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Determining Interphase Identity and Directing Cation Transport at Mg and Ca Electrodes

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236th ECS Meeting

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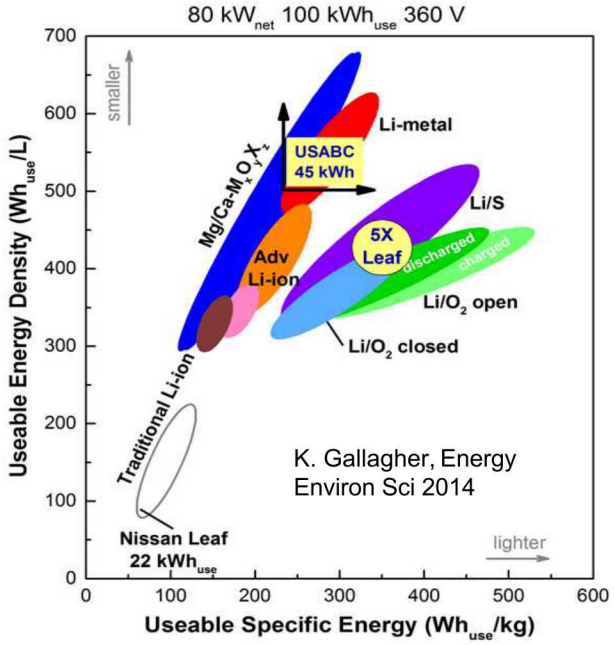
Snapshot of MV Electrolyte Development

- ***MV metal anode + high voltage cathode = transformative energy storage***
- Significant growth in Mg electrolyte development – expansion of stability window
- Growing electrolyte toolkit provides opportunity for systematic investigation - predictive electrolyte design



Mg Electrolyte Concept Development

$R_2Mg:AlR_xCl_{3-x}$ "DCC" — $RMgCl:AlCl_3$ "APC" — $MgX_2:MgCl_2$ X = OR, NR_2 — $MgTFSI_2:MgCl_2$

Cl-based Electrolytes

($Mg_2Cl_3^+$ + etc.)

more basic/reactive (lower anodic stability)

less basic/reactive (higher anodic stability)

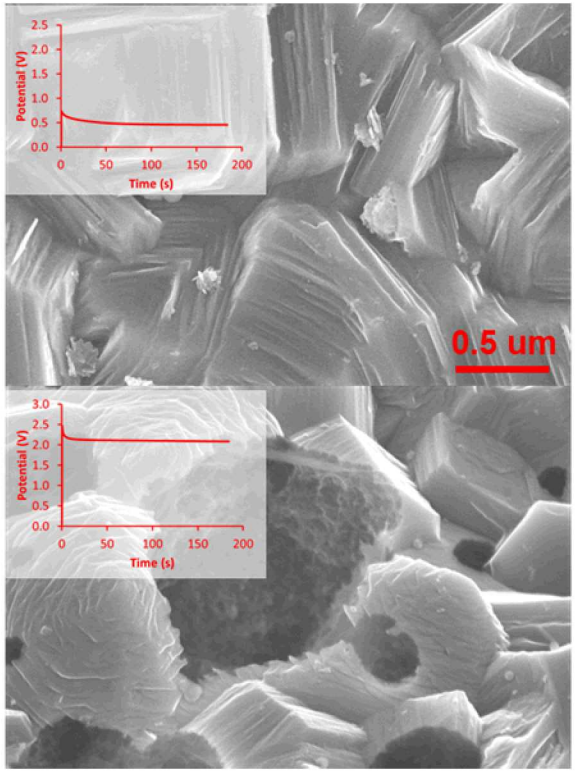
$Mg(BR_4)_2$ — $MgTFSI_2$ — $Mg(RCB_{11}H_{11})_2$ — $Mg(MOR^F{}_4)_2$

WCA-based Electrolytes

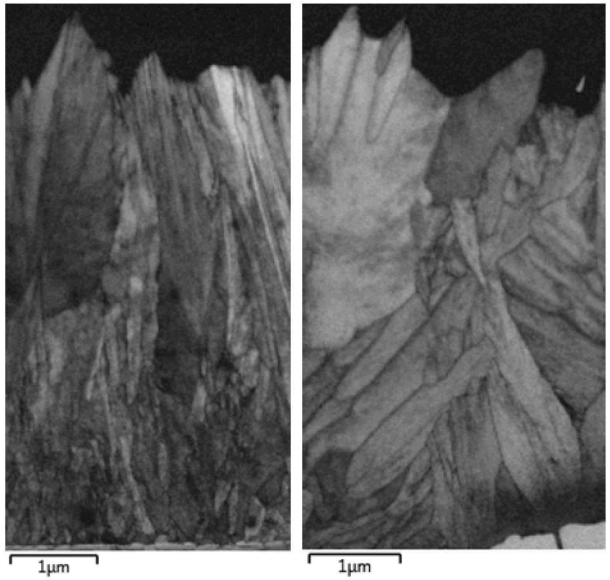
(Mg^{2+})

Interphases dictate the feasibility of MV metal anodes

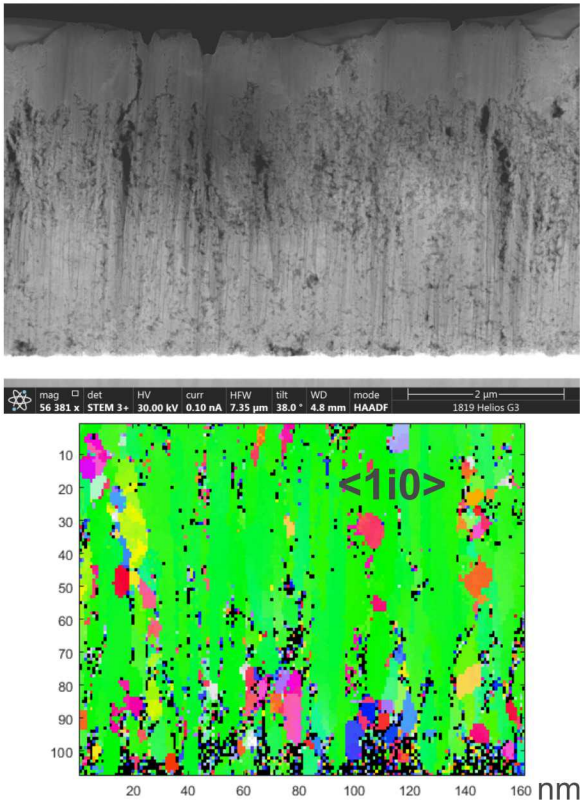
Mg requires activation of the anode interphase



Structure directing role: trace H_2O impacts Mg deposit microstructure



Morphology evolution: Porosity evolution in cycled Ca anodes

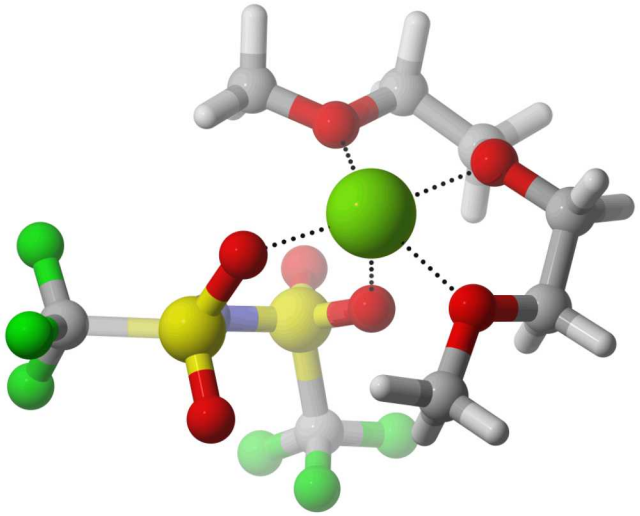


Design and directed formation of MV interphases is challenging - nanometric, structurally unstable, and largely undetermined

Outstanding Questions – New Approach

Science Question What is the role of the solvent in dictating the following:

- TFSI reactivity?
- the limits of efficiency?
- performance of WCA's?



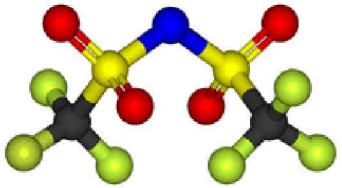
Our approach:

Explore impact of competitive solvent and anion complexation on efficiency.

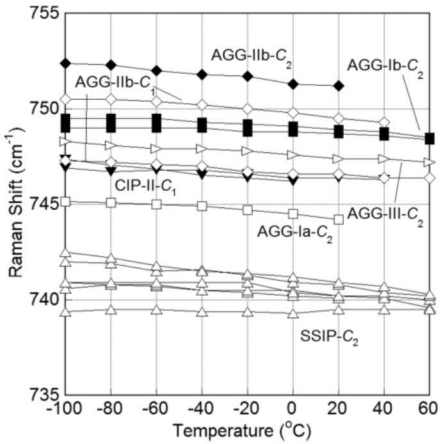
- Treat the ether – glyme solvent series as a continuum of energy of complexation
- Treat contact ion pairing anions as displacive ligands
- Bulk speciation – interfacial speciation - reactivity

$TFSI^-$ as a Benchmark Weakly Coordinating Anion

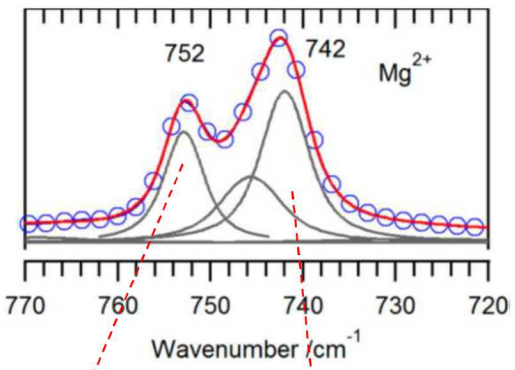
TFSI provides diverse conformations and interactions



TFSI Conformational Sensitivity

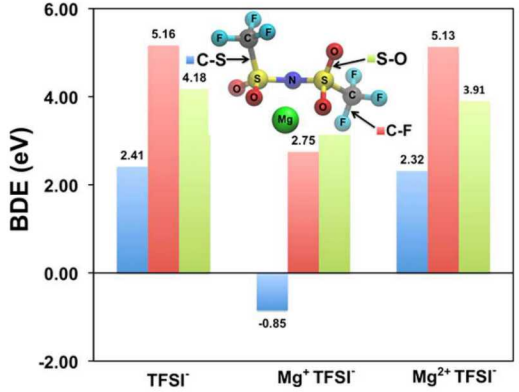


Seo et al. J. Phys. Chem. B 2014, 118, 13601−13608

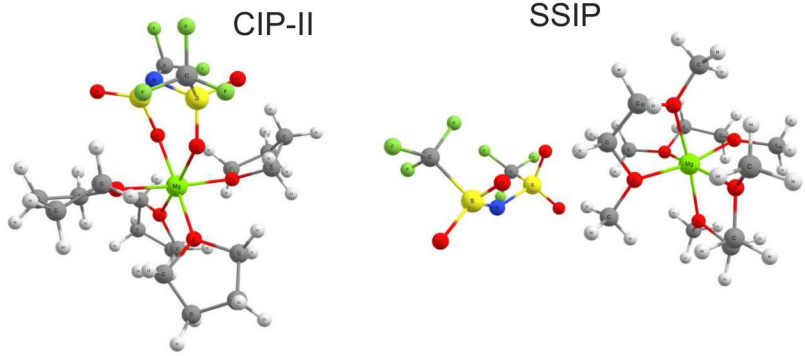


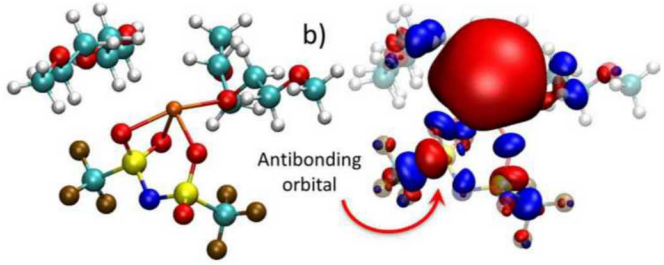
Giffin et al. J. Phys. Chem. C 2014, 118, 9966−9973

Predicted Stability Dependence



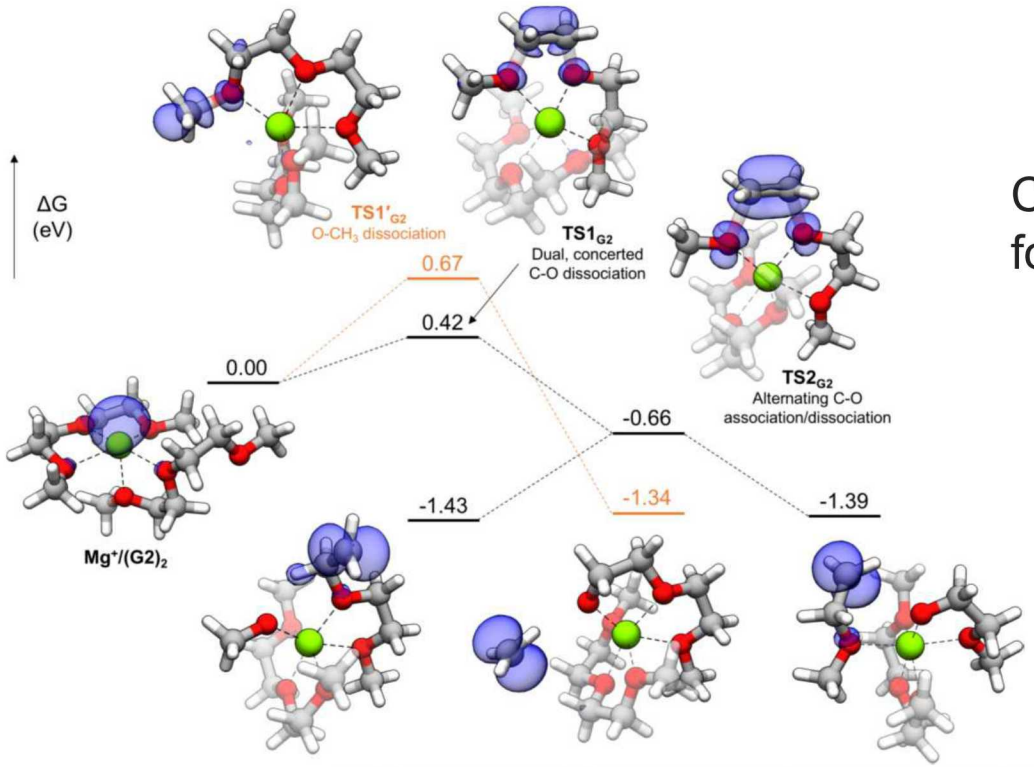
N. Rajput et al. J. Am. Chem. Soc. 2015, 137, 3411−3420





A. Baskin et al. J. Phys. Chem. C, 2016, 120 , 3583–3594

The reductive stability of the solvent alone is not the concern?



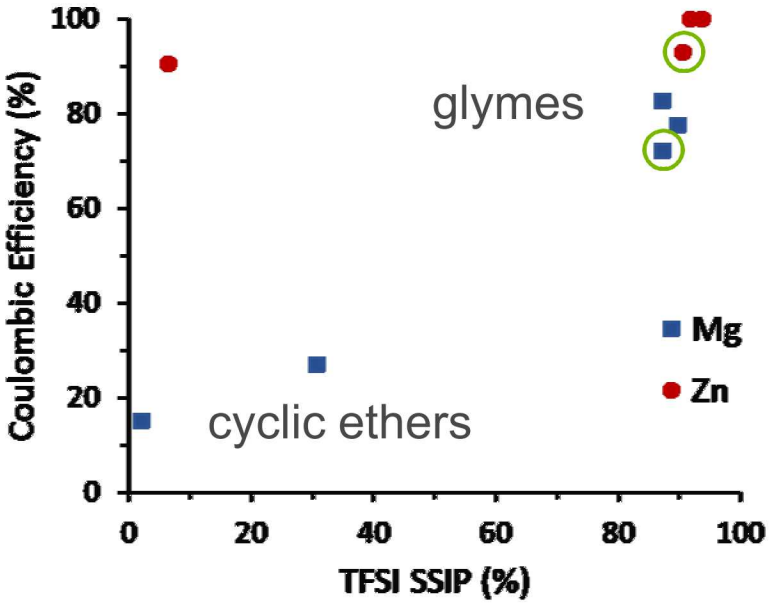
Comparable free energy barriers for Mg^+-solv reduction

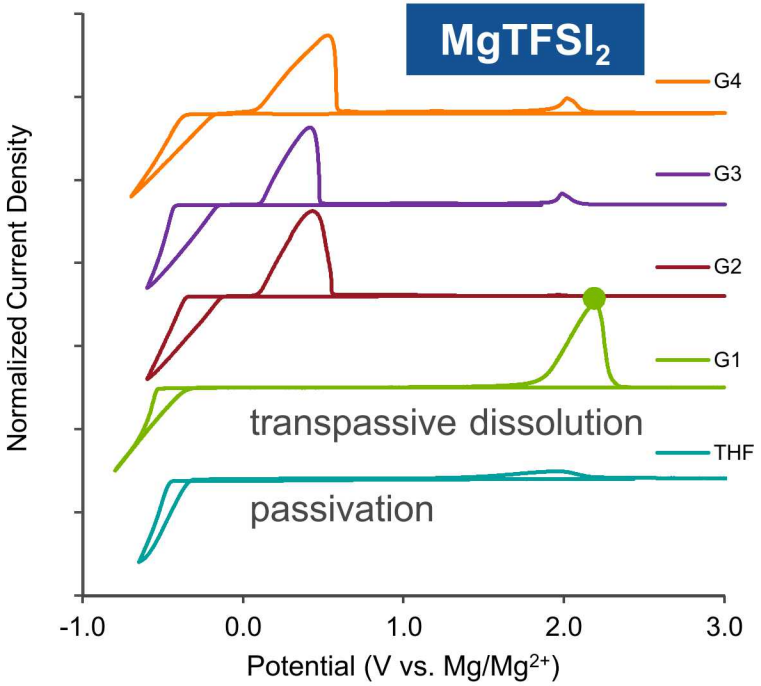
$$\Delta E^{\ddagger} = \Delta E_{dist}(glyme) + \Delta E_{int} + \Delta E_{red}(glyme) + \Delta E_{ox}(Mg^+)$$

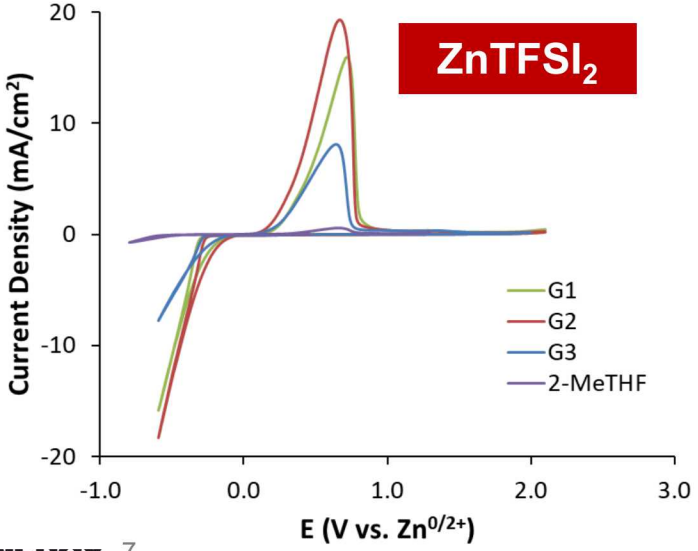
Solvent	$\Delta G^{\ddagger}$	$\Delta E^{\ddagger}$	ΔE_{dist}(glyme)	ΔE_{red}(glyme)	ΔE_{int}	$\Delta E_{ox}(Mg^+)$
G1	0.54	0.68	0.91	1.63	-16.56	14.70
G2	0.42	0.55	0.98	1.68	-16.81	14.70
G3	0.51	0.58	0.77	1.56	-16.44	14.70

N.T. Seguin et al. Frontiers in Chemistry. 2019, 10.3389/fchem.2019.00175

Solvent-anion combination has a strong impact on activity







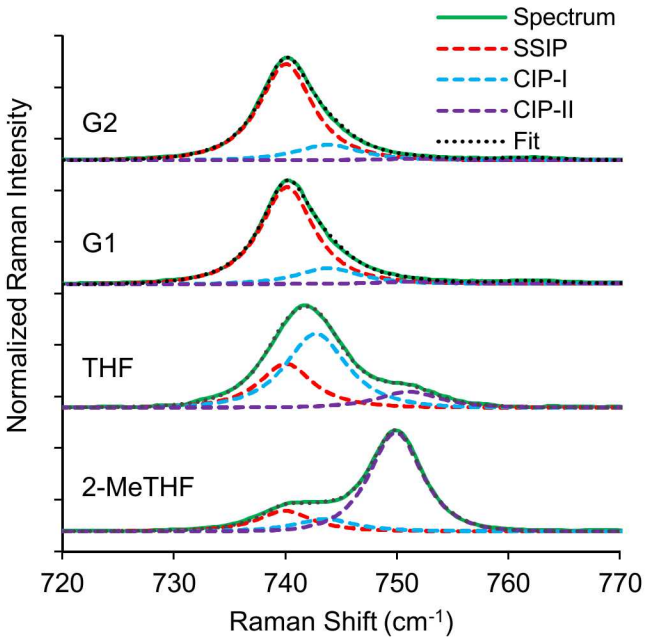
Activity = efficiency, kinetics, overpotential

DME test case:
Low CE, sluggish kinetics, transpassive behavior

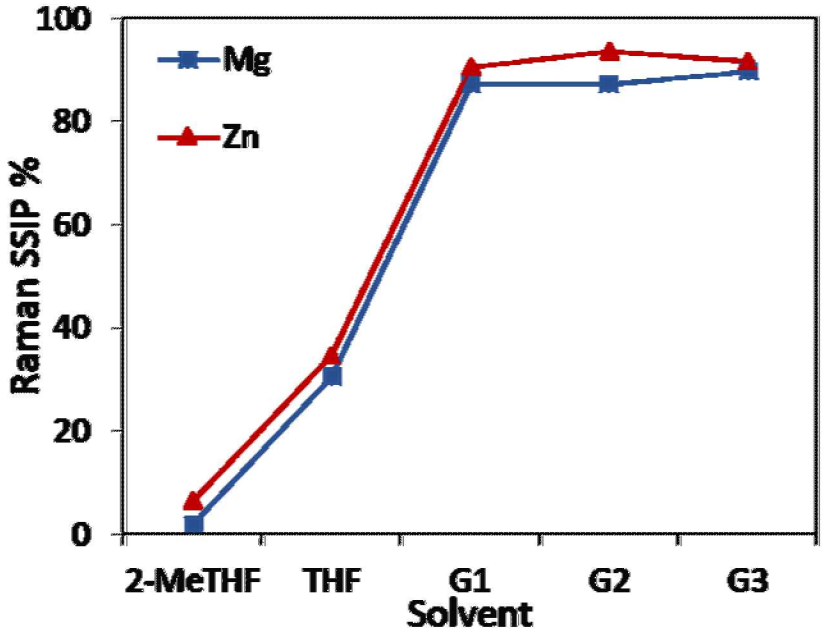
Ion Pairing is prominent across the ether series

Bulk Speciation is determined with Raman

0.5 M $MgTFSI_2$:solvent



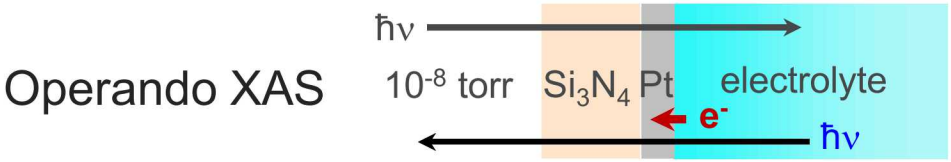
degree of dissociation with ether



- Free or solvent separated ion pairs are dominant in multidentate ethers
- Contact ion pairs and aggregates are dominant in the cyclic ethers

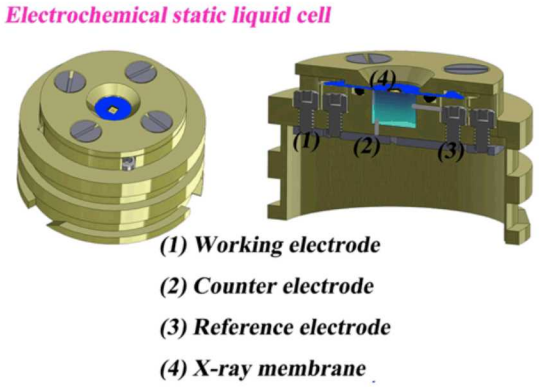
How does bulk speciation translate to the interface?

Tools are necessary to probe interfacial speciation

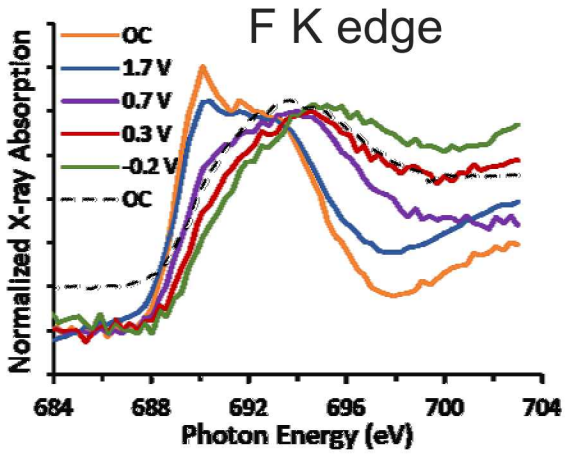


Total electron yield (TEY) e^- out = interfacial

Total fluorescent yield (TFY) ħν out = bulk electrolyte



potential dependent response of interface



soft and tender x-rays enable an interfacial compositional inventory

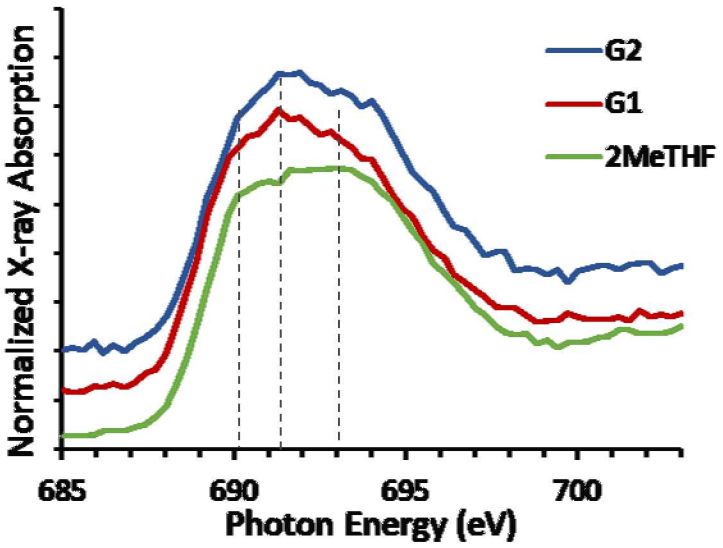
Cations: Mg, Ca, Zn

Ligands: B , Cl, C, O, F

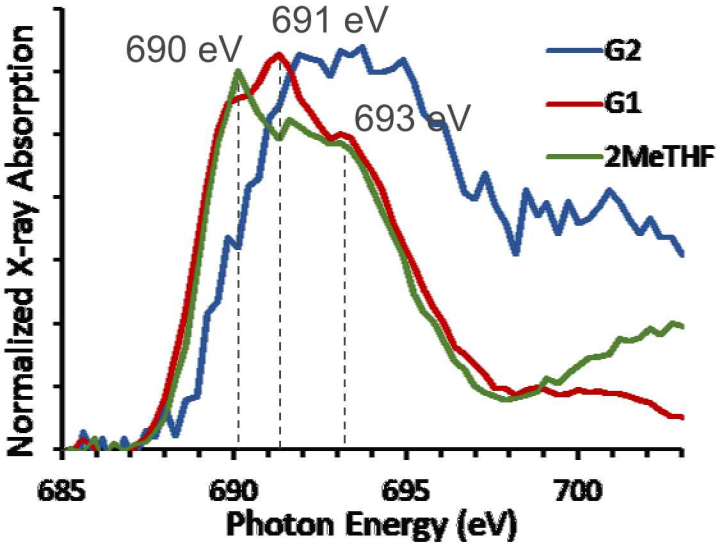
Unique speciation exists at the interface

0.5 M $MgTFSI_2$:solv Au working electrode at open circuit potential

Bulk Electrolyte (TFY)



Interface (TEY)



Modest change across IP range
95 - 10%

3+ distinct bands – vary across IP range

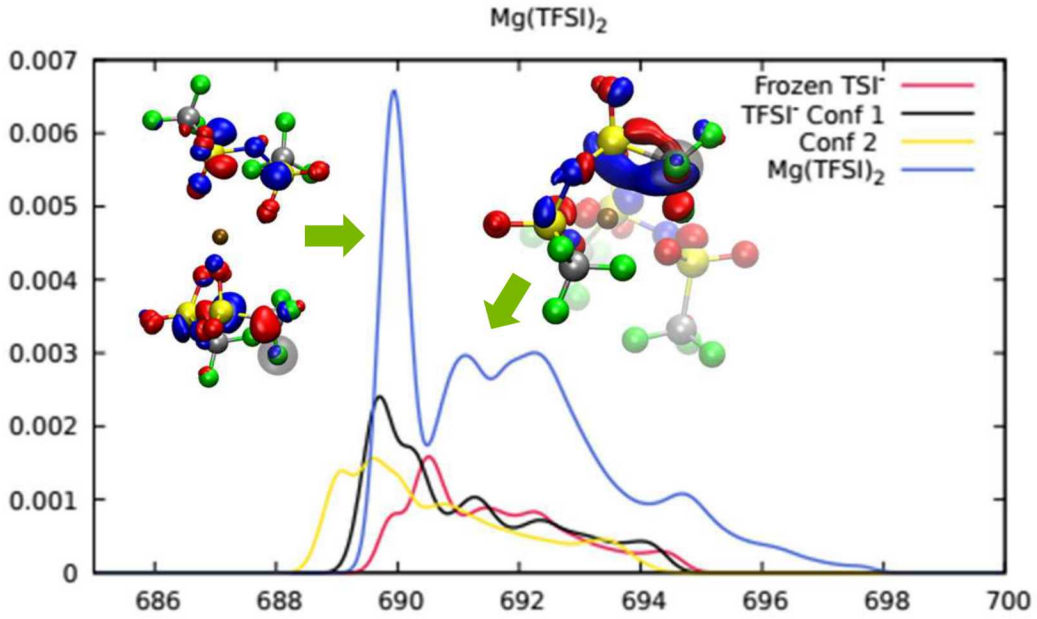
DME – variation within IP range

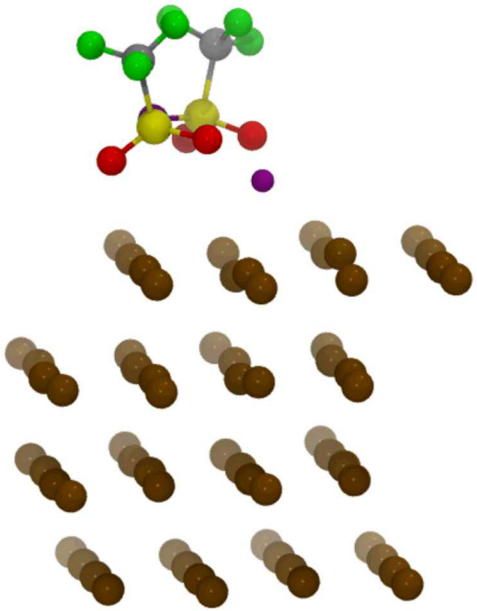
The interface is a unique environment for reconfiguration of the M-TFSI-solv coordination complex

Probable structures determined using computational spectral simulation

First-principles electronic structure simulation and interpretation of F K-edge XAS

Informed by AIMD for stable TFSI- conformation





Gas phase simulations to start

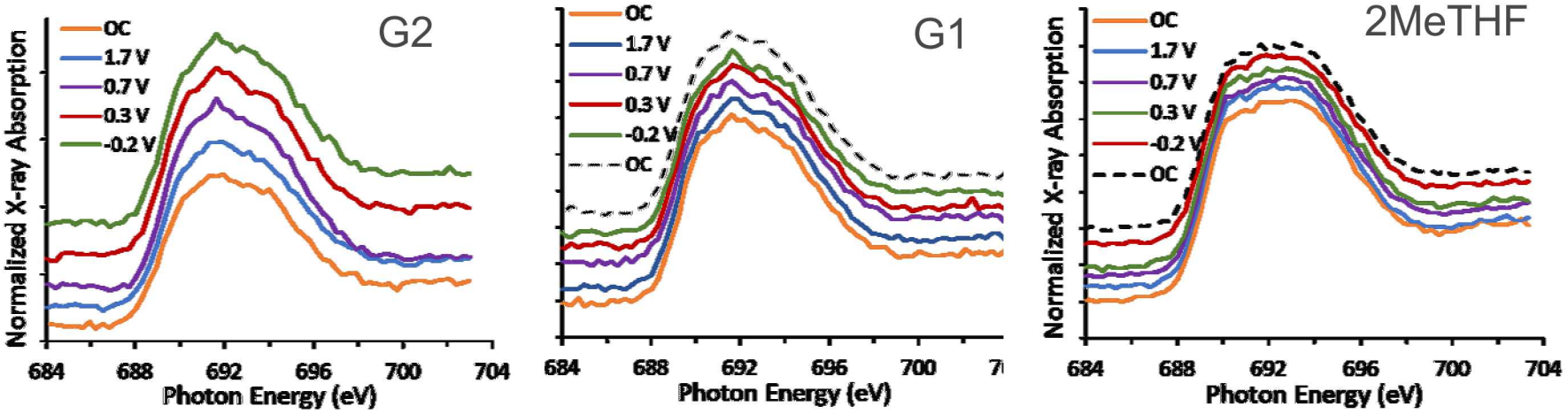
- incorporate solvent as a ligand

- account for metal electrode
- charge screening of solvent

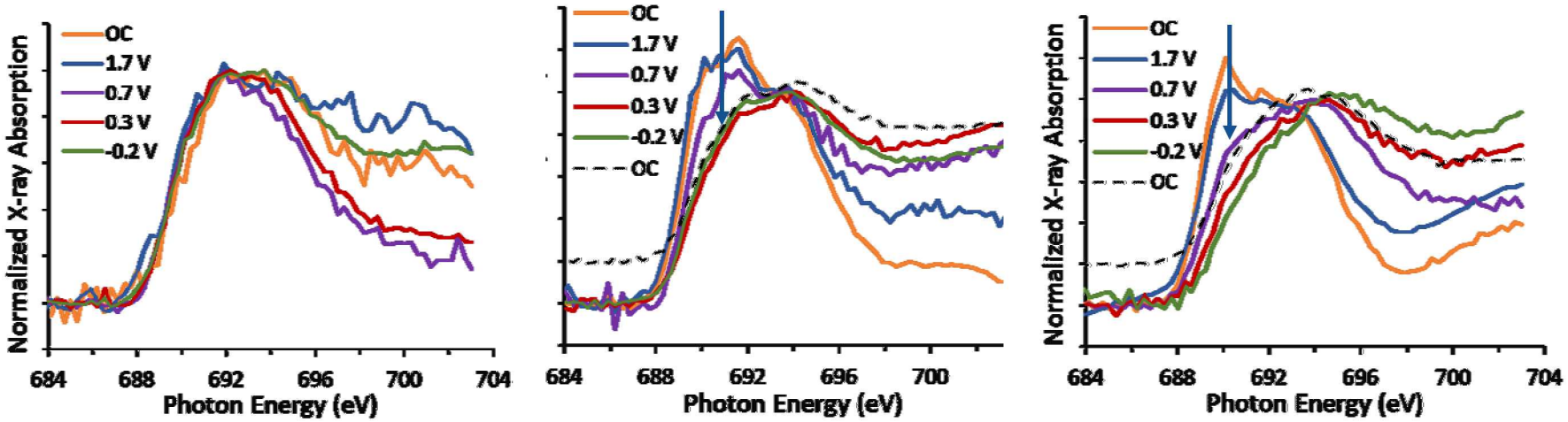
Liang, Y. and Prendergast, D. Phys. Rev. B, **96**, 205127 (2018)

Unique interfacial speciation correlates with reactivity

Bulk electrolyte spectra are unchanged with cathodic polarization

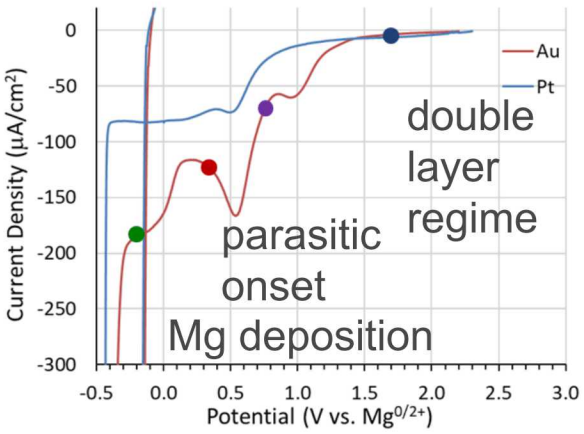


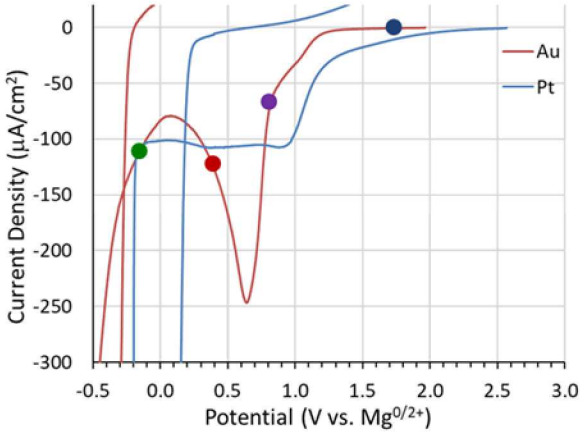
Interfacial spectral show attenuation of 690 - 691 eV peaks (irreversible)

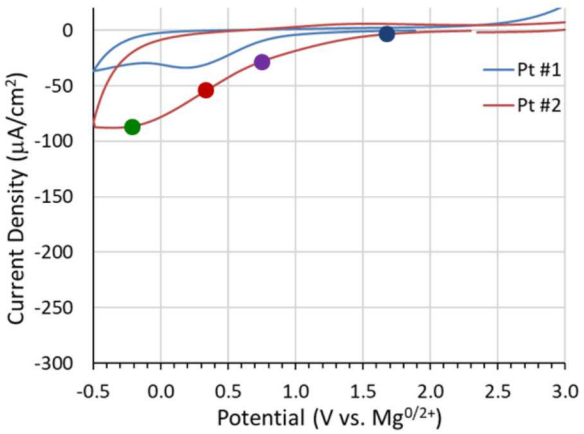


Interfacial speciation changes correlate with parasitic reactions

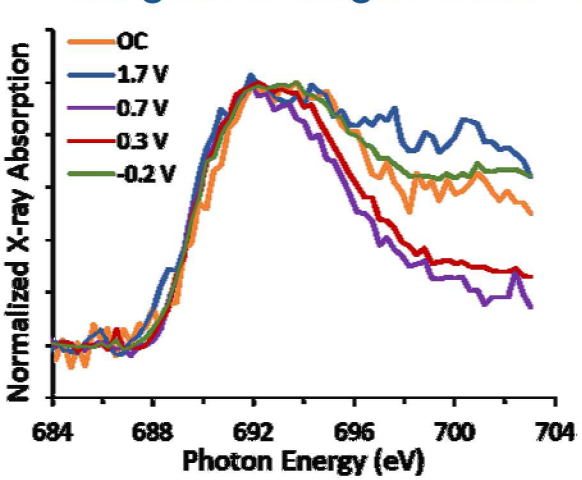
Irreversible redox is observed well below the Mg nucleation potential

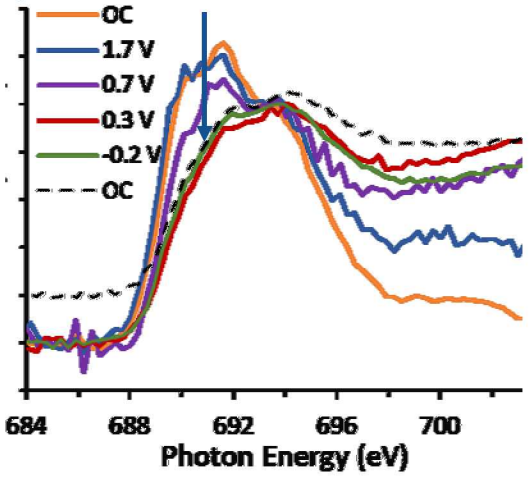


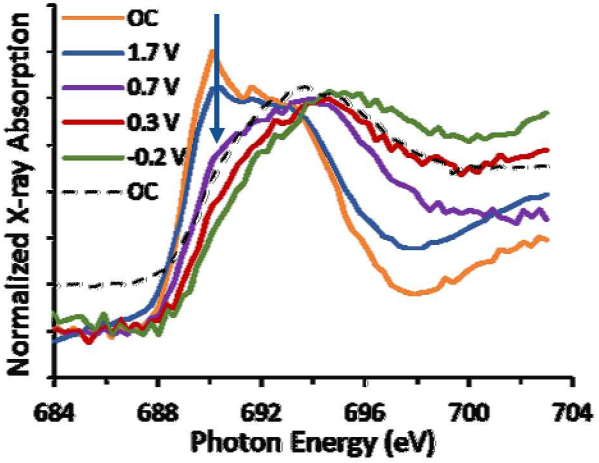




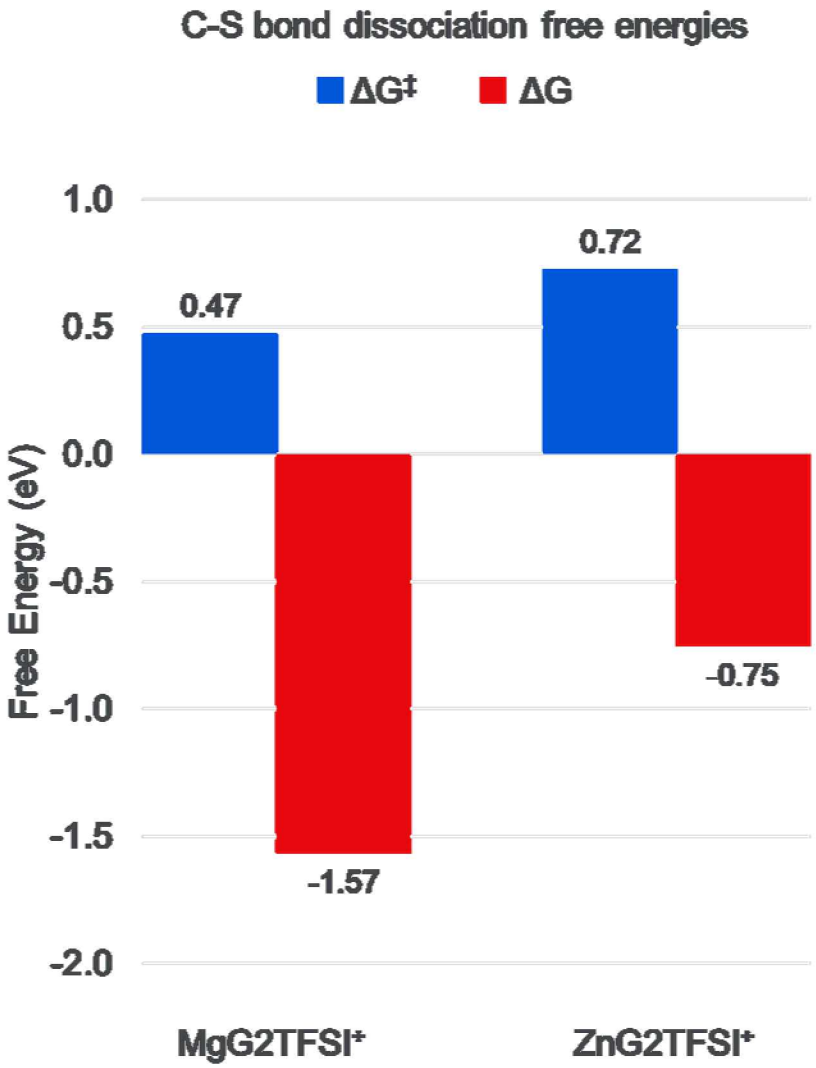
Largest changes occur at parasitic onset



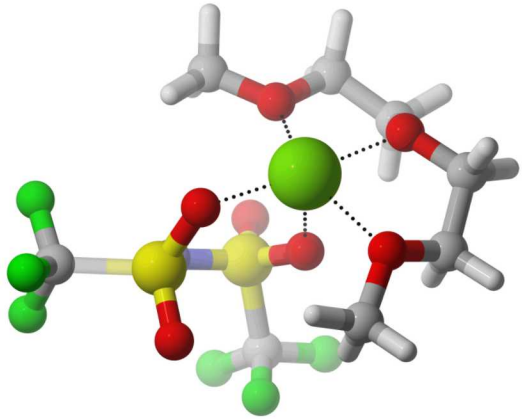




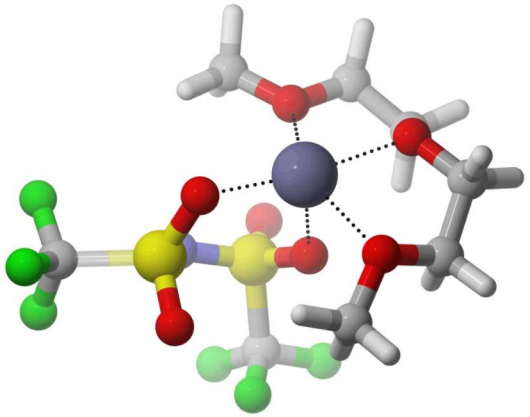
Computation confirms ZnTFSI(G2)^0 stability



C-S cleavage transition states



$MgG2TFSI^+$

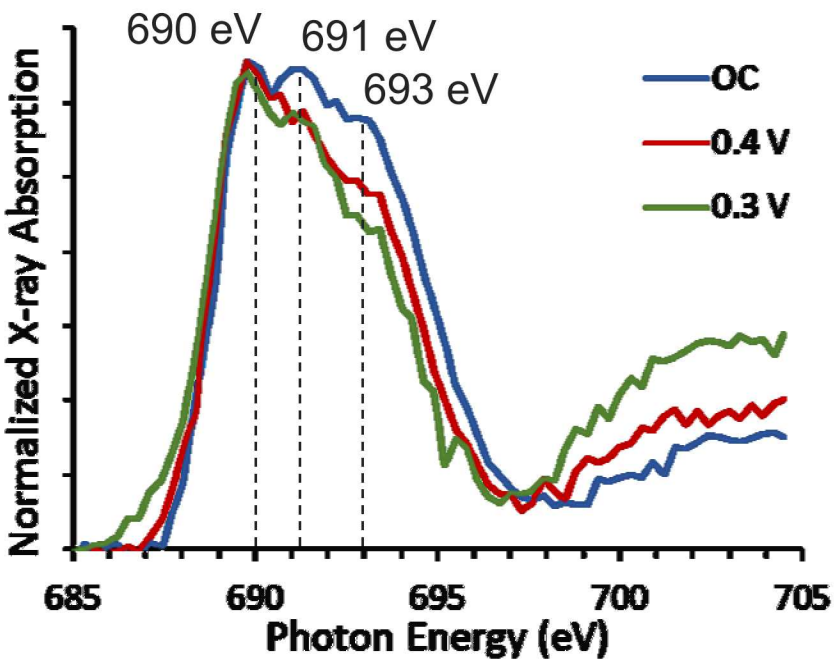


$ZnG2TFSI^+$

T. Seguin, K.A. Persson et al.

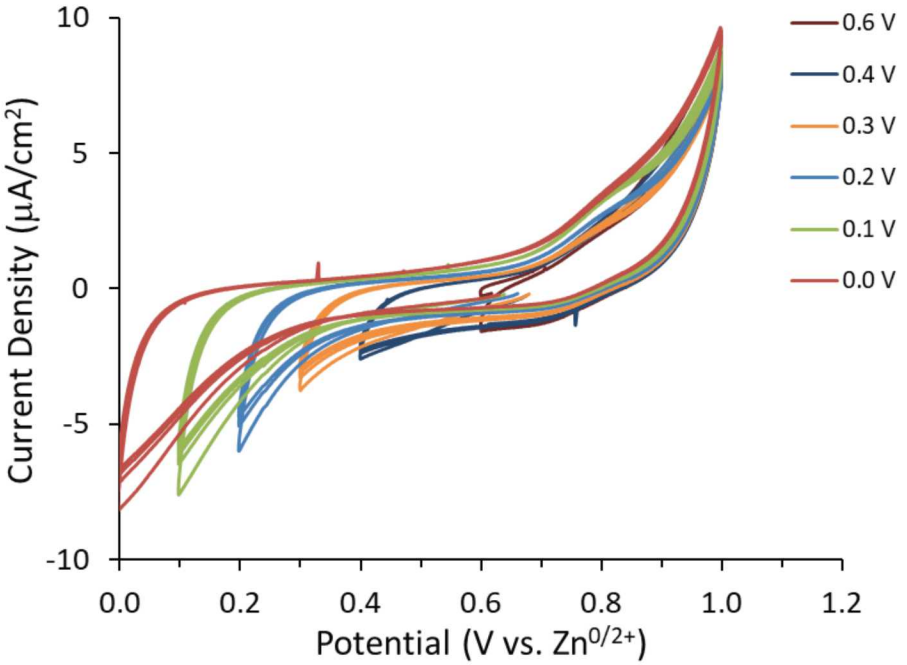
Interfacial speciation of $ZnTFSI_2$ as a control

0.5 M $ZnTFSI_2$:2-MeTHF



Minor interfacial changes due to $ZnTFSI(solv)^0$ stability

Similar absorption features for MgTFSI2 in 2MeTHF and G1



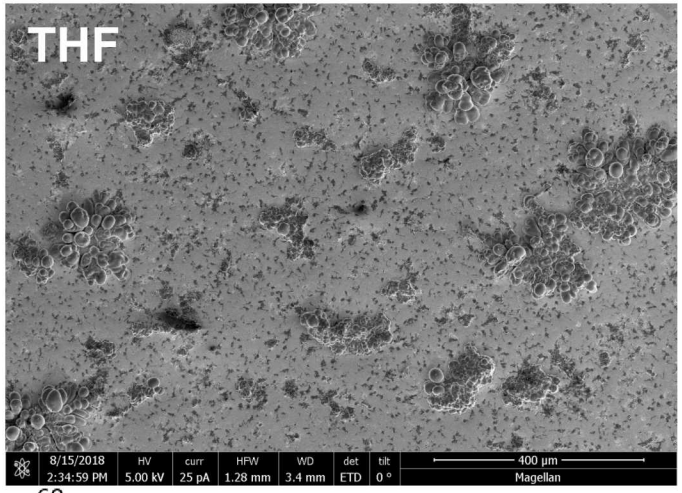
reduced parasitic reactivity at higher potential $E(Mg^{0/2+}) - E(Zn^{0/2+})$

Zn-Au alloying is impaired in 2MeTHF

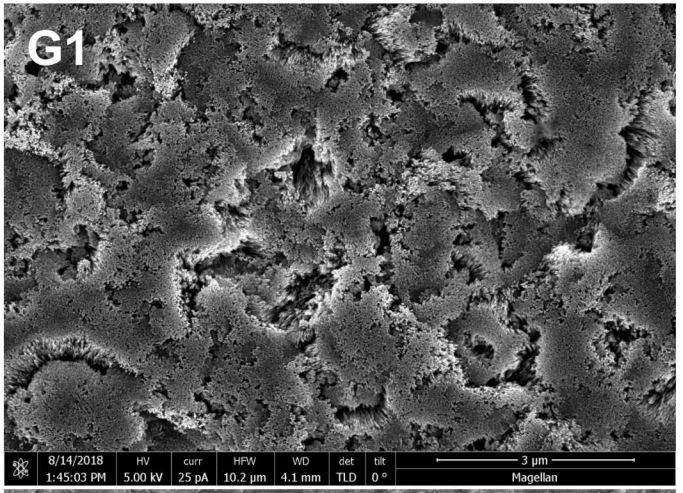
Reduced TFSI Decomposition with Displacement

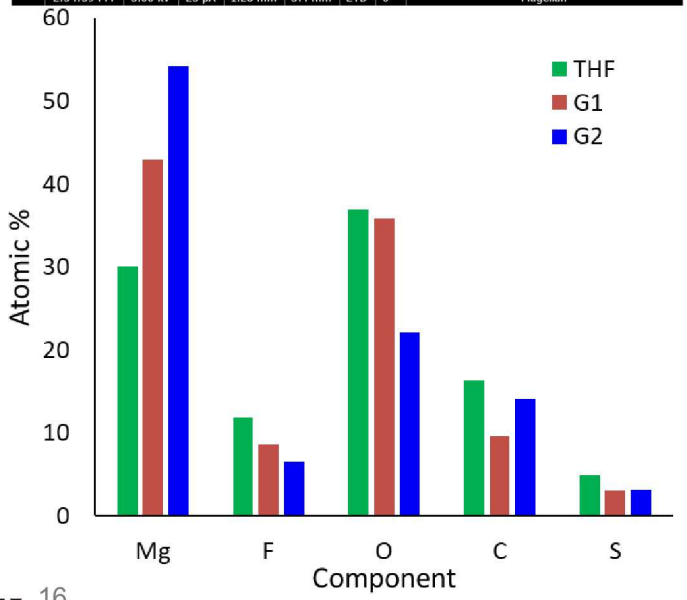
Interphase composition should yield less TFSI products with THF ⇢ G2

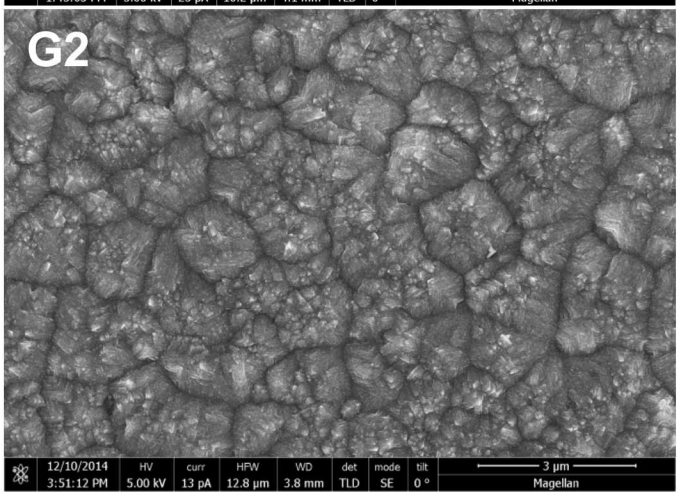
Localized deposit – filmed substrate



Localized deposit – fibrous morphology





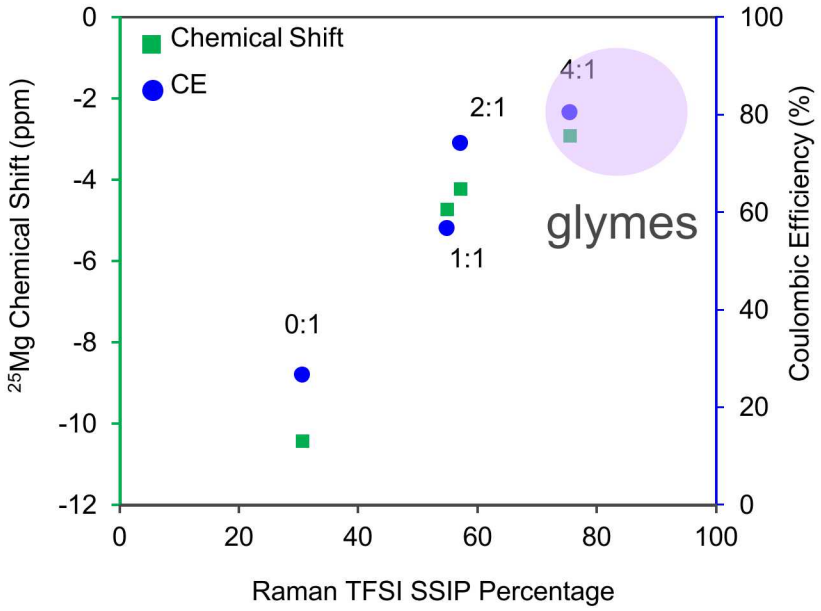


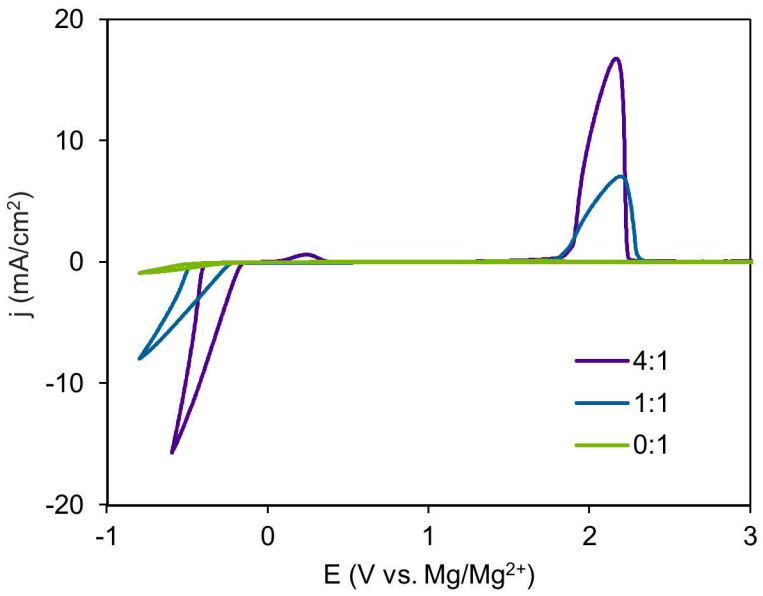
Localized deposit –dense platelets

Demonstration of Solvent Controlled Ion Separation

Add a stronger coordinating solvent to a highly ion associated electrolyte

G2 addition to THF at select G2:Mg^{2+} molar ratios while maintaining Mg^{2+} at 0.5M





- G2 up to 17 mol% yields descriptors consistent with a glyme electrolyte
- Mg deposition is greatly enhanced
- Generalized strategy for regulating reactivity

Key Lessons

- Interfacial speciation is probed in the $MgTFSI_2$:solv system using EC-XAS
- Interface is a unique environment aiding in creation of reactive complexes
  - These are prescribed by and regulated by bulk speciation
  - But are unique to the interface
- Directed formation of stable, functional interphases requires this knowledge

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David Prendergast

Vijayakumar Murugesan
Jian Zhi Hu