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Studies of Electrolytes and Interfaces for Mg Batteries

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Sandia National Laboratories

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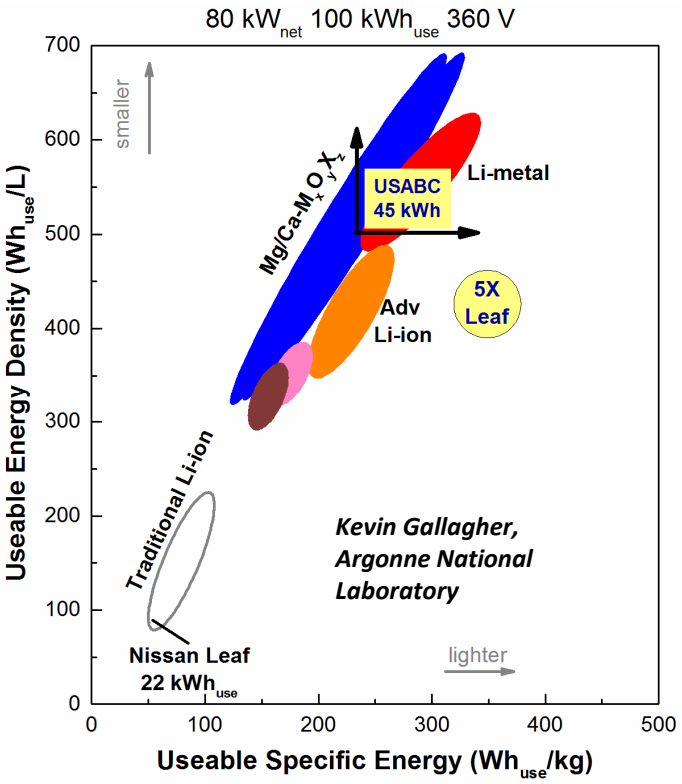
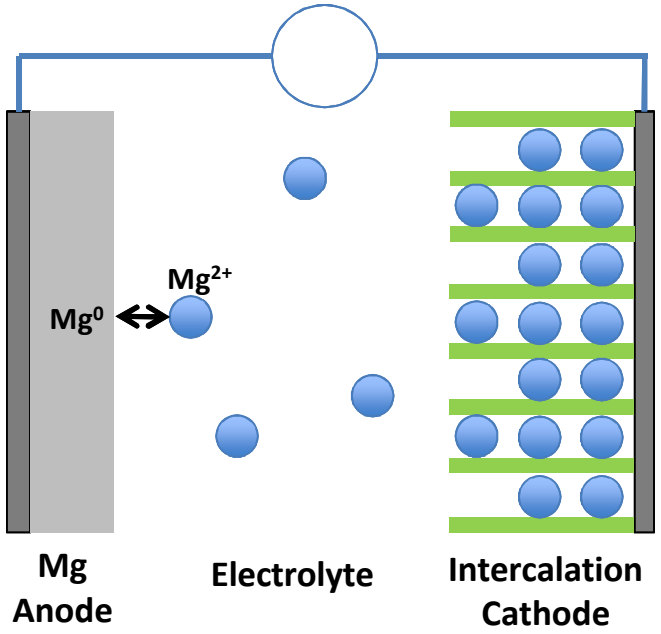
Magnesium Battery Promises

Pack-level calculations:
Mg anode + high voltage cathode = success



Mg metal plating and stripping comprise anode charge/discharge

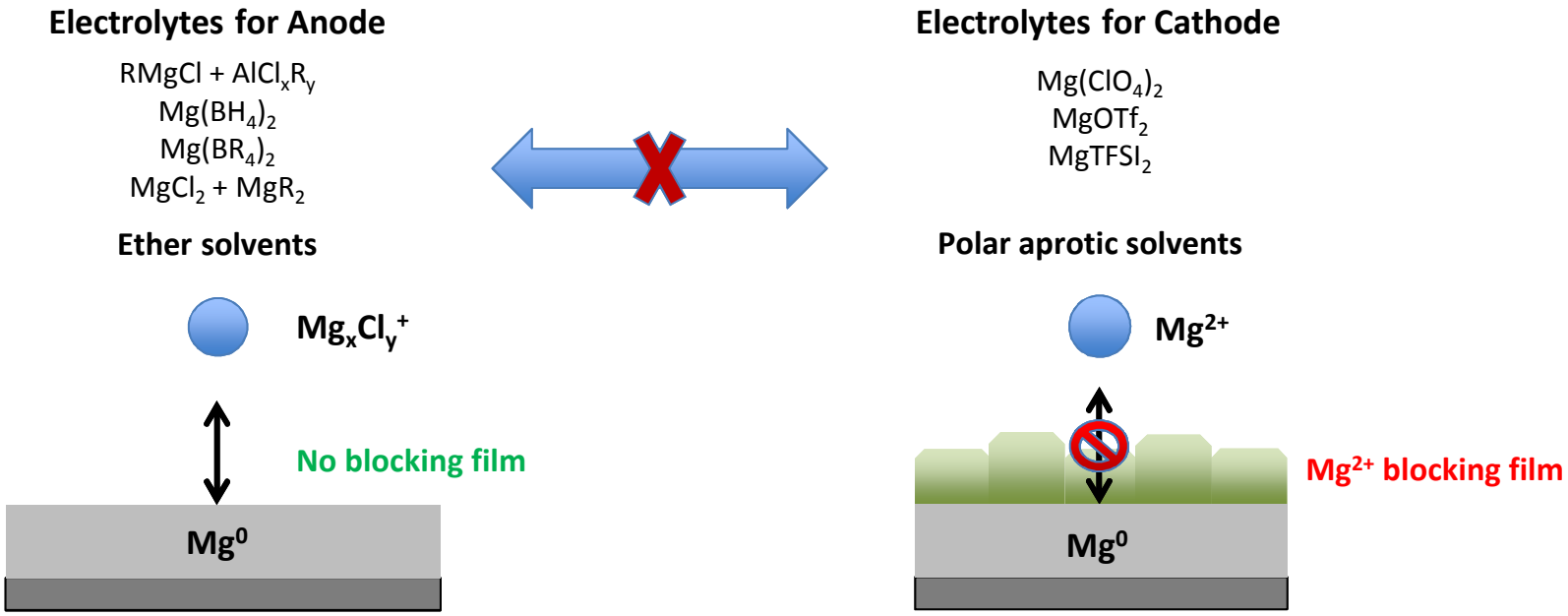


Anode	mAh/cm^3	V vs. SHE
LiC_6	780	-2.9
Mg	3830	-2.4

- **Metal anode drives improvement in overall energy density**

Magnesium Battery Confessions

- Electrolytes must support Mg deposition cycling at ≥ 99.8% coulombic efficiency (CE) and reasonable current densities (1-6 mA/cm^2)… while maintaining wide electrochemical window and compatibility with cathodes of reasonable voltage

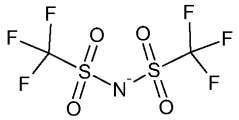


- Electrolyte development must marry the anode and cathode functionality
  - Reductive **and** oxidative stability
  - Non-corrosive toward cathode materials

Pushing the Limits of Conventional Electrolytes

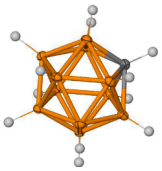
- Weakly coordinating anions
- Wide electrochemical windows
- Oxide-compatible
- Mg susceptible to passivation

TFSI



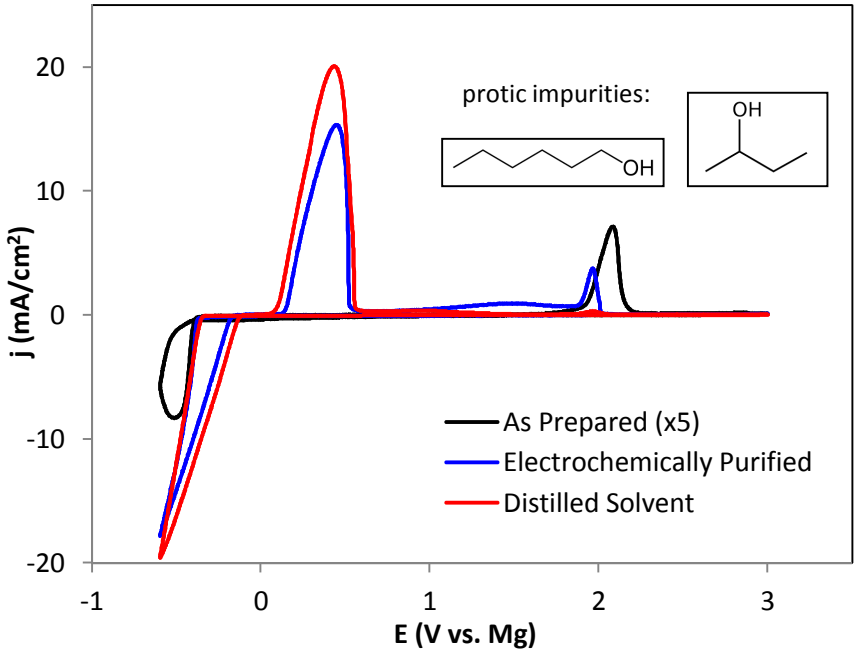
- Commercially available
- Soluble in glymes
- Susceptible to reductive decomposition

$CB_{11}H_{12}^-$

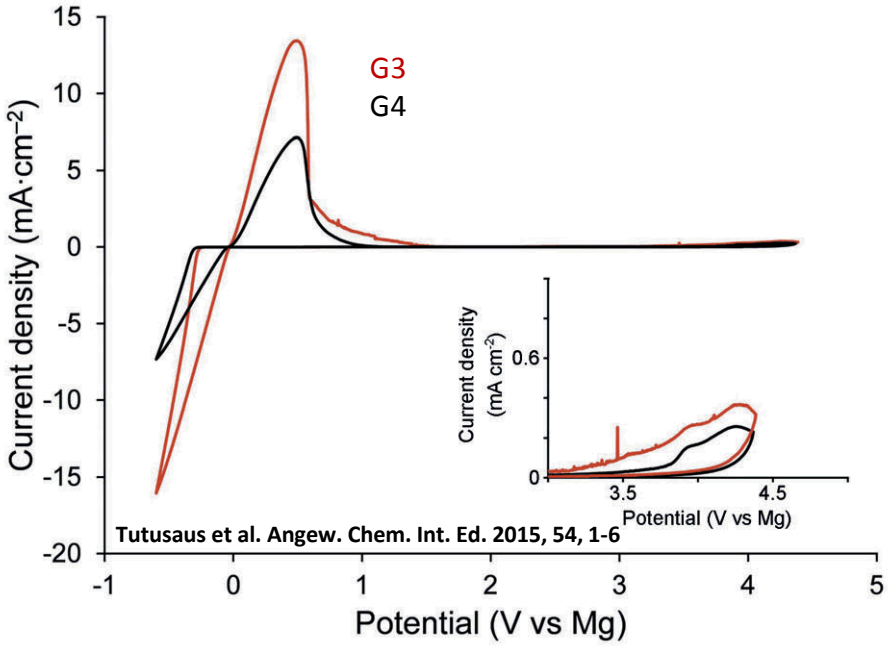


- Synthesized
- Soluble in long-chain glymes
- High reductive stability

$MgTFSI_2$ in diglyme – purity matters



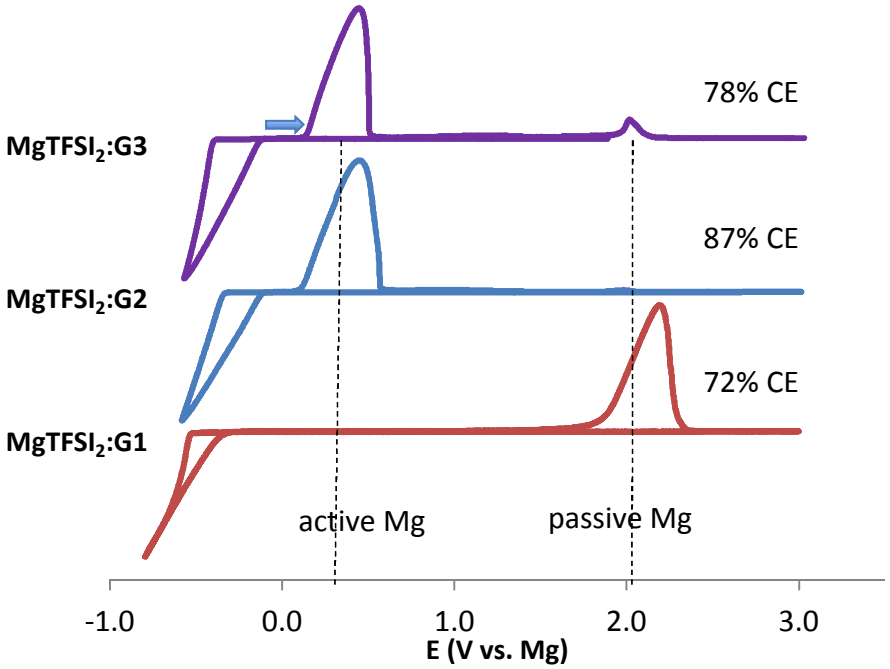
$MgCB_2$ in triglyme and tetraglyme - high stability



TFSI and Carborane Systems Afford Instructive Comparison

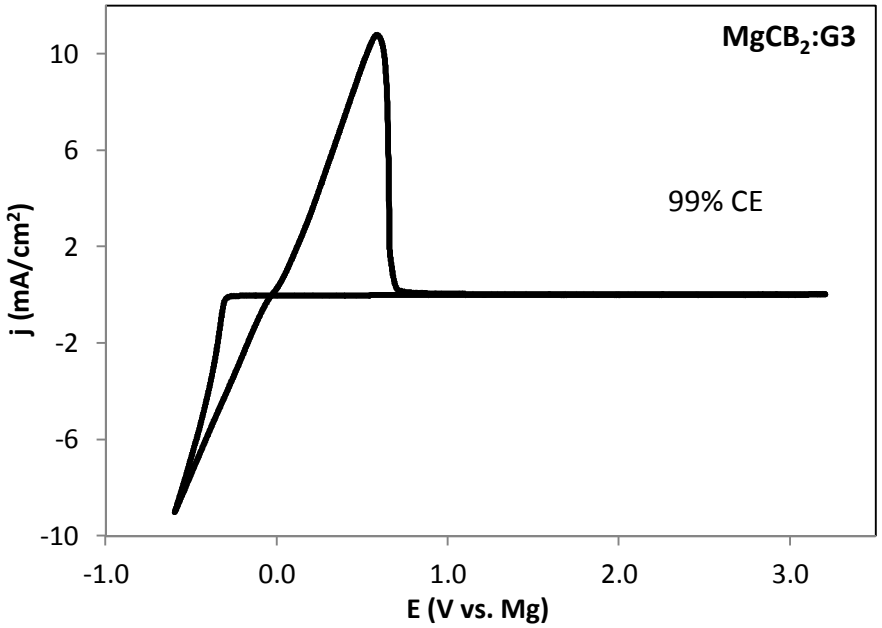
$MgTFSI_2$ system : rapid passivation, low CE

- **Regulated by impurities + anion**

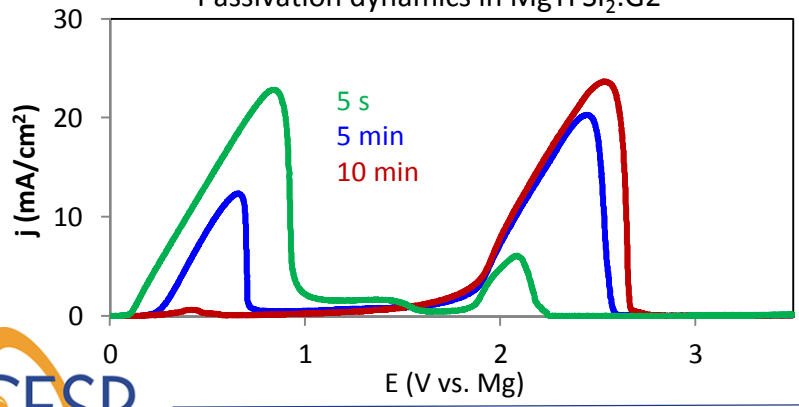


$MgCB_2$ system: slow passivation, high CE

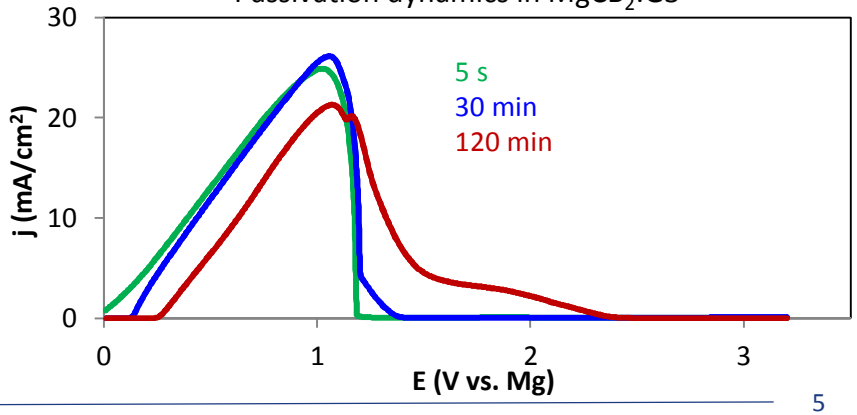
- **Regulated by impurities**



Passivation dynamics in $MgTFSI_2$:G2

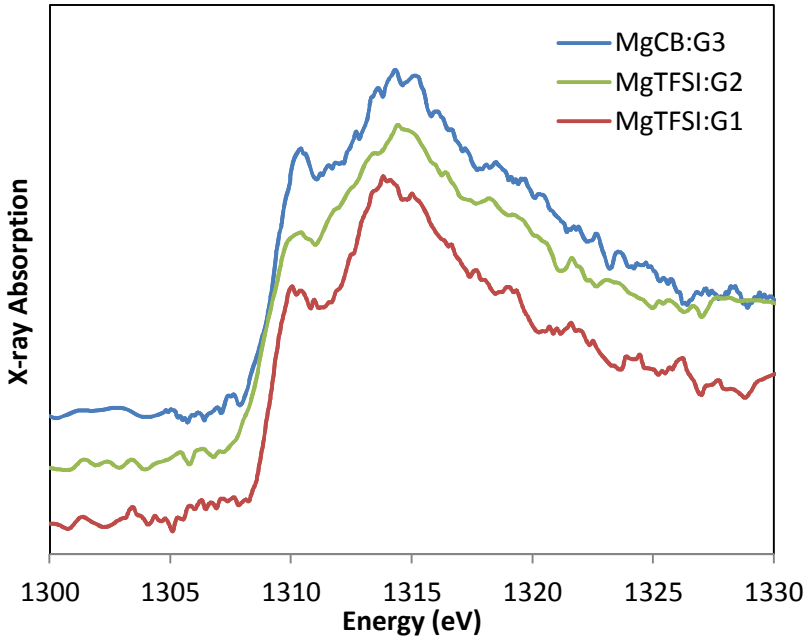


Passivation dynamics in $MgCB_2$:G3

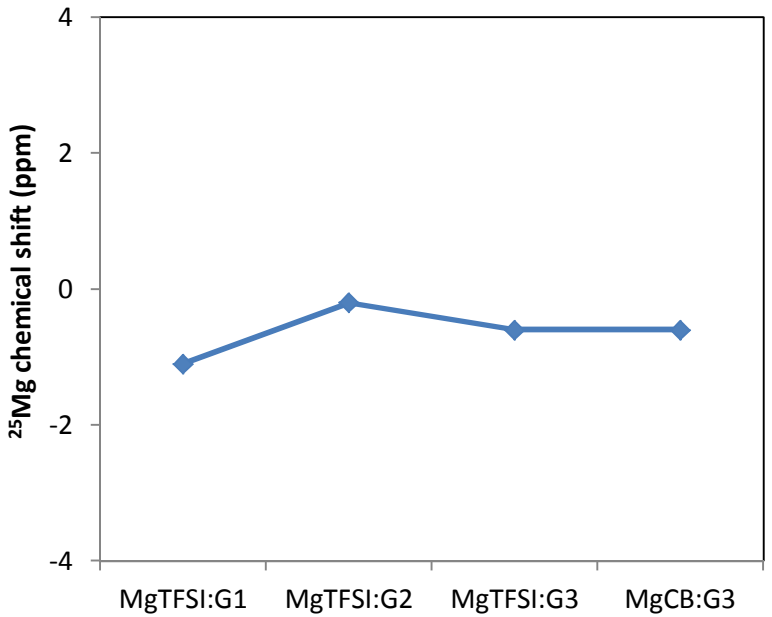


Average Bulk Speciation Doesn't Explain Differences

subtle variations in complex structure



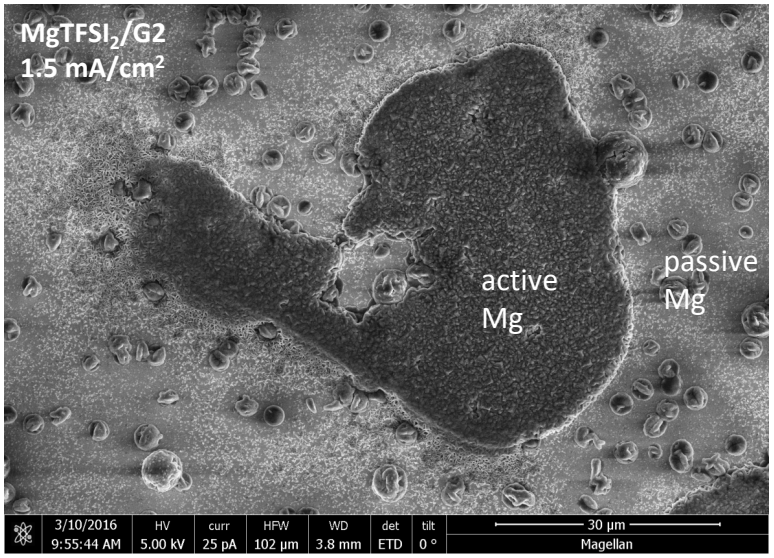
similar average Mg^{2+} environment

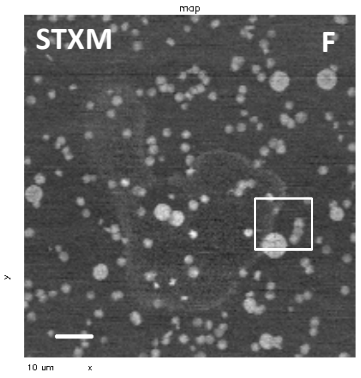


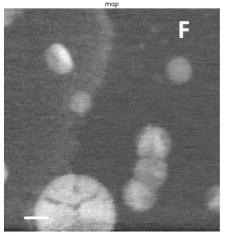
- Mg deposition reversibility and passivation are not strongly dependent on Mg^{2+} complexation in weakly-coordinating electrolytes
- Unique interfacial processes must explain differences in electrolyte behavior
- Interfacial stability appears to be the key determinant

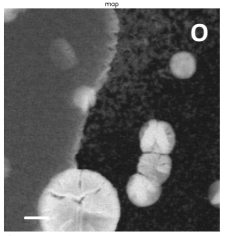
Interfacial Stability Controls Deposit Morphology

Unstable anions enforce low nucleation density and 3D growth









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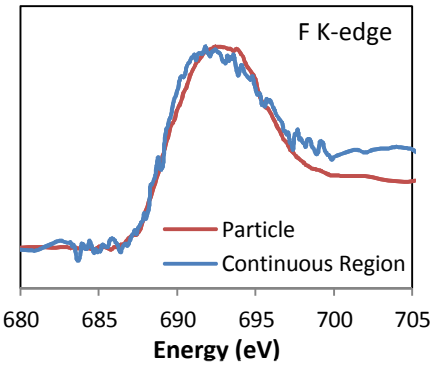
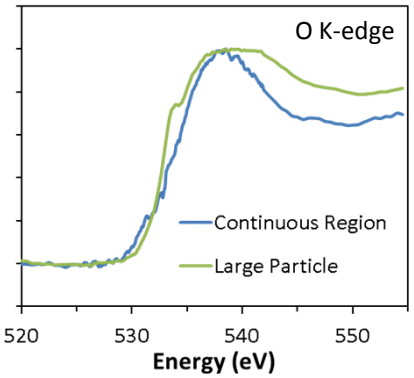
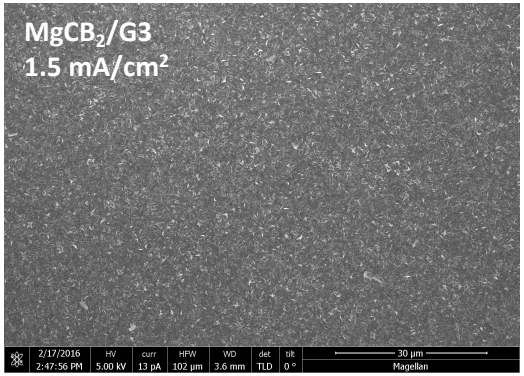
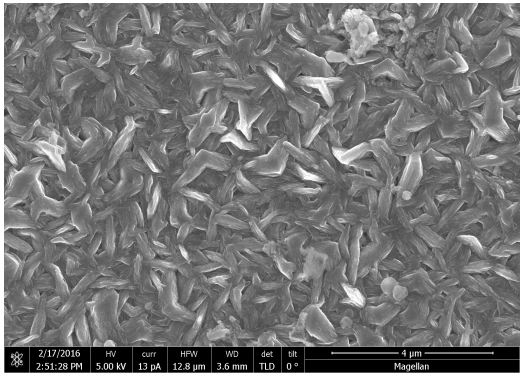
Passivated structures dominated by fluorine/oxygen signatures





Stable anions enable continuous, compact deposit structure



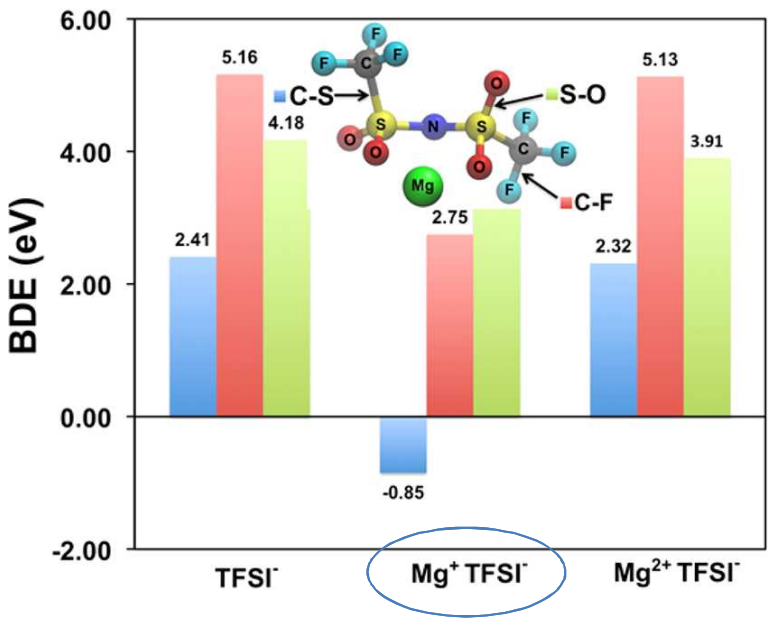


- Anion/byproduct adsorption directs non-uniform growth

Origins of Interfacial TFSI Instability

Computationally derived bond dissociation energies
(K. Persson group, LBNL)

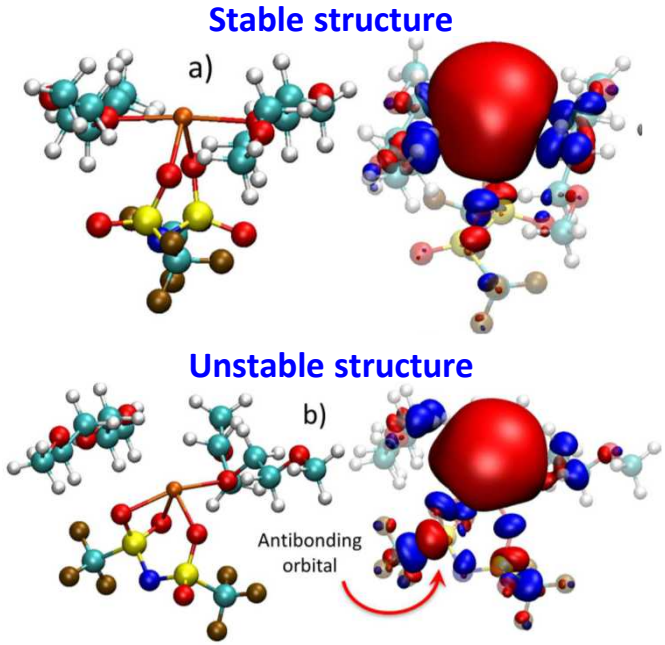
J. Am. Chem. Soc. 2015, 137, 3411−3420



C-S bond scission predicted during Mg^{2+} -> Mg^{+} reduction
If TFSI is coordinated to $Mg^{2+/+}$

DFT-derived complex structures
(D. Prendergast group, LBNL)

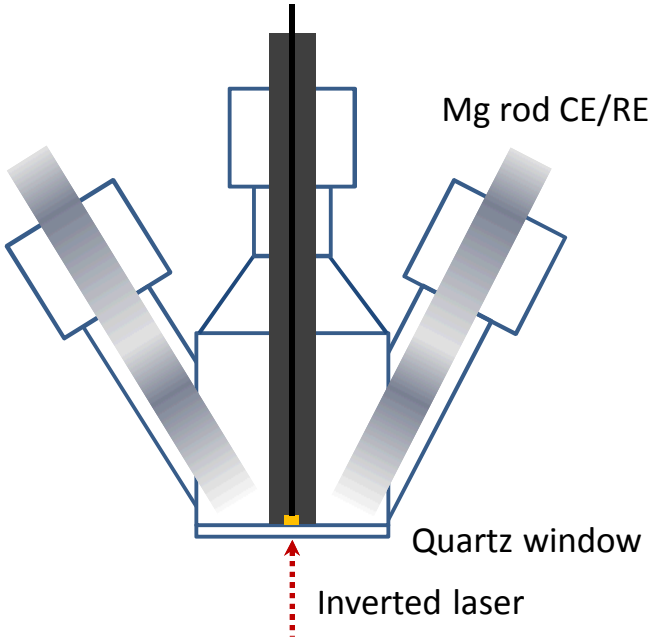
J. Phys. Chem. C, 2016, 120 , 3583–3594

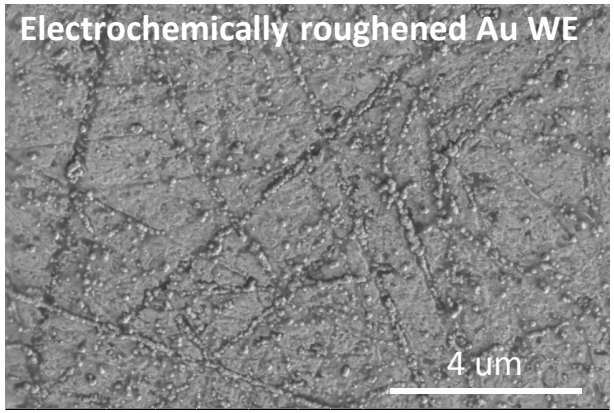


Geometry of G2:Mg^{2+}:$TFSI^{-}$ complex controls likelihood of C-S bond scission

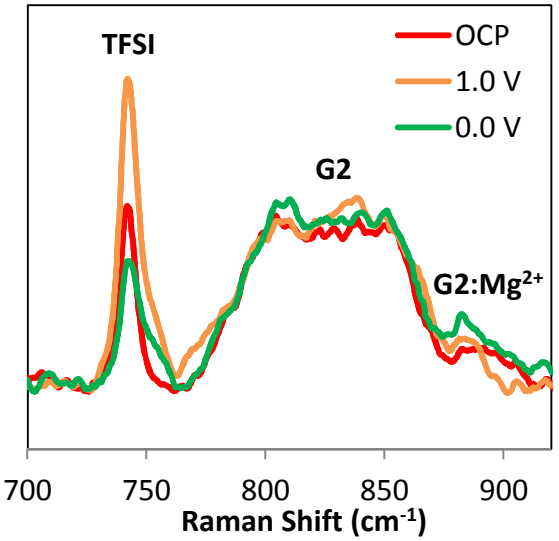
In Operando Characterization of TFSI Instability

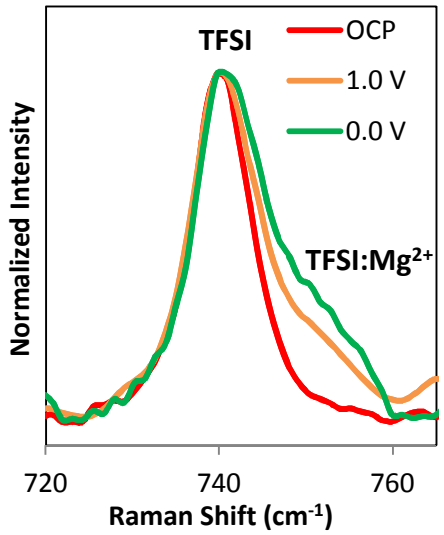
In situ Raman Spectroscopy



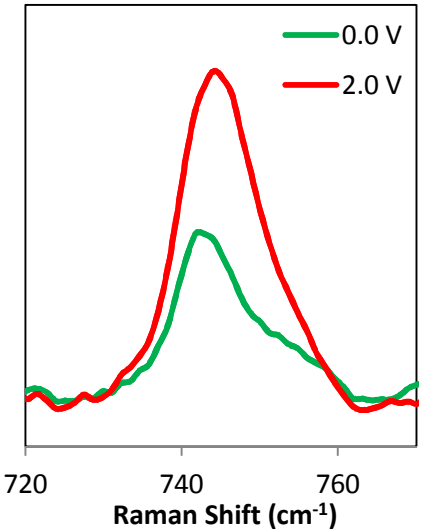


cathodic polarization induces changes in TFSI signature in $MgTFSI_2$:G2

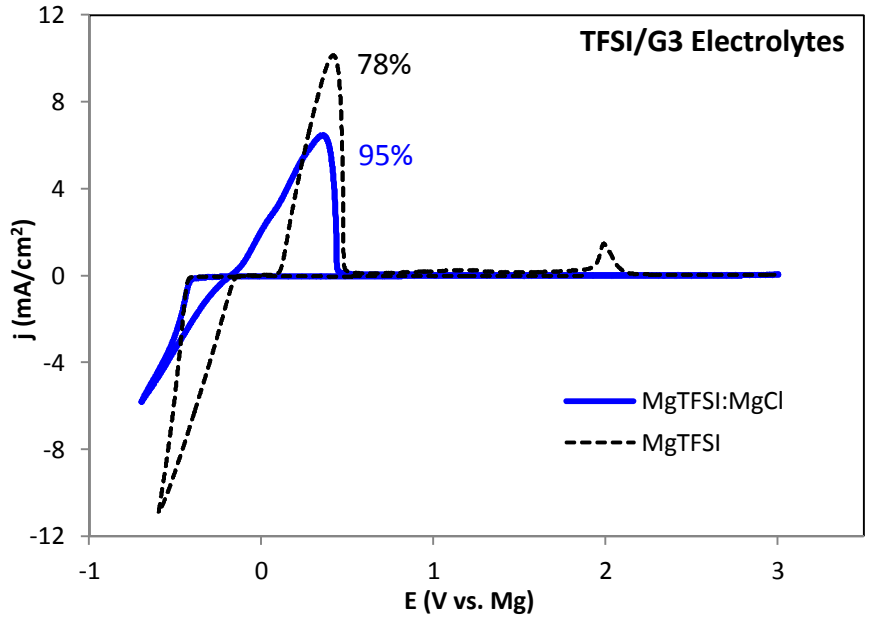


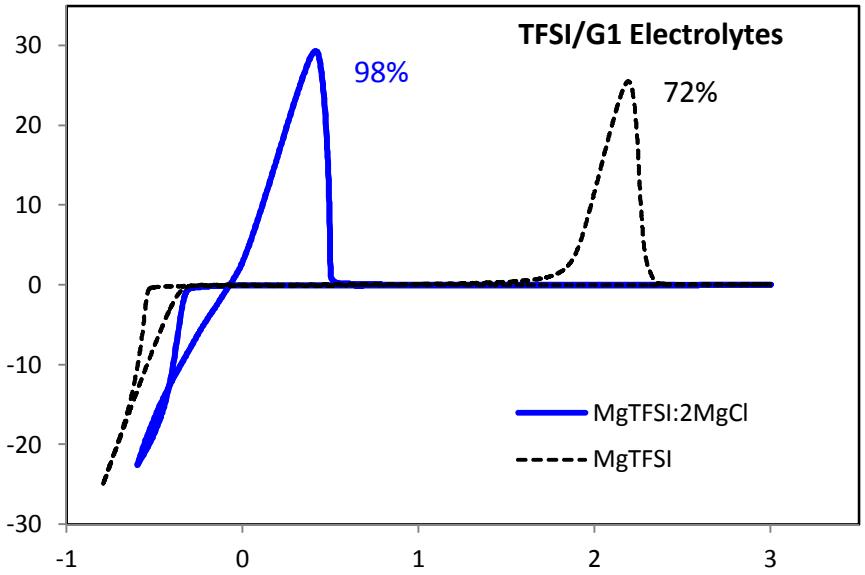


- Perturbation of TFSI coordination structure near Mg potentials
- Persistent changes in TFSI spectra signify formation of a surface layer

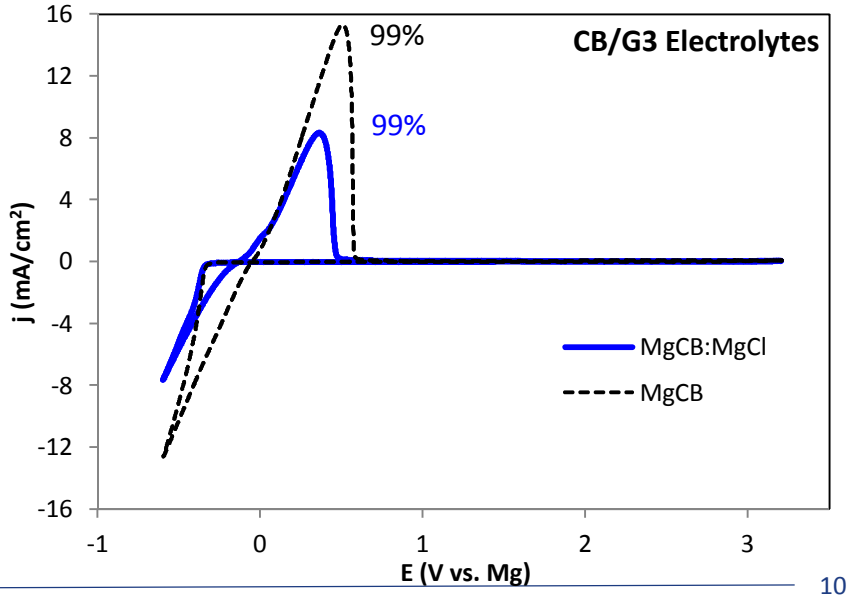


Chloride Mitigates Instability in TFSI Electrolytes





- Cl^- increases CE and reduced stripping overpotential in TFSI, but not in carborane system
  - Demonstrates the role of reducible vs. non-reducible anion species
- What role(s) does Cl^- play?
  - Unique complexation facilitates rapid Mg^{2+} delivery?
  - Exclusion of TFSI from Mg^{2+} coordination at interface?
  - Protection of fresh Mg^0?



Chloride Drives Complex Formation

Changes in Mg K-edge XANES are consistent with Cl-complex formation

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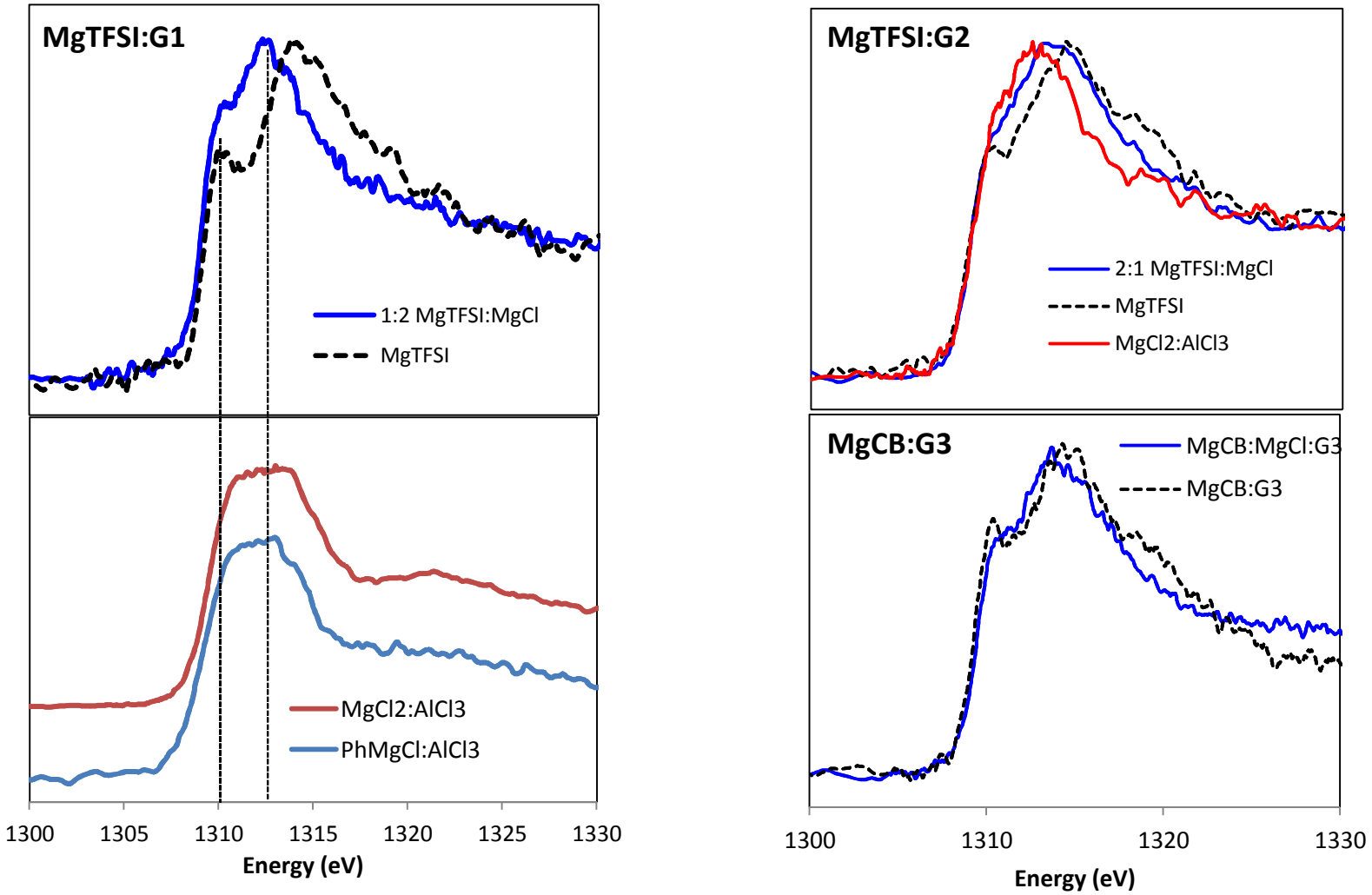
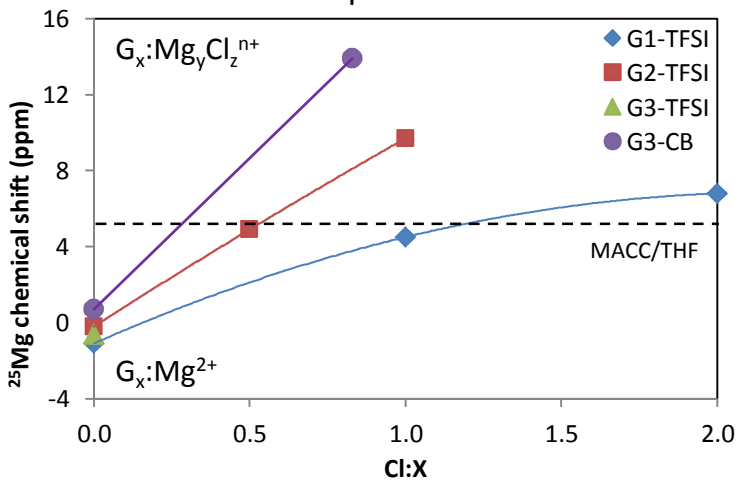
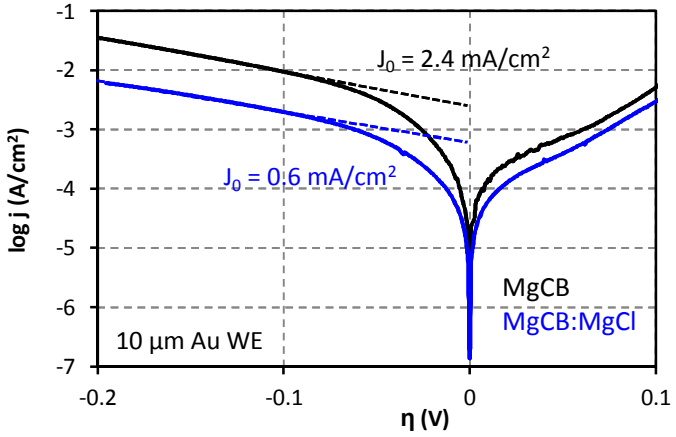


Electrochemical Kinetics Depend on Nature of Mg^{2+}-Complex

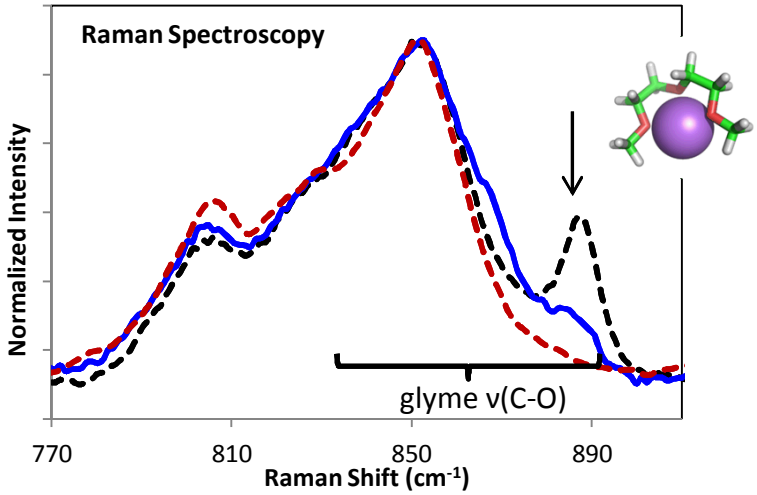
Cl-complexation induces a de-shielded ^{25}Mg NMR response



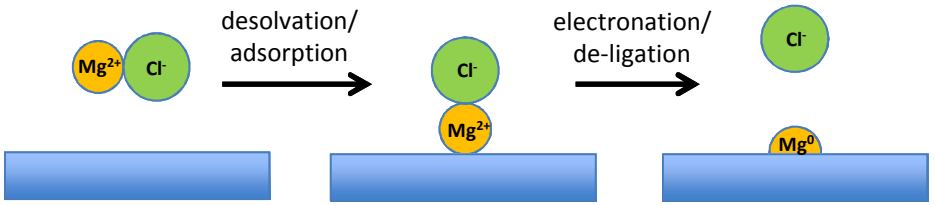
Cl-complexation down-regulates deposition kinetics



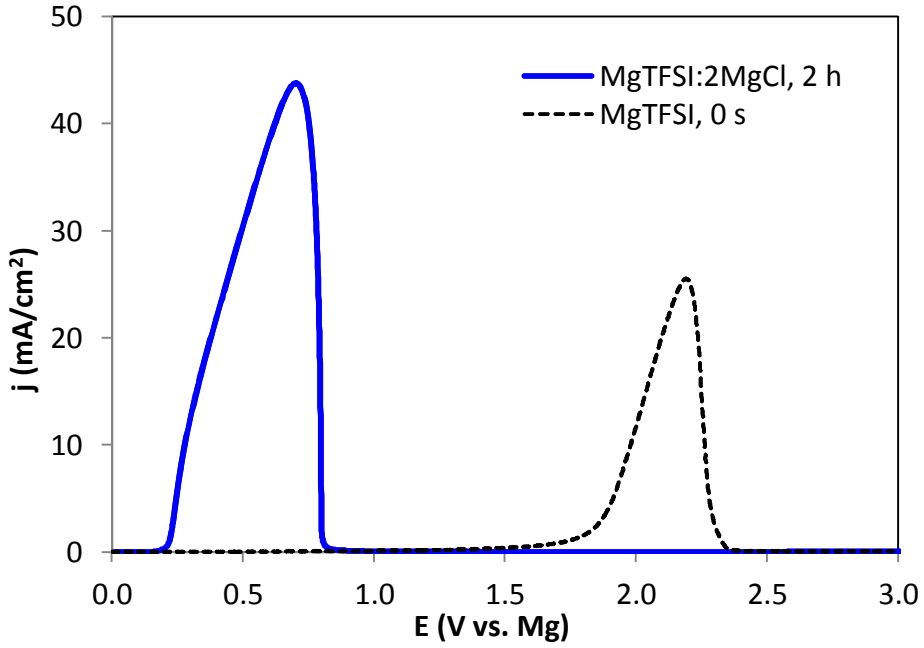
Cl-complexation reduces glyme:Mg^{2+} chelation

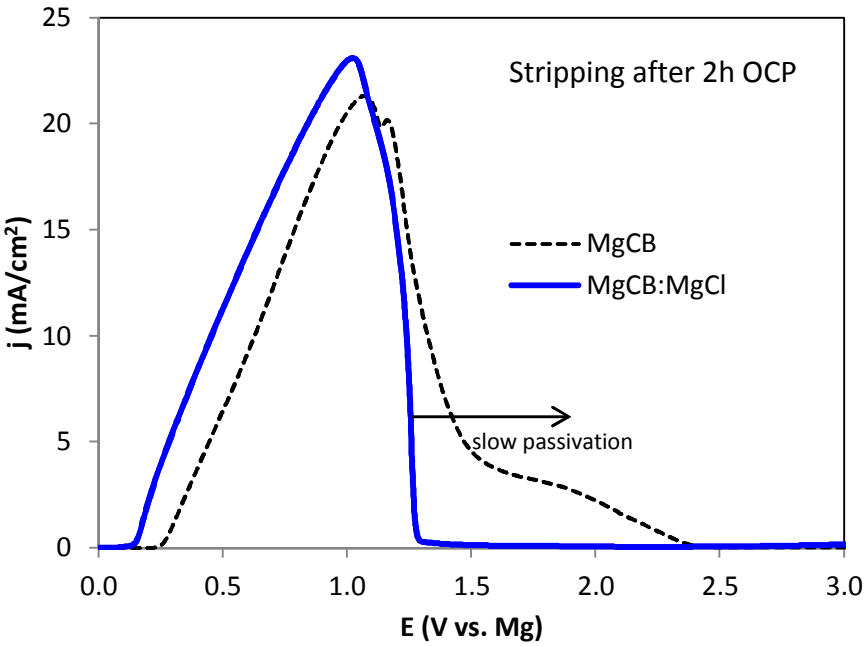


- Chloride-ligands expected to reduce solvation energy of Mg^{2+}
- Deposition kinetics are hindered with the addition of Cl^- in G2 and G3, but not in G1!
- Rate-limiting step depends on solvent and ligand interplay



Chloride Preserves the Active Mg^0 Interface





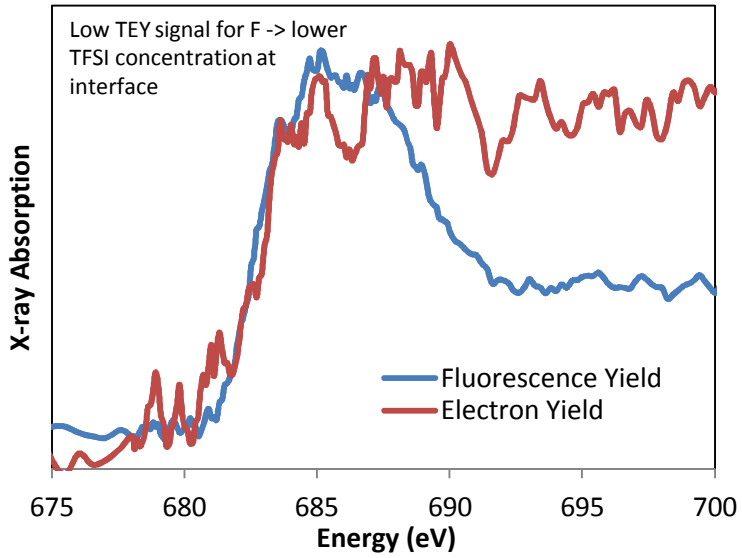
- Activity could be maintained by two routes
  - Cl-adsorption to Mg^0 prevents reaction with anion/impurities
  - Cl-mediated breakdown of rapidly formed passivating layer

- Presence pf persistent self-discharge suggests Mg^0 is not completely protected from reactants

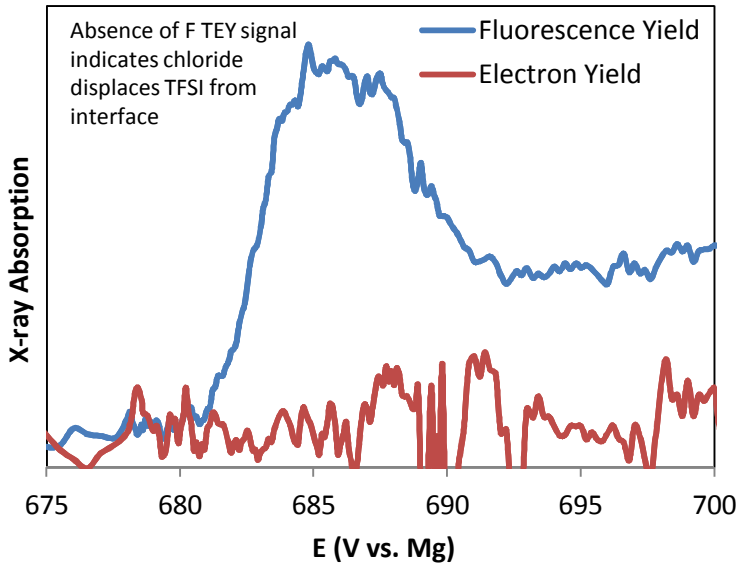
Chloride Alters Interfacial TFSI Population

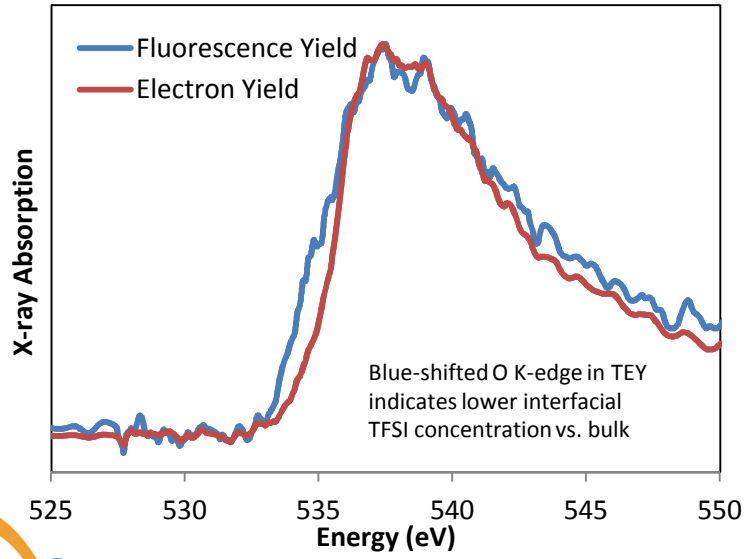
ALS BL 8.0.1

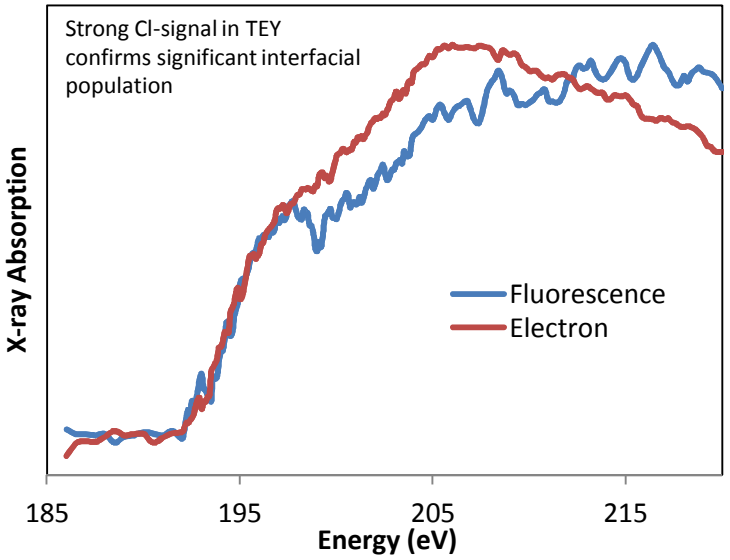
MgTFSI:G1



MgTFSI:2MgCl:G1







Take Home Messages

- $MgTFSI_2$ and $MgCB_2$ electrolytes provide fertile ground for understanding the links between bulk, interface, and activity
- These electrolyte systems are primarily limited by both impurities and, in the $MgTFSI_2$ case, instability of the anion species
- Reversibility of Mg deposition and Mg passivation are primarily determined by interfacial processes not necessarily reflective of the bulk speciation
- Chloride additives alter both the bulk complexation of Mg^{2+} and the interfacial behavior of reactive species

Acknowledgements

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A. David Kilcoyne
Jinghua Guo

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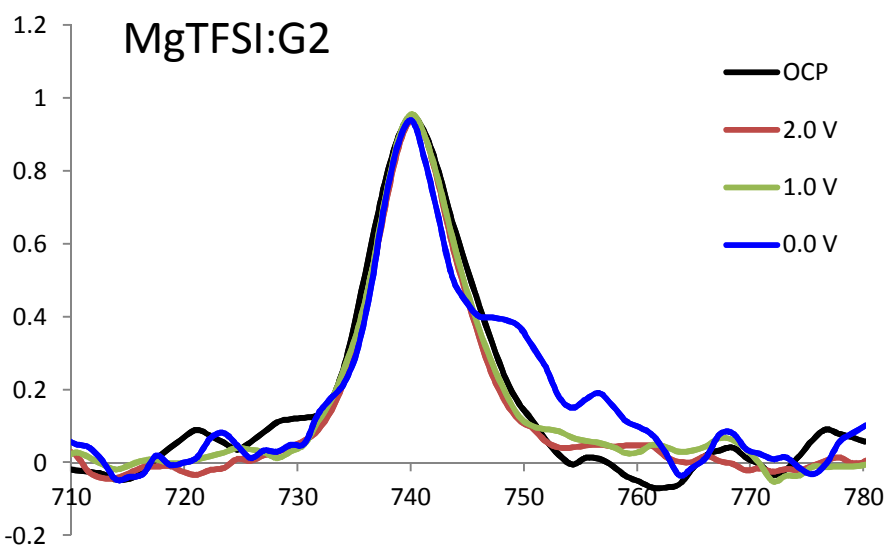
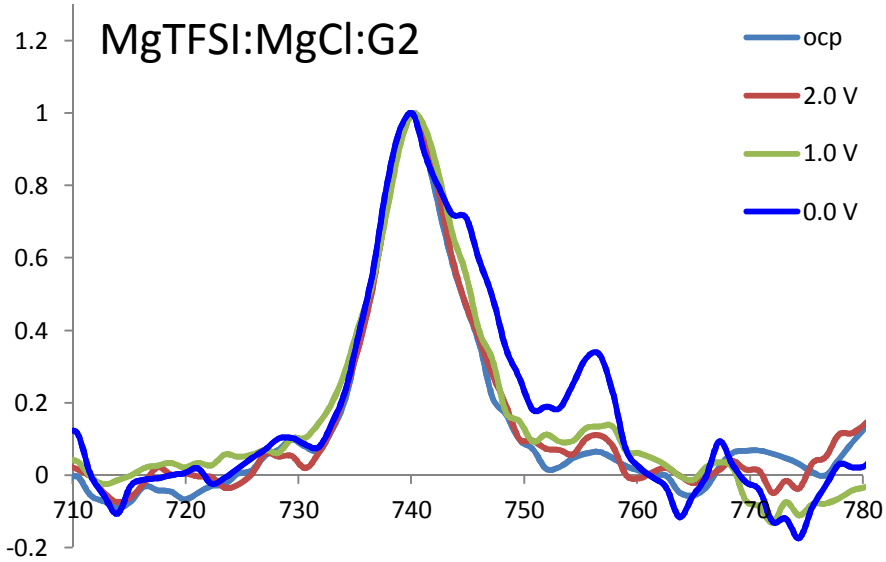
Chloride Modifies Interfacial Behavior

Raman comparison





- Chloride alters TFSI interactions at Mg^0 potentials