

Magnesium Battery Anode Processes in Conventional Electrolytes

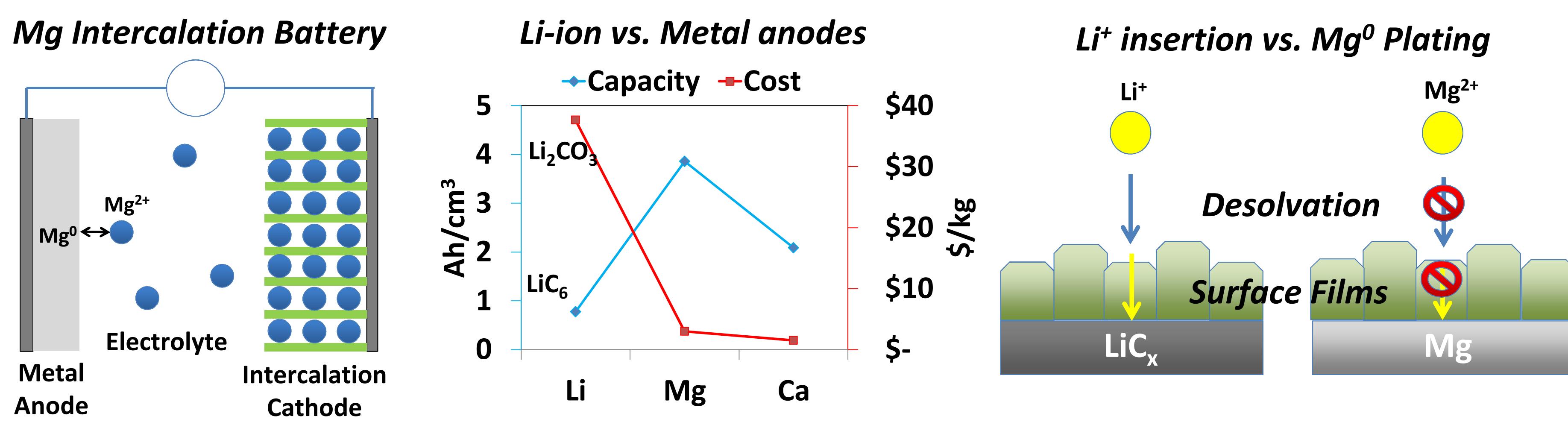


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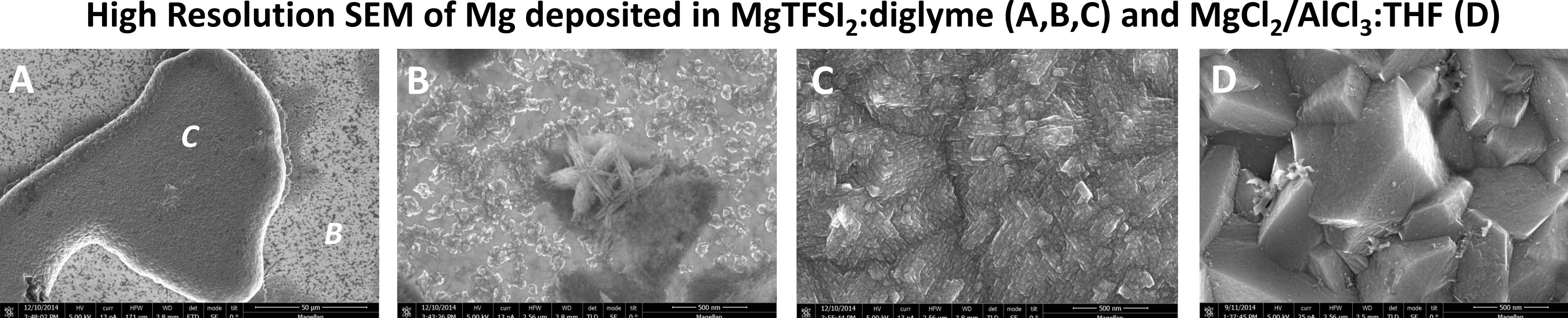
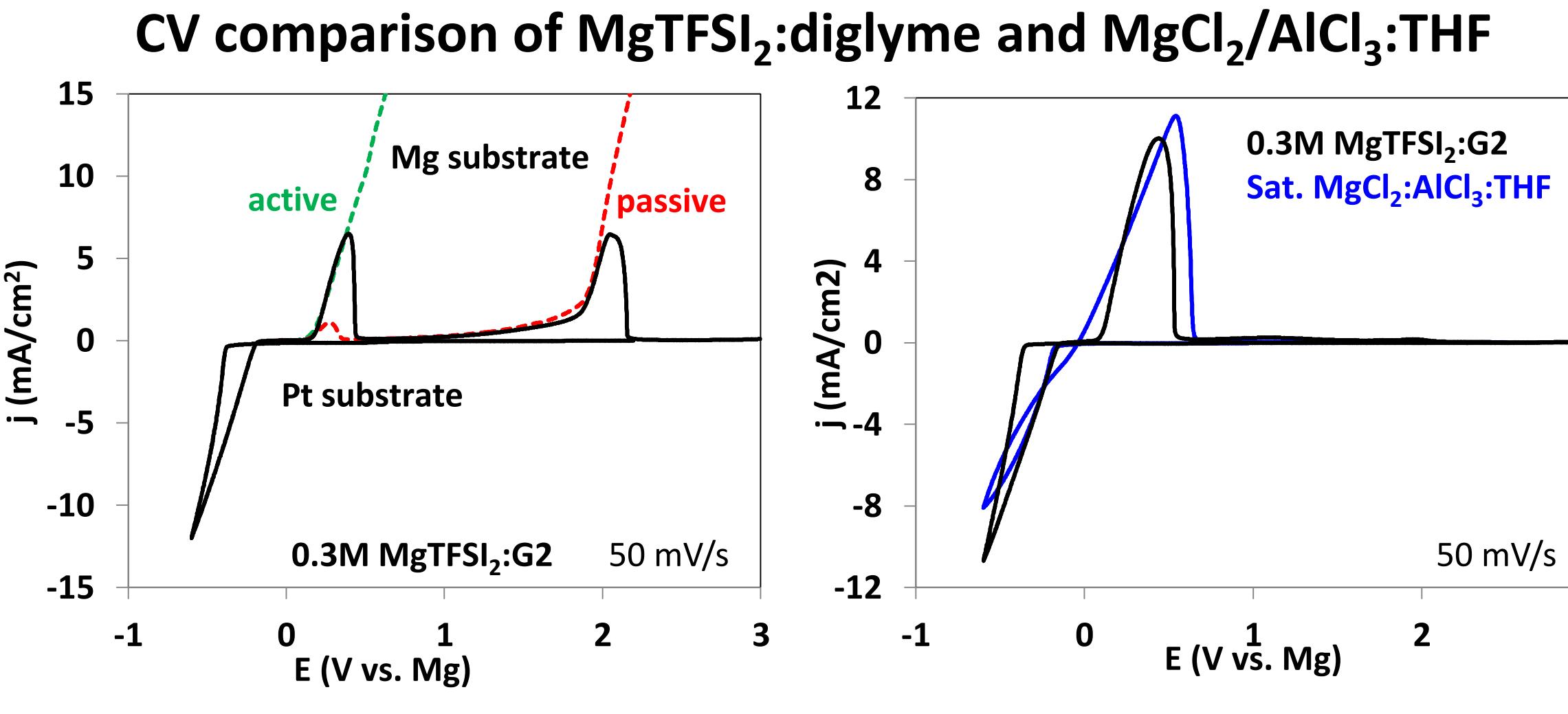


Background and Motivation

- Rechargeable batteries utilizing divalent metal anodes (Mg, Ca) provide pathways to increase energy storage density and decrease cost vs. Li-ion analogs.
- Most electrolytes enabling reversible Mg plating and dissolution contain high Cl^- or reducing agent concentrations, inducing corrosion at the cathode and current collector.
- Historically, “conventional” Mg salt electrolytes (PF_6^- , BF_4^- , SO_3CF_3^- , $\text{N}(\text{SO}_2\text{CF}_3)_2$, etc.) were regarded as incapable of supporting Mg plating due to passive film formation.^{1,2}
 - Recent results show that this assumption is not true.³
- The goal of this work is to establish the origins of activity and inactivity in electrolytes based on inorganic ligands system to understand the rules of design for improved Mg-battery electrolytes.

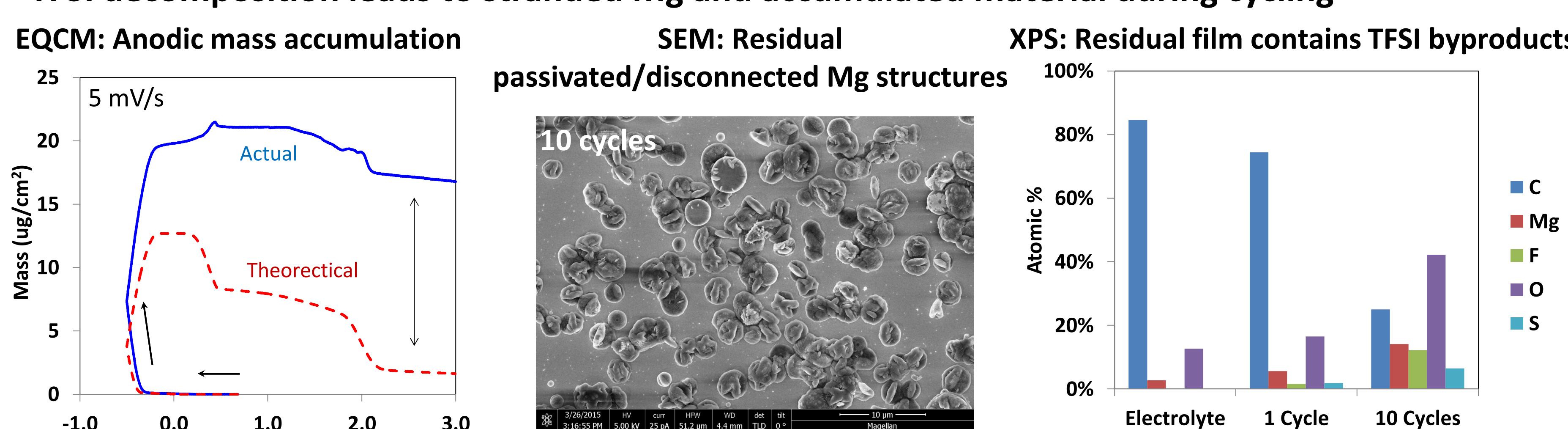


Mg⁰ Plating Without a Strongly Coordinating Anion



Parasitic Loss and Passivation in MgTFSI₂:G2

- Two problems: low coulombic efficiency (<90%) and Mg passivation over time; are they related?
- Open Circuit Equilibration Experiment: Mg on Pt → Film formation → OCP → LSV
- Trend in passivation does not match coulombic efficiency
- Efficiency loss and passivation are decoupled processes
- TFSI decomposition leads to stranded Mg and accumulated material during cycling



- Aurbach, et al. Journal of Electroanalytical Chemistry 466 (1999) 203–217.
- Lossius, et al. Electrochimica Acta 41 (1996) 445–447.
- Ha, et al. ACS Appl. Mater. Interfaces 6 (2014) 4063–4073.

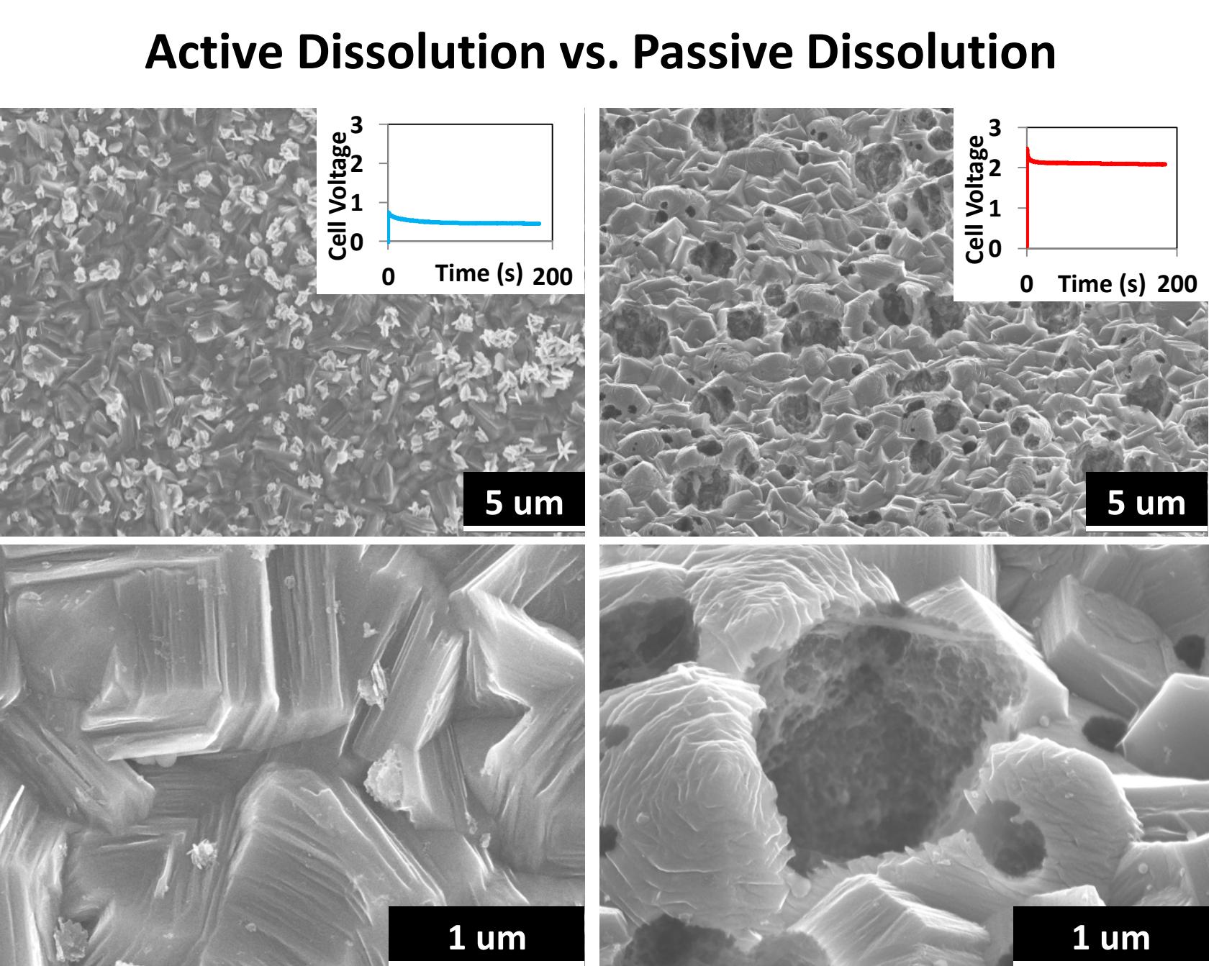
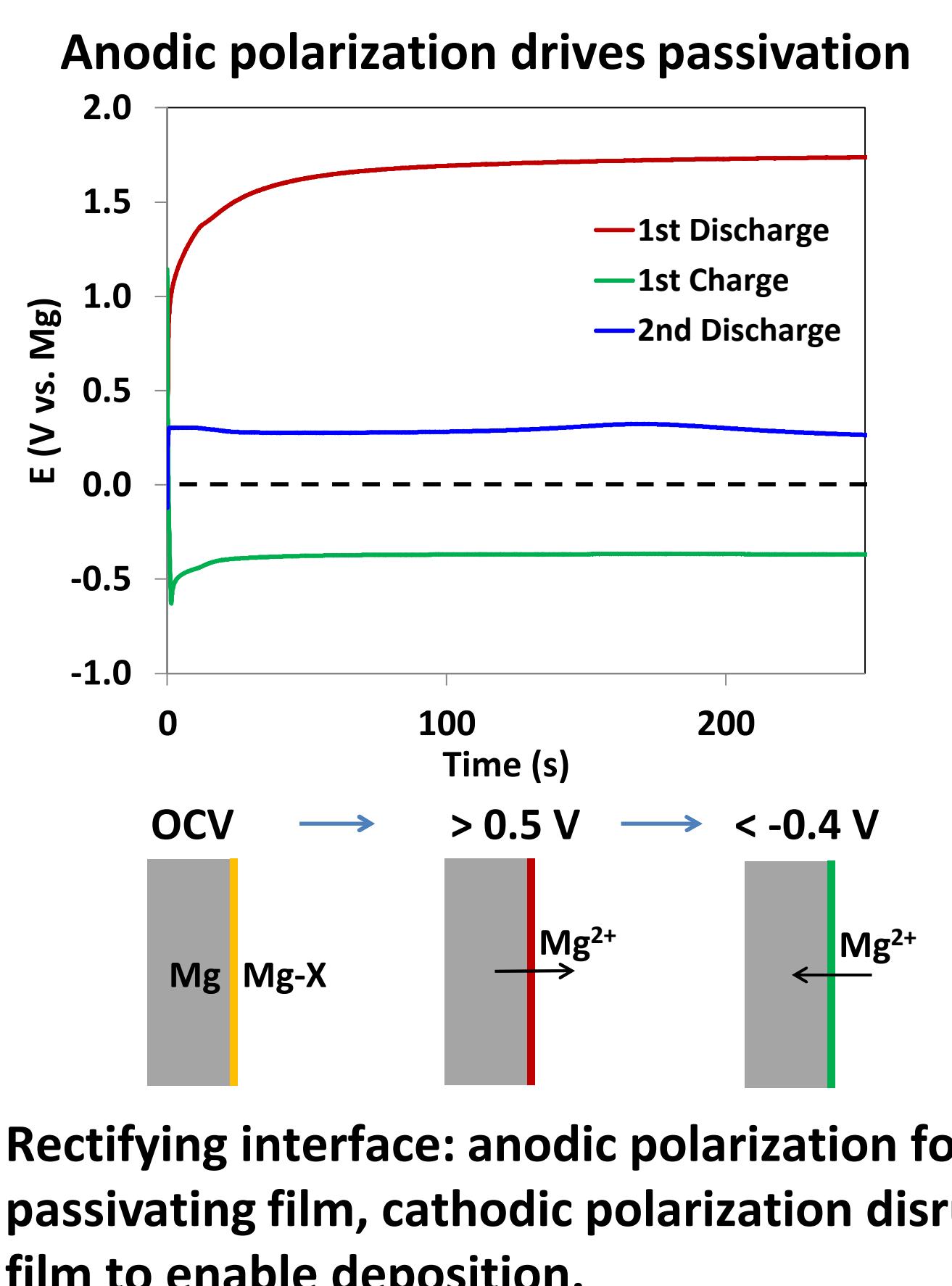
Experimental Tools



- In-situ tools:
 - AFM, QCM, Raman, FTIR, XAS
- Ex-situ tools:
 - SEM, TEM, XPS, ToF-SIMS, NMR

Surface Film Regulation of Electrodeposition/Dissolution

- TFSI byproducts on surface, yet Mg deposition activity is still maintained - how do surface films regulate charge transport to/from anode?

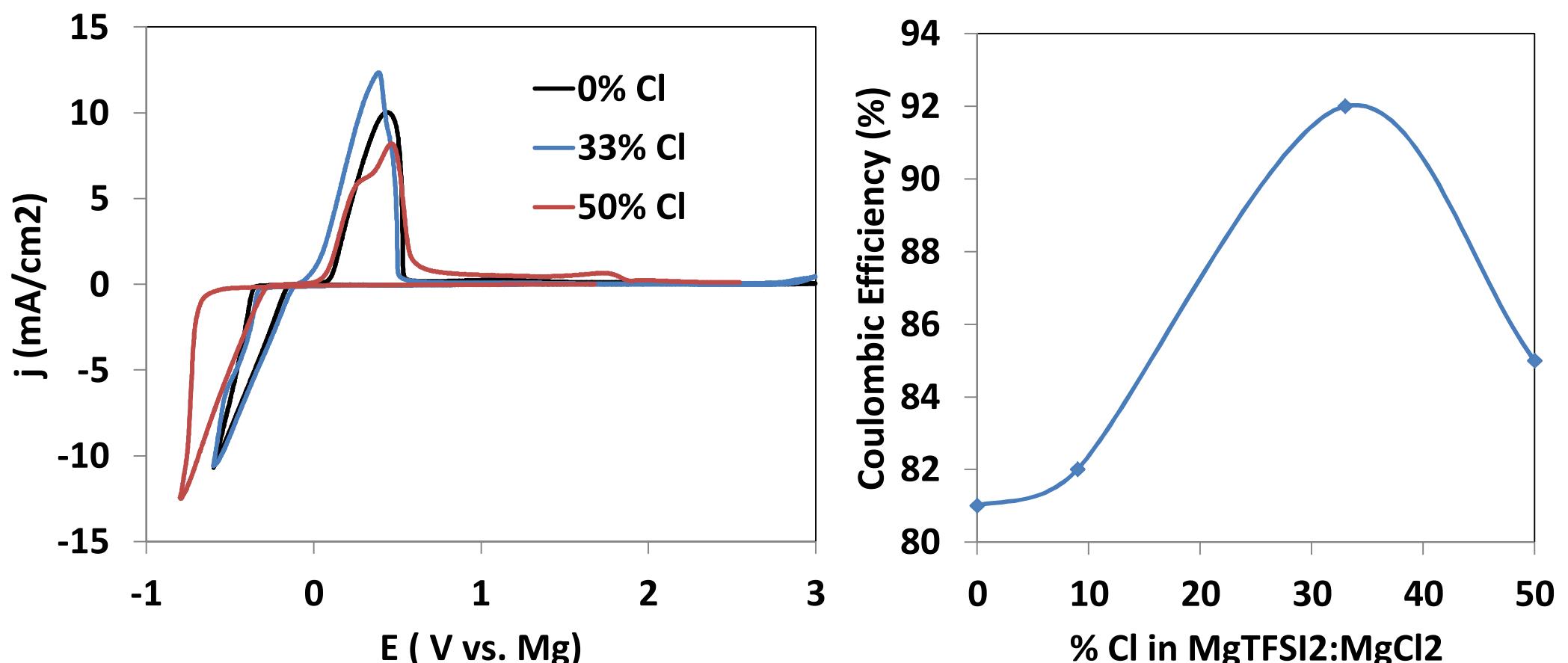


- Corrosion behavior: dissolution in active state (disrupted film) is crystallographic; dissolution in passive state (intact film) proceeds via localized pitting.

The Role of Chloride

- How does the re-introduction of Cl^- influence Mg deposition and dissolution?
- Can small Cl^- additions improve anode passivation resistance by modifying the anode surface?

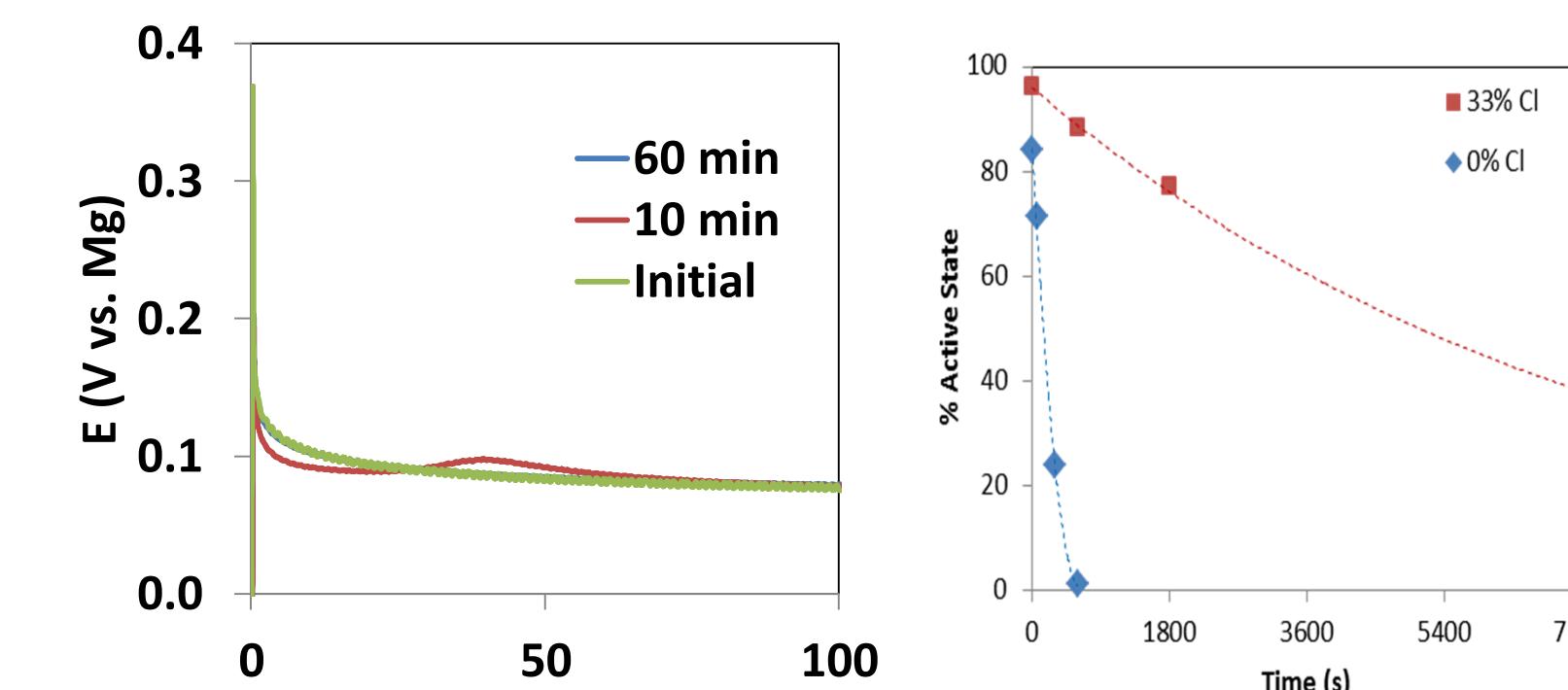
Significant amounts of MgCl_2 are required to improve MgTFSI₂ deposition reversibility



NMR: Mg-Cl species created in bulk solution

Composition	^{25}Mg -δ (ppm)	FWHM (Hz)
1:1 MgTFSI₂:MgCl₂	+9.7	685
2:1 MgTFSI₂:MgCl₂	+4.9	669
MgTFSI₂	0.0	294
2:1 MgCl₂:AlCl₃	+5.7	191

Cl-addition to MgTFSI₂ slows passivation of equilibrating Mg anodes



Conclusions

- Facile deposition of Mg is possible in the absence of chloride or reducing agents, i.e. in “conventional” electrolytes
- Mg anode reversibility in MgTFSI₂:G2 is plagued by low coulombic efficiency and passivation due to breakdown of the TFSI anion
- Chloride addition provides some improvement but substantial concentrations required - bad for cathodes and current collectors
- Future work aimed at understanding the origins of activity and inactivity in MgTFSI₂ and similar systems will provide valuable insight into electrolyte development for Mg batteries

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