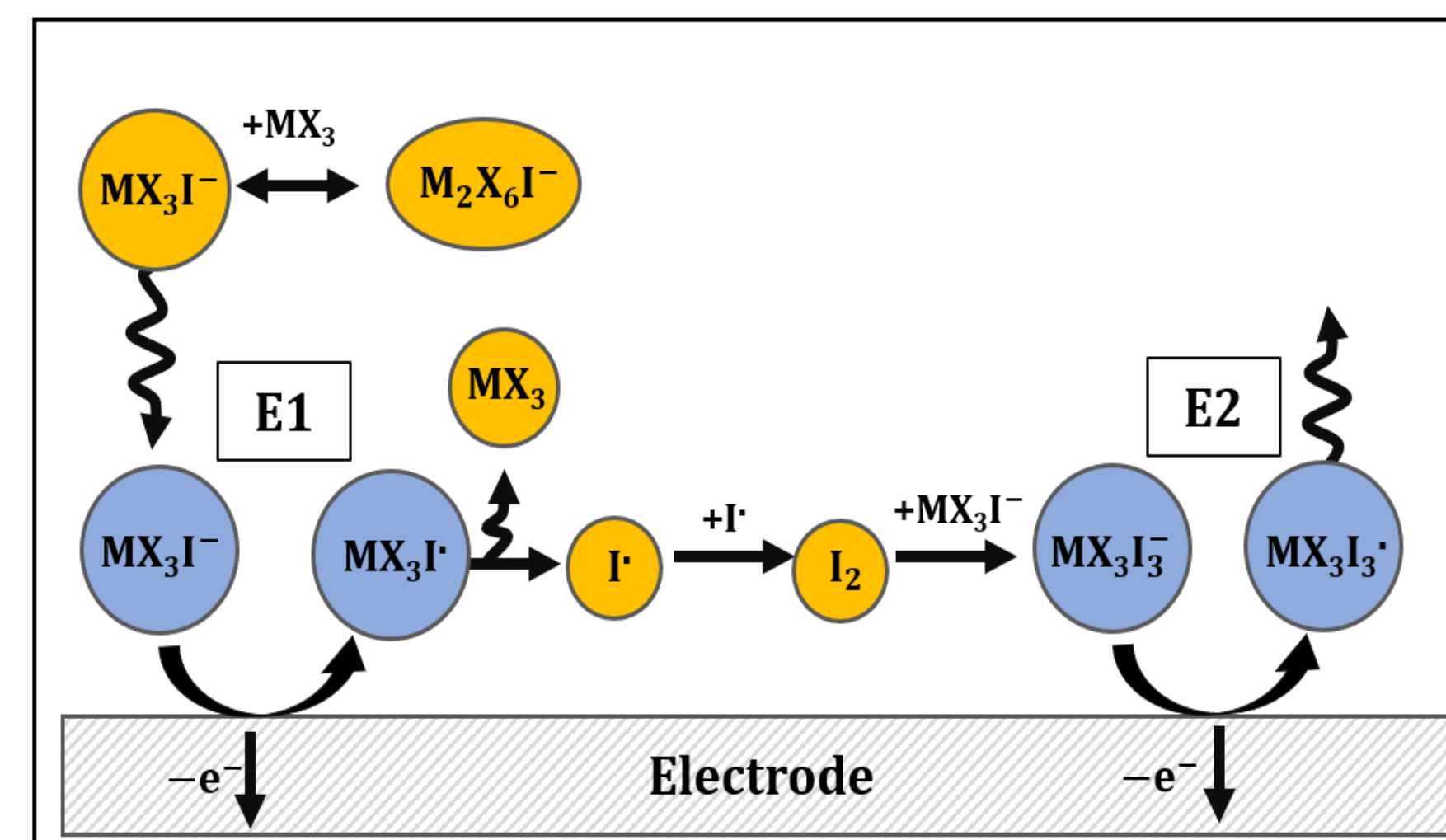
Maraschky, et al. *J. Phys. Chem. C*, 2023, 127, 1293.

## 2. Simulation Chem/Electrochem Model

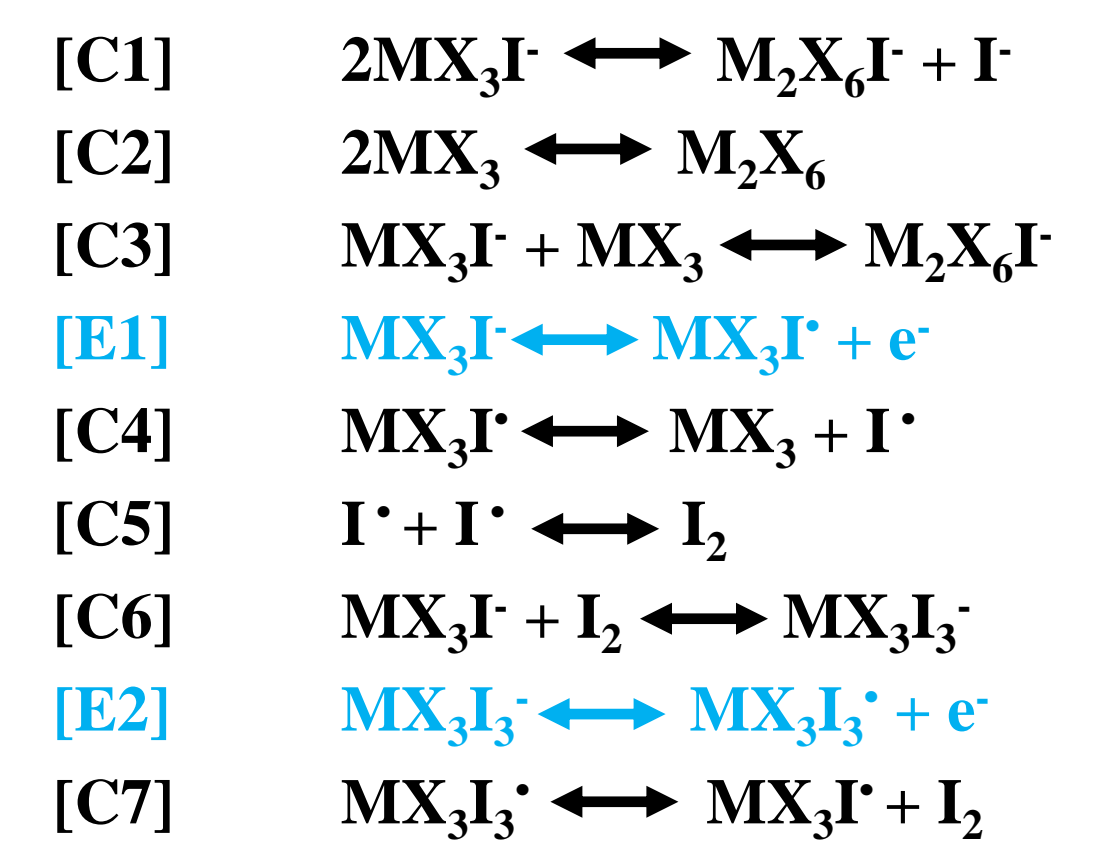
Model consists of two electrochemical steps (shown in blue) and multiple chemical steps

Accounts for multiple species: radical intermediates, the electrochemically active “monomers” ( $MX_3I^-$  and  $MX_3I_3^-$ ) and inactive “dimers” ( $M_2X_6I^-$ ) -

- $M_2X_6I^-$  not considered active at these potentials - effectively lowers reactant concentration



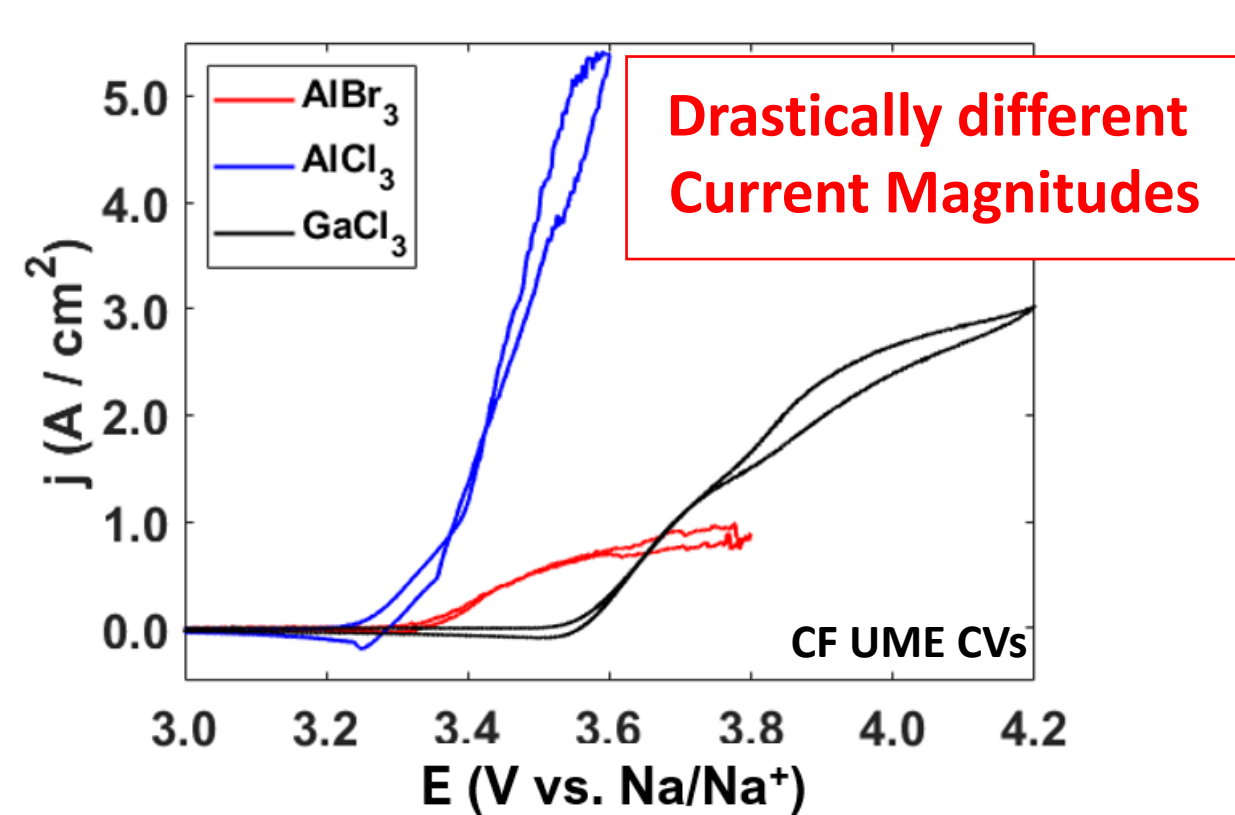
Percival, et al. *J. Electrochem. Soc.*, 2021, 168, 126511.



Chemical equation number corresponds to equilibrium constants

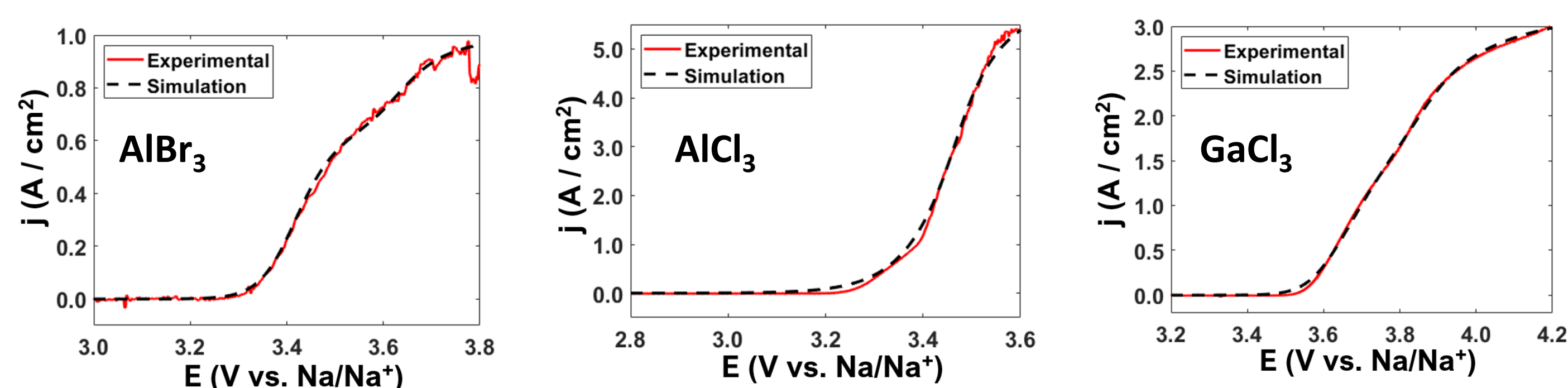
Microelectrode CV analysis - current differences in melts with the same reactant concentration

Some reactant is inaccessible!



Percival, et al. *J. Electrochem. Soc.*, 2021, 168, 126511.

## 3. Speciation vs. Kinetics



Simulated CVs match experimental CVs and Electron Transfer (ET) kinetics determined:

- The standard heterogeneous electron transfer rate constant ( $k_0$ )
- The charge transfer coefficient ( $\alpha$ )

$AlBr_3$  had the highest ET kinetics despite having the lowest currents

$AlBr_3$  shows a speciation profile that favors the dimer decreasing available reactant

An ideal system would have a very fast ET kinetics and high reactant concentration

	E1			E2		
	$E^0$ (V)	$k^0$ ( $cm\ s^{-1}$ )	$\alpha$	$E^0$ (V)	$k^0$ ( $cm\ s^{-1}$ )	$\alpha$
$AlBr_3$	3.79	0.30	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

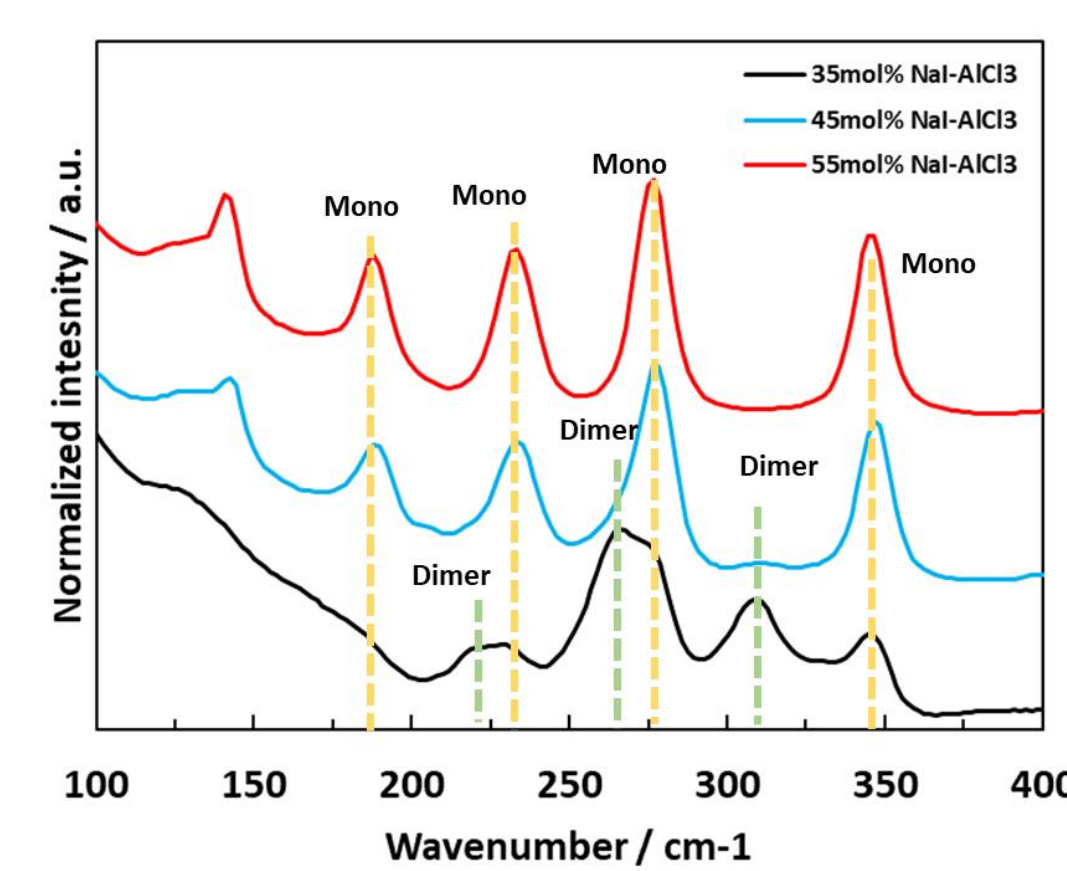
  

	$MX_3I^-$ Concentration		
	Initial ( $mol\ l^{-1}$ )	Equilibrium ( $mol\ l^{-1}$ )	Reactant available (%)
$AlBr_3$	3.10	1.37	44.2
$AlCl_3$	6.09	4.91	80.6
$GaCl_3$	3.42	2.41	70.5

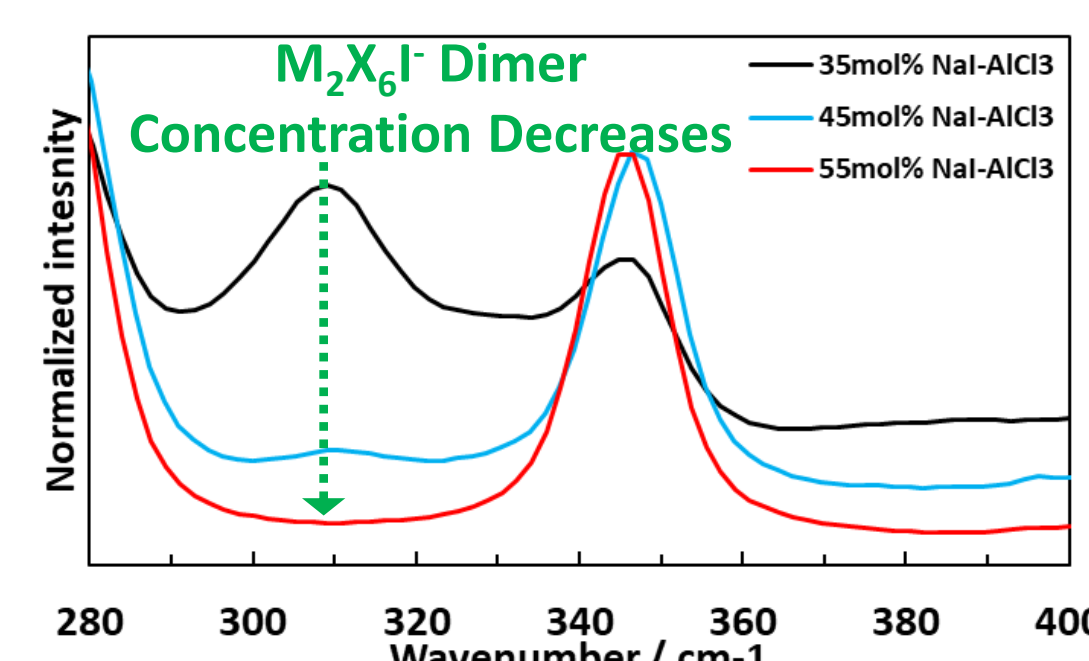
Percival, et al. *J. Electrochem. Soc.*, 2021, 168, 126511.

## 4. Spectroscopic Verification of Species

Raman spectroscopy was performed with pristine molten salt catholytes and reveals monomer and dimer species peaks



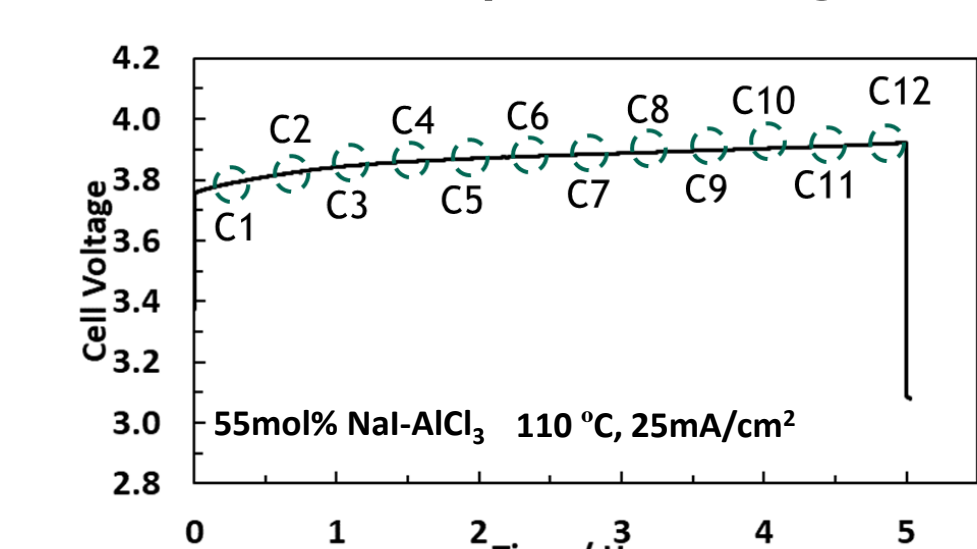
Analysis of Raman spectra revealed changing composition from acidic to basic melts leads to elimination of the reactive dimer species that was attacking the NaSICON.



Maraschky, et al. *J. Phys. Chem. C*, 2023, 127, 1293.



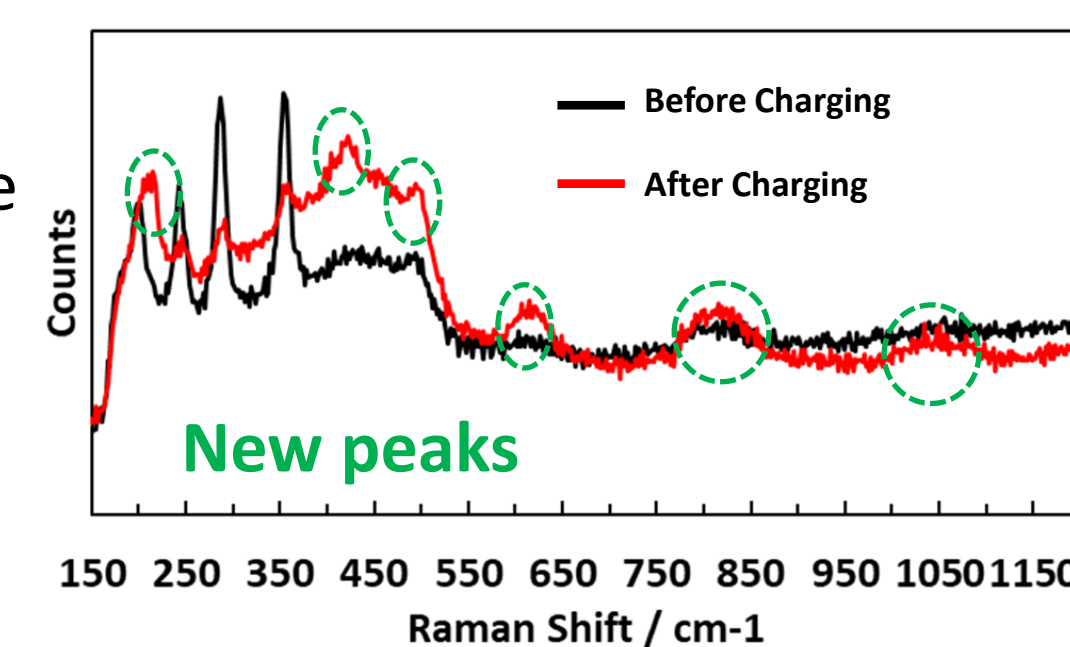
New fiber optic *in-situ* Raman system setup inside glovebox and new battery cells designed for spectroscopic analysis.



Battery charged and Raman spectra taken periodically from the bulk catholyte melt

New peaks appear as battery charged to ~5% DoD

New peaks show growing intensity with DoD and are theorized to be attributable to new  $I_3^-$  monomer ( $MX_3I_3^-$ ), and dimer ( $M_2X_6I_3^-$ ) species.



## Summary

- Using a detailed electrochemical and chemical model to simulate data revealed differences in different Lewis-acid-base molten salts with a positive shift in  $E_{1/2}$  with softer Lewis acid and ultimately, speciation can matter more to an applied electrochemical system than fast kinetics alone.
- Composition will also affect speciation and can lead to dramatic differences in observed battery cycling behavior and overpotentials due to increased interfacial resistances where presence of Lewis acid-base “dimers” will have a detrimental affect on the NaSICON catholyte interface and thus affects battery performance.
- New *in-situ* Raman system setup and preliminary data shows new Raman peaks associated with a change in salt species as the battery is being charged.
- Future work will continue to probe the catholyte speciation using *in-situ* Raman spectroscopy, in the salt and at the electrode surface, combined with electrochemical modeling to determine how changing compositions will effect the battery behavior and how to improve the battery performance and cycle lifetime.

### Acknowledgments:

This work was supported by the U.S. Department of Energy Office of Electricity, Energy Storage Program.