SAND2015-10420C

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Magnesium Metal Anode Interfaces and Performance in Chloride-Free Electrolytes

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Sandia National Laboratories

2015 Fall MRS Meeting

Supported as part of the Joint Center for Energy Storage Research, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science. Sandia is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Company, for the U.S. DOE's NNSA under contract DE-AC04-94AL85000.

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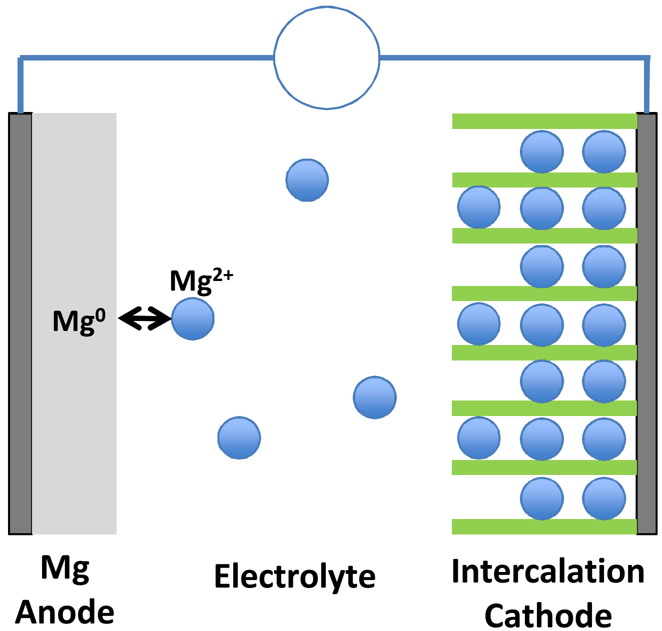
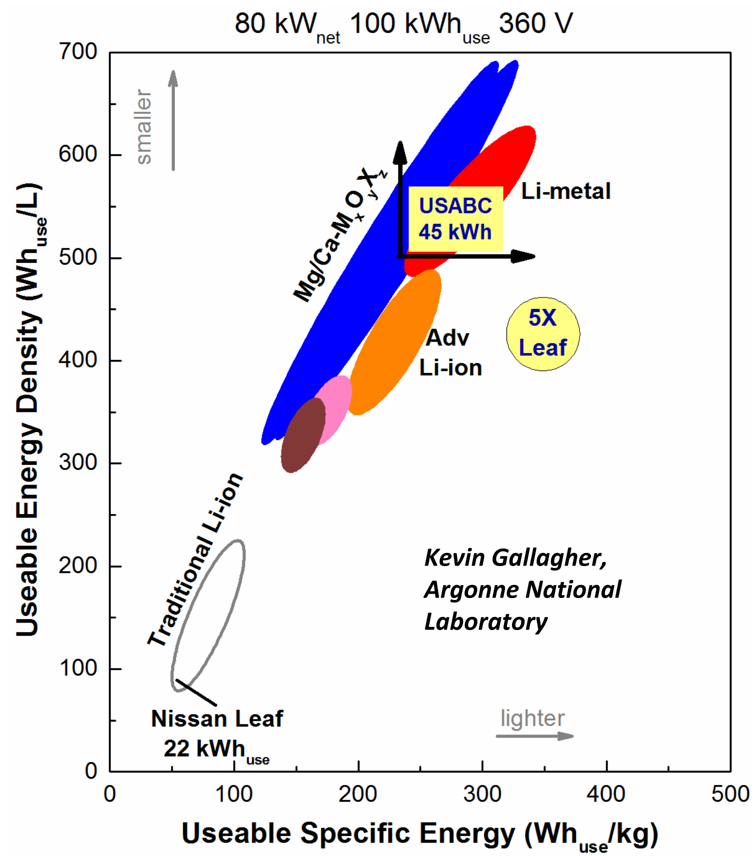
Mg Batteries as a Beyond Li-ion Energy Storage Technology



Anode	mAh/cm³	$/1000 kg metal[1]	V vs. SHE
LiC_6	780	$ 39600[2]	-2.9
Mg	3830	$ 2700	-2.4
Ca	2090	$ 3500	-2.9

Mg anode + high voltage cathode = success



- **Competitiveness of Mg batteries hinges on the utilization of a metal anode**

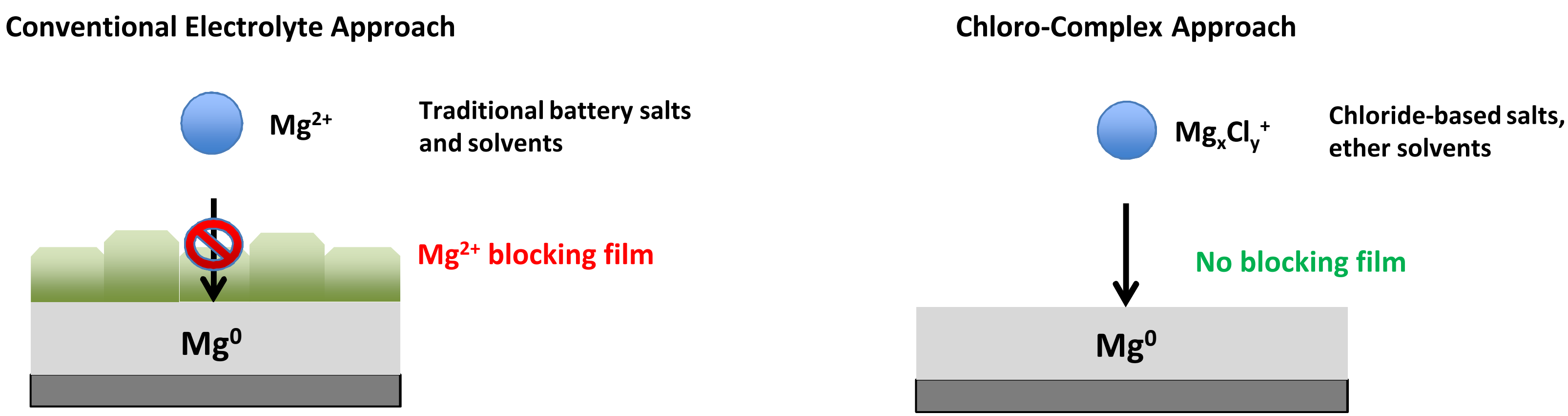
[1]www.alibaba.com
[2]Based on Li_2CO_3 price of $7500

Magnesium Anode Challenges

Technical challenge

- Develop and implement the design rules necessary to achieve Mg cycling at > 99.8% coulombic efficiency (CE) under relevant conditions

Electrolyte Approaches to Mg Electrodeposition

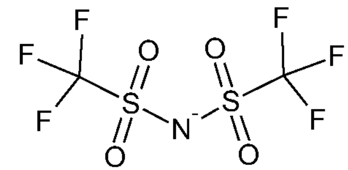


- **Mg electrodeposition has historically been accomplished using chloride-rich electrolytes**
  - Target oxide cathodes not expected to be stable in high-chloride environments
- **Push to develop Cl-free electrolytes for Mg electrodeposition**
  - Need to understand the role of alternative anions at the interface

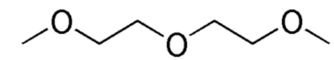
MgTFSI$_2$/glyme Electrolytes

- Weakly coordinating, wide electrochemical window
- First "conventional" electrolyte to show reasonable electrodeposition activity
- Sub-optimal electrochemical behavior
  - Low CE
  - Passivated dissolution

TFSI

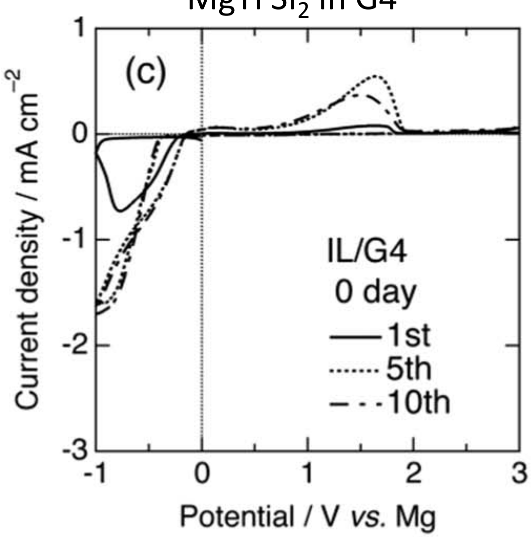


G2



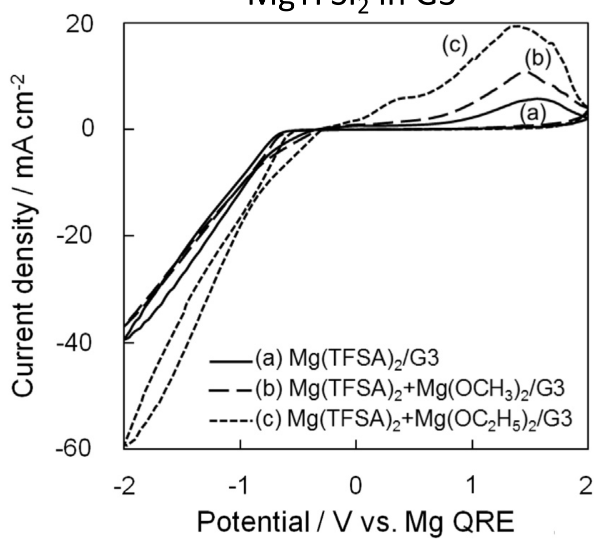
Cyclic voltammetry on Pt

MgTFSI$_2$ in G4



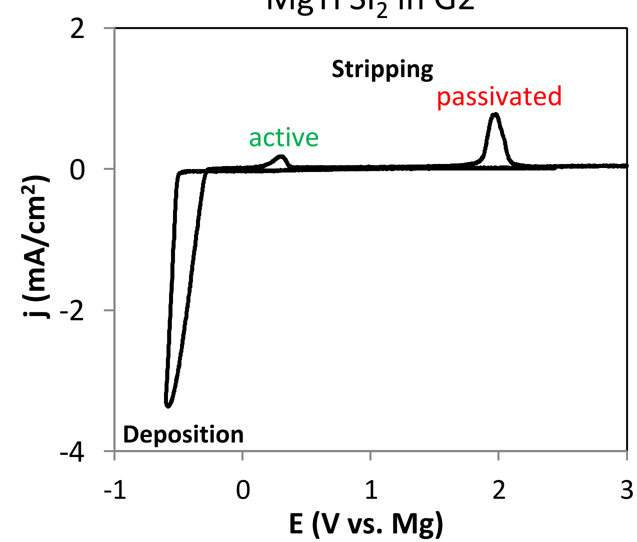
***JECS*, 162 (8) D389-D396 (2015)**

MgTFSI$_2$ in G3



JPS 278 (2015) 340

MgTFSI$_2$ in G2



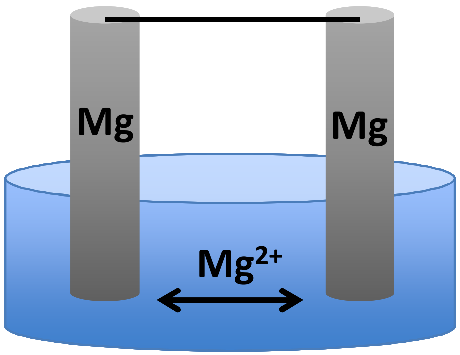
This Work

What feature(s) of these electrolytes impose low CE and passivation?

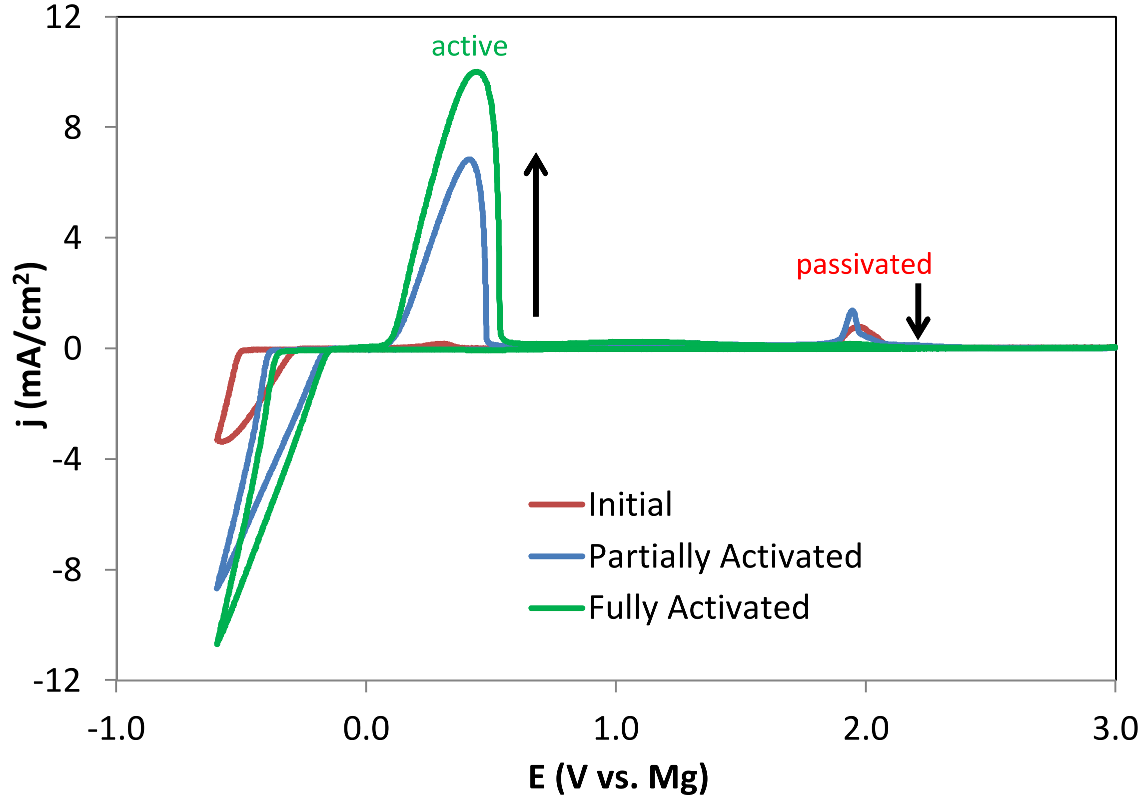
Electrochemical cycling enhances activity

- Bulk electrolysis improves subsequent electrochemical behavior
  - Increased CE from < 50% to over 80%
  - Suppression of passive state
- Something in the as-prepared electrolyte restricts CE and imposes passivation

2-electrode electrolysis



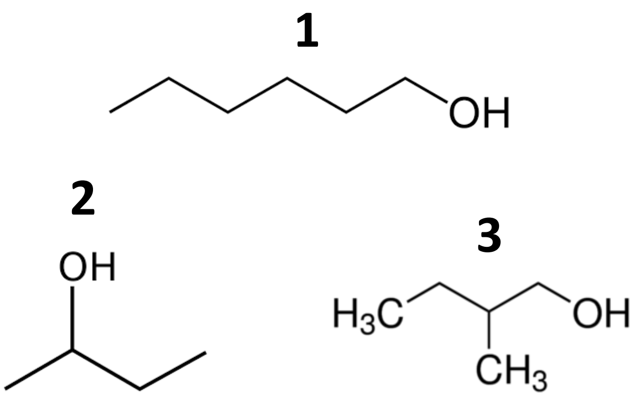
3-electrode characterization on clean Pt

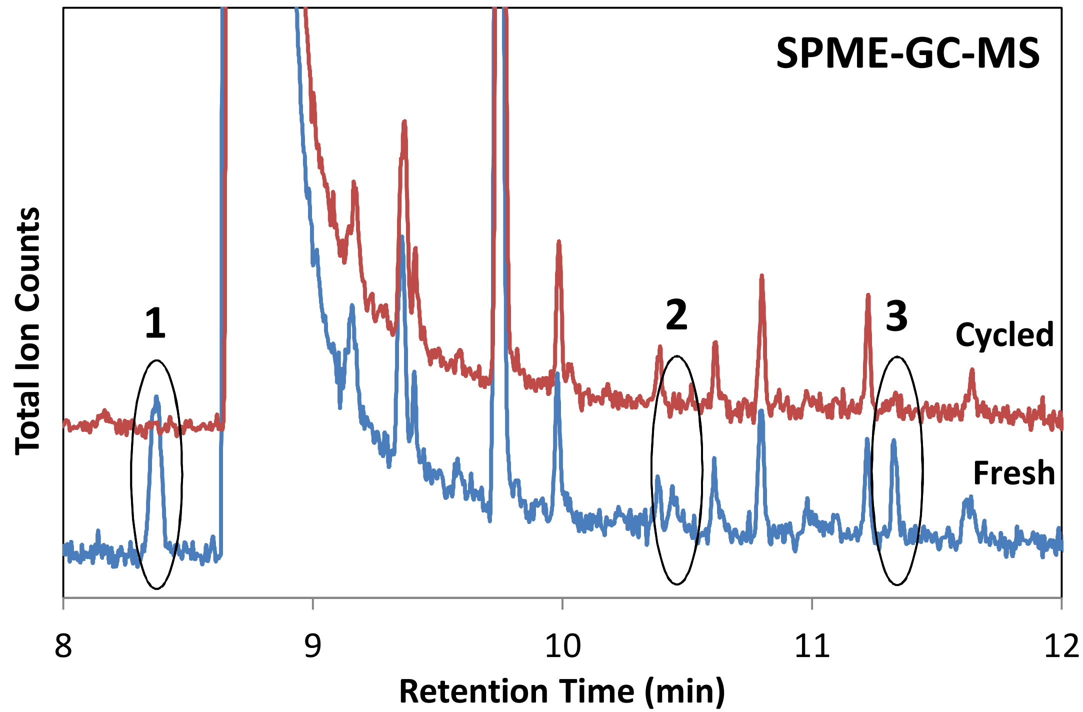


➢ **Behavior suggests that passivating impurities are being removed**

Cycling removes organic impurities

Cycling breaks down residual protic molecules:

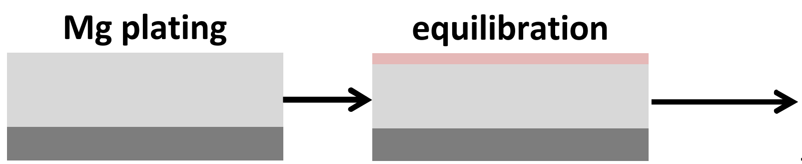


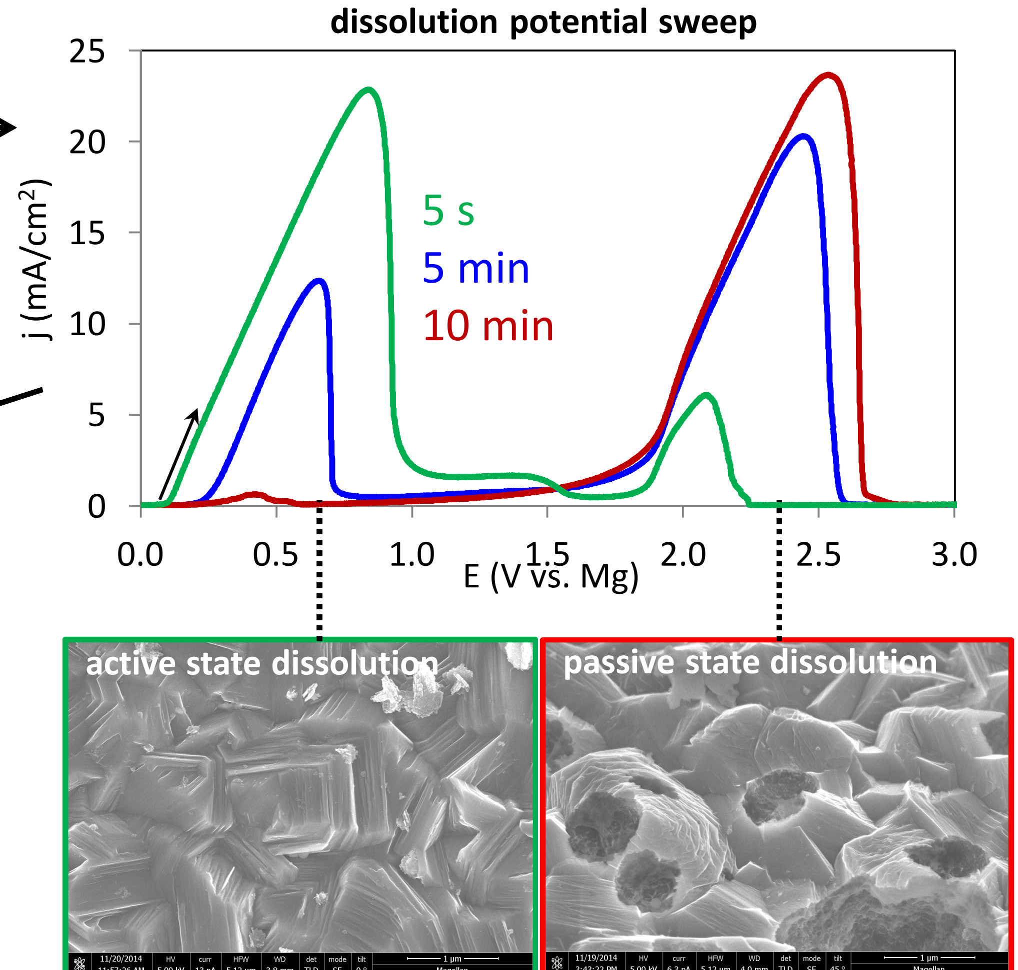


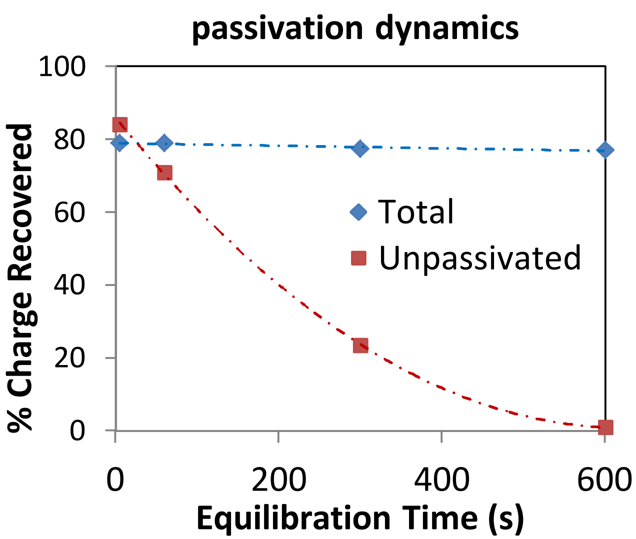
- Methods of attaining improved electrolyte performance without cycling
  - Aggressive distillation of the glyme solvent
  - Addition of trace amounts of reducing agents ($Mg(BH_4)_2$, R_2Mg)
- **Solvent-borne contaminants impose the activation requirement**

Purified $MgTFSI_2$/G2 activity is still limited

- CE limited to < 95%
- Mg^0 passivates over time

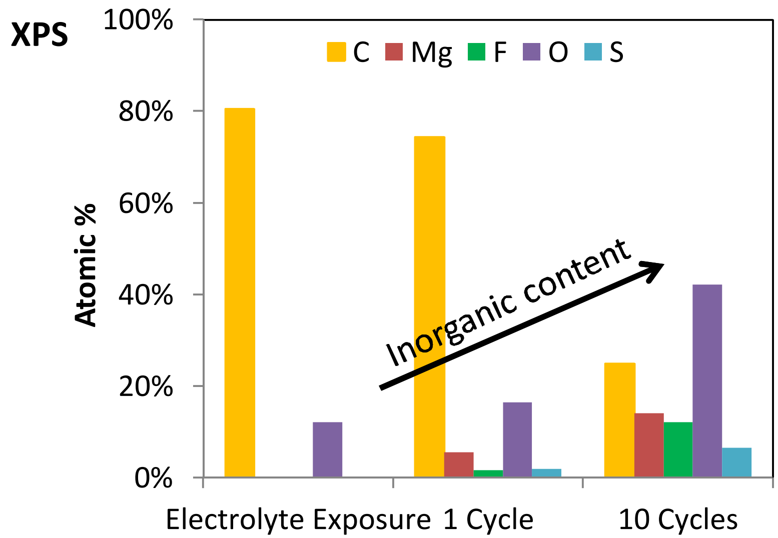


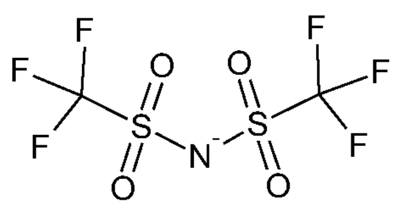




Formation of anion-derived species on electrode

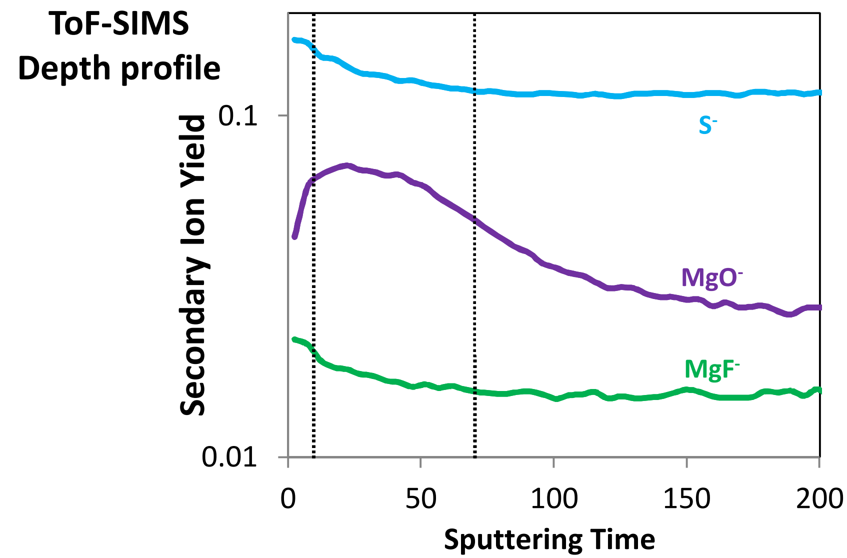
- ➢ **Byproduct buildup on current collector during cycling**



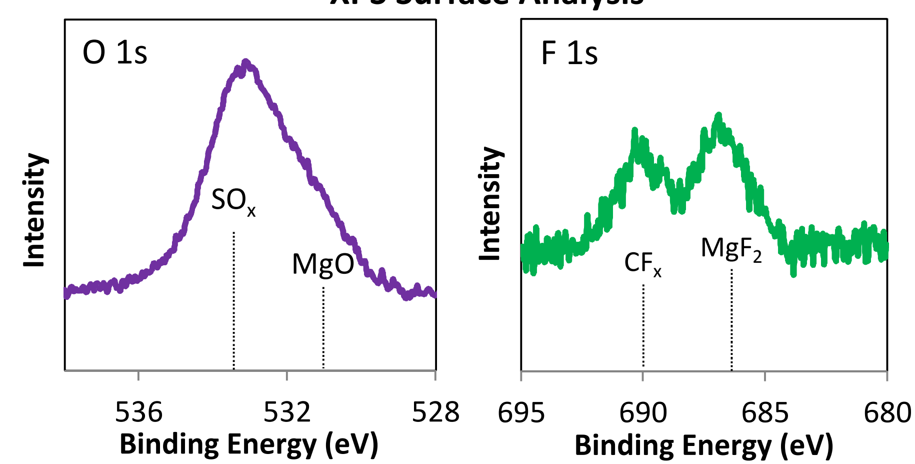


- ➢ **Signs point to decomposition of TFSI**

- ➢ **Surface film formation on thick Mg deposits**



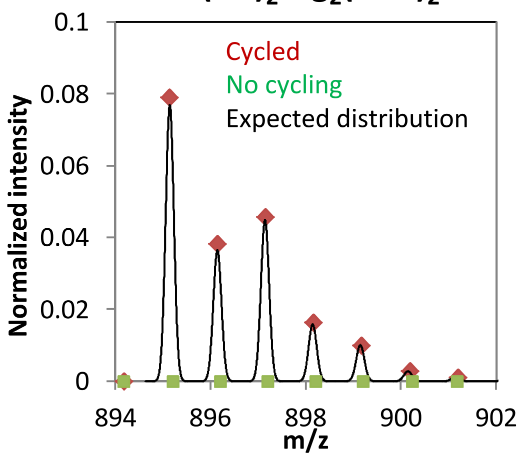
XPS Surface Analysis



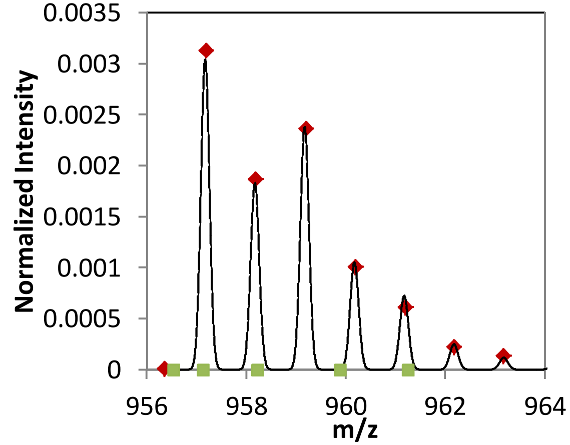
Formation of anion-derived species in solution

ESI-MS reveals creation of new species with cycling

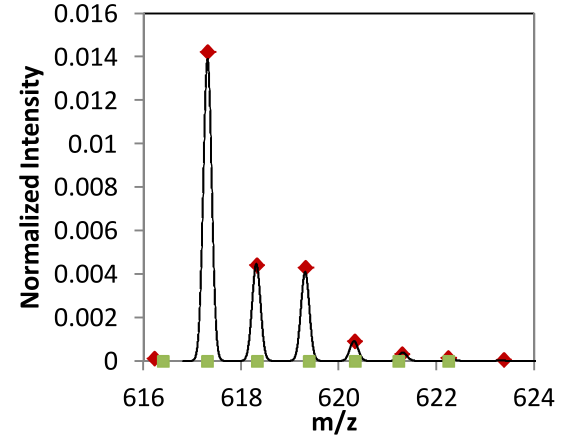
895 = $(G2)_2Mg_2(TFSI)_2F^+$



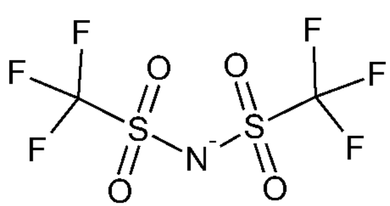
957 = $(G2)_2Mg_3(TFSI)_2F_3^+$



617 = $(G2)Mg(TFSI)(CH_3ON)^+$

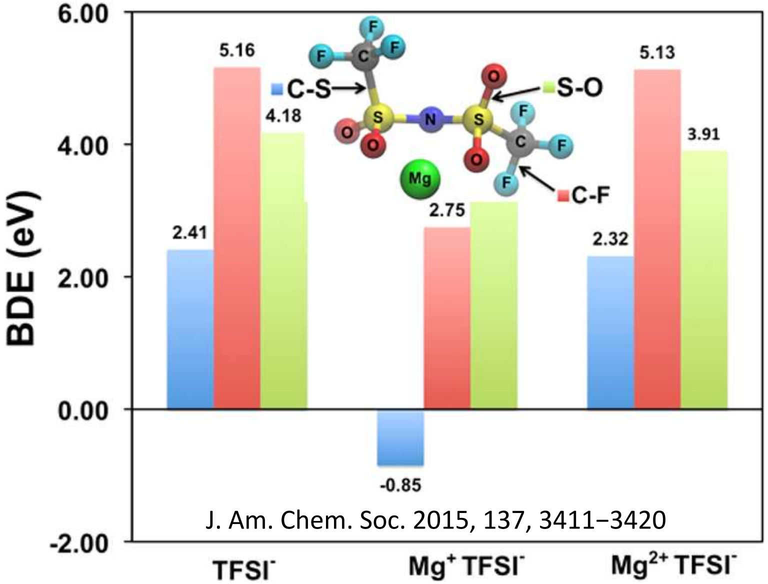


- Fluorine and nitrogen are liberated from $TFSI^-$
- **Data suggests that TFSI instability limits electrolyte activity**



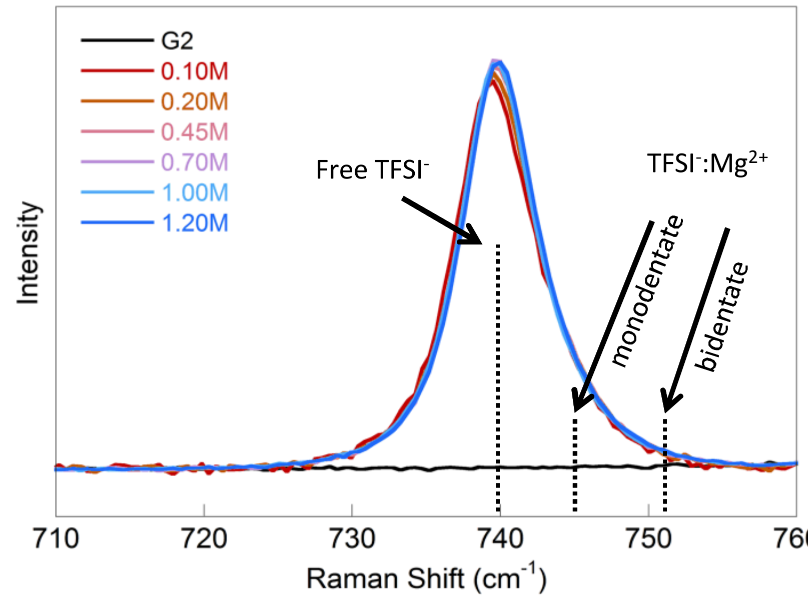
TFSI instability is promoted by Mg^{2+} coordination

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



C-S bond scission predicted during Mg^{2+} -> Mg^{+} reduction
Proposed mechanism requires TFSI-Mg^{2+} coordination

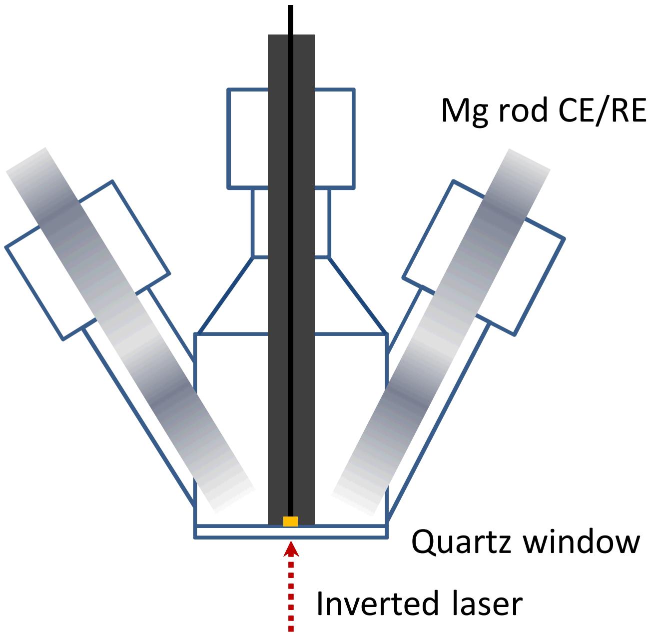
Raman spectroscopy of TFSI electrolytes is sensitive to coordination
(W. Henderson, PNNL)

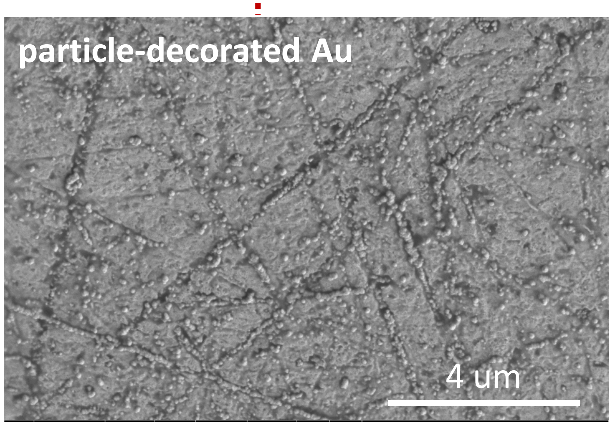


$MgTFSI_2$/G2 solutions show little ion pairing!

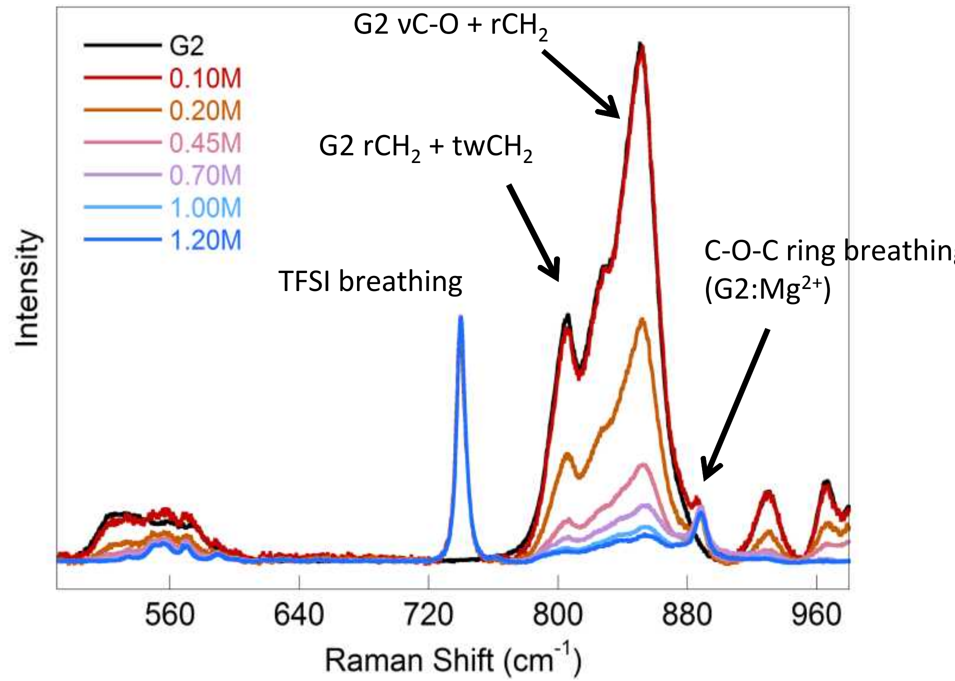
➢ **Interfacial speciation may differ from bulk speciation**

In Situ Raman Spectroscopy



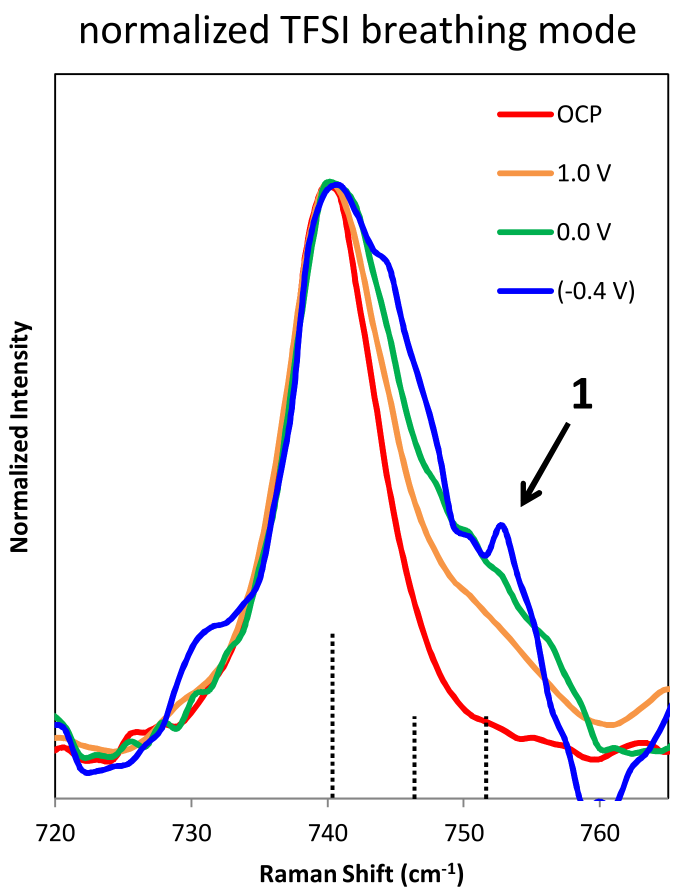


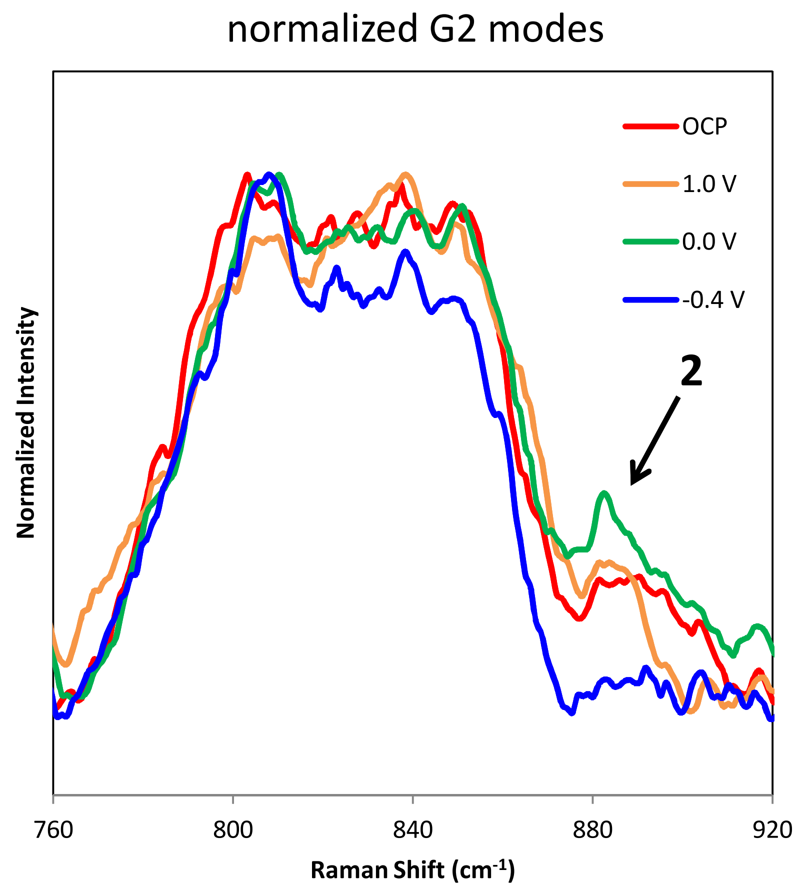
Raman spectra provide information on Mg^{2+} speciation



➢ **Goal: detection of Mg^{2+} environment changes at the anode interface**

Speciation changes during cathodic polarization





1. Increasing 752 cm^{-1} shoulder at 1.0 V and below - **enhanced interaction between $TFSI^-$ and Mg^{2+}**
2. Suppression of 885 cm^{-1} peak below 0.0 V - **reduced interaction between G2 and Mg^{2+}**

➢ **TFSI-Mg coordination at interface during Mg deposition promotes TFSI instability**

Take Home Messages

- Impurity management is critical to enabling efficient Mg electrodeposition/dissolution in conventional electrolytes
- Purified $MgTFSI_2$/glyme electrolytes still suffer from limited coulombic efficiency and rapid passivation due to TFSI instability
- In operando detection of speciation changes at the anode interface are consistent with increased coordination of $TFSI^-$ and Mg^{2+} at Mg^0 potentials
- Experimental findings are consistent with computationally derived coordination-induced instability mechanism

Acknowledgements

Sandia National Laboratories

Michael Brumbach
Richard Grant
Curtis Mowry
James Ohlhausen
Adam Pimentel

Argonne NATIONAL LABORATORY

<u>Electrochemical Discovery Laboratory</u>
Nenad Markovic
Justin Connell
Bostjan Genorio
Pietro Lopes
Dusan Strmcnik

BERKELEY LAB

Kristin Persson
Xiaohui Lu
Nav Nidhi Rajput

Pacific Northwest NATIONAL LABORATORY

Wesley Henderson