

Magnesium Battery Anode Processes in Conventional Electrolytes



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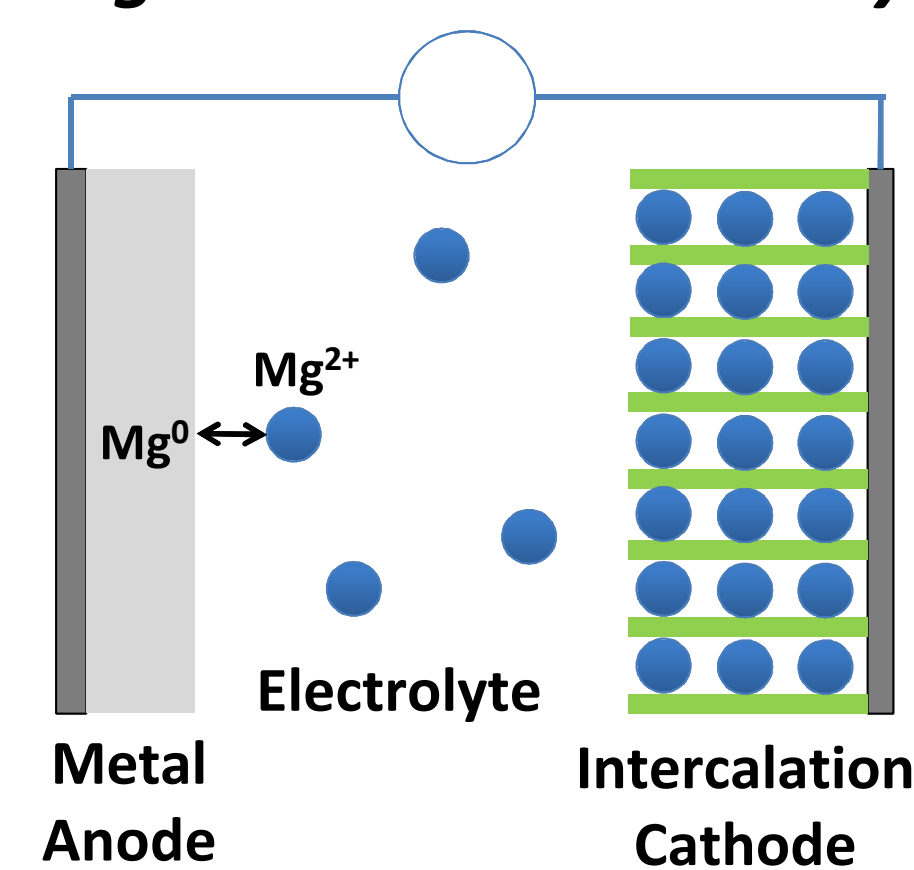
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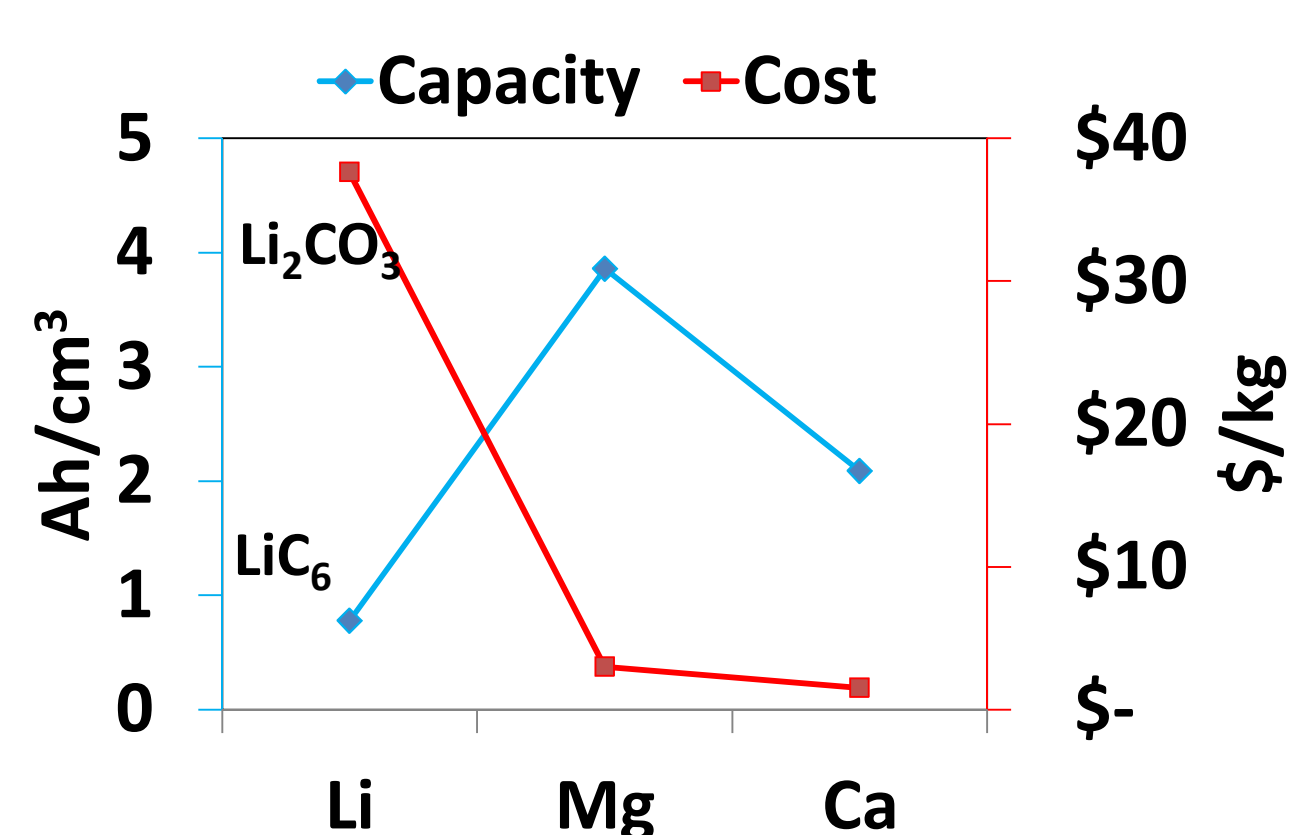
Background and Motivation

- 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.

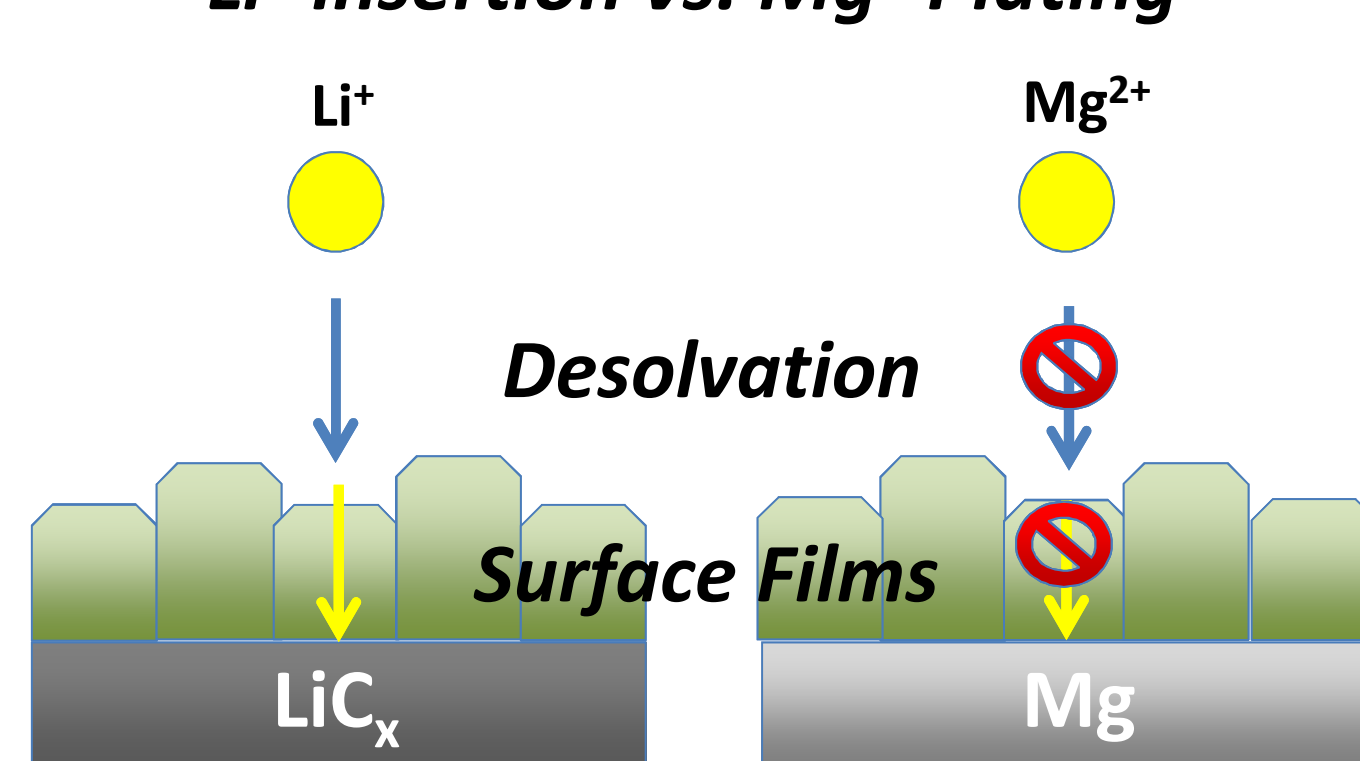
Mg Intercalation Battery



Li-ion vs. Metal anodes

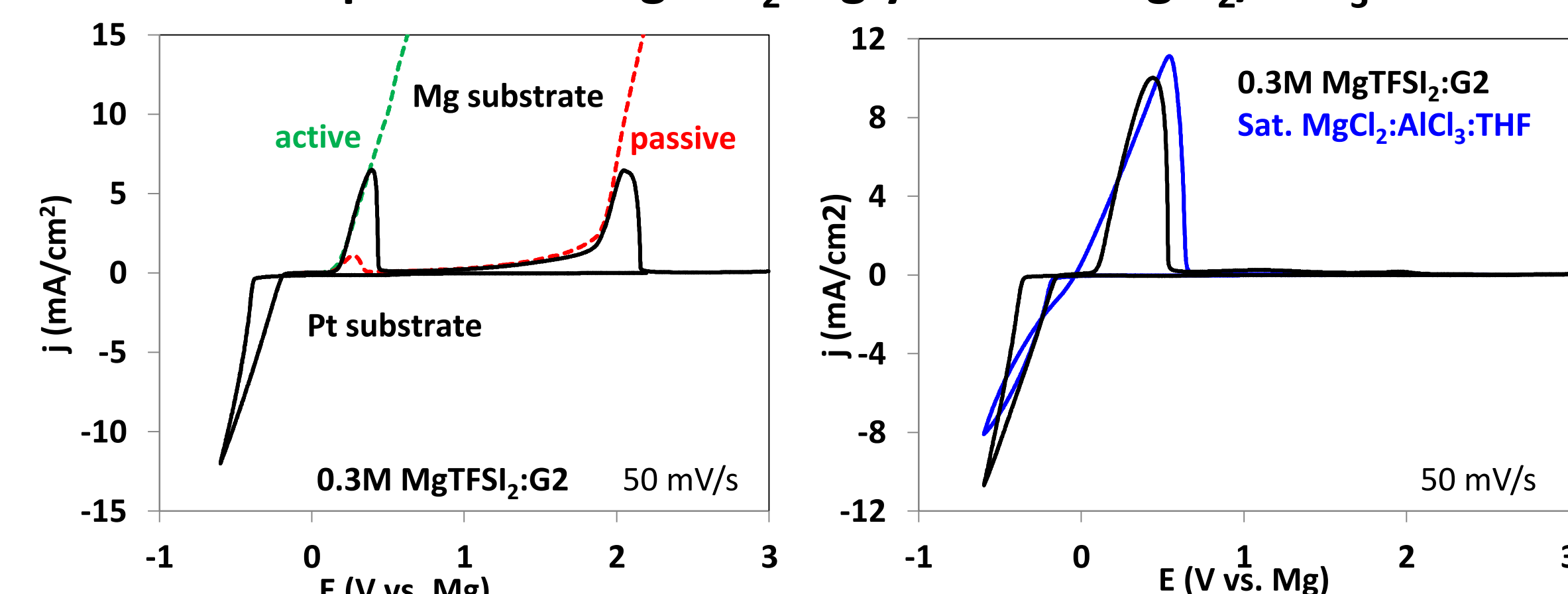


Li+ insertion vs. Mg0 Plating



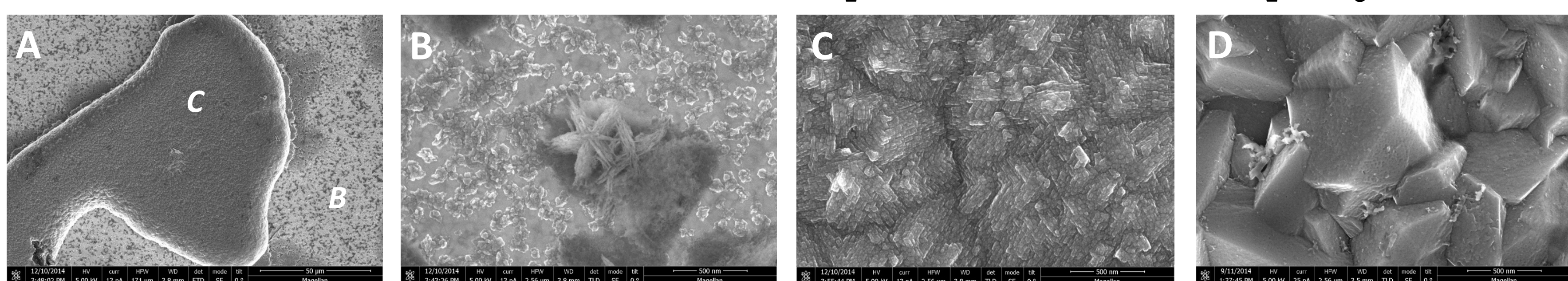
Mg0 Plating Without a Strongly Coordinating Anion

CV comparison of MgTFSI2:diglyme and MgCl2/AlCl3:THF



- High-rate (10 mA/cm^2) deposition
- Two anodic signatures implying active and passivate state dissolution
- Potential hysteresis about E^0 evidence for inhibition at low overpotential
- Unique deposit structure without hexagonally faceted crystals

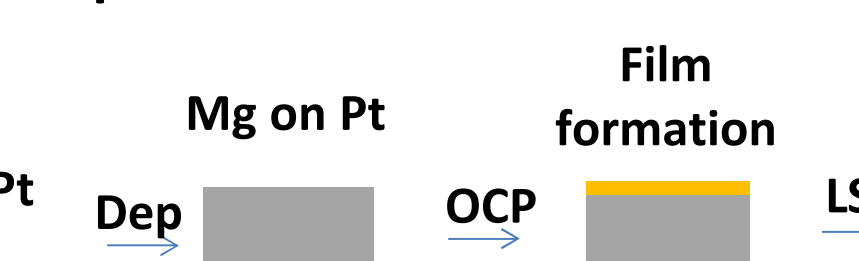
High Resolution SEM of Mg deposited in MgTFSI2:diglyme (A,B,C) and MgCl2/AlCl3:THF (D)



Parasitic Loss and Passivation in MgTFSI2:G2

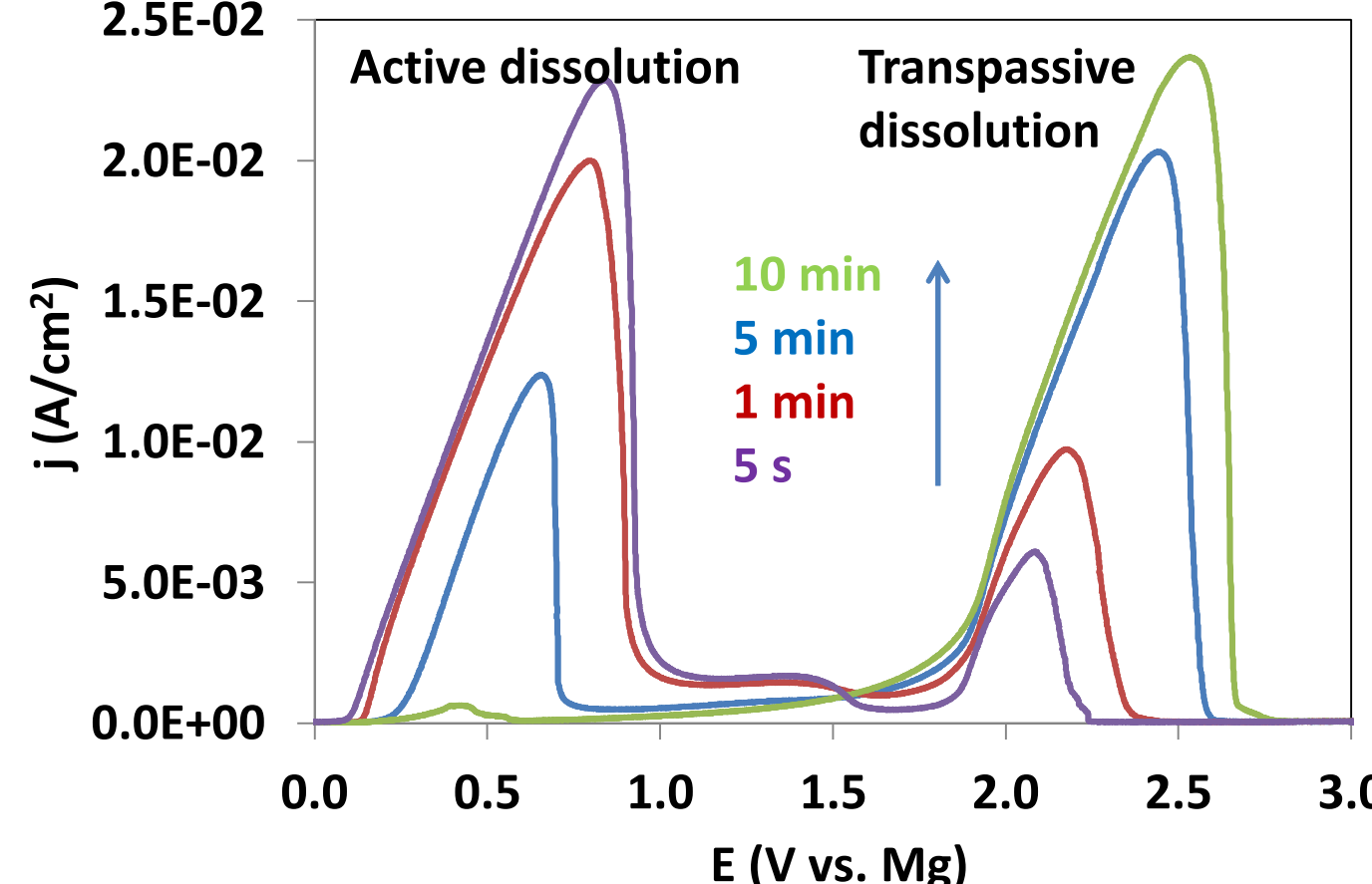
- Two problems: low coulombic efficiency (<90%) and Mg passivation over time; are they related?

Open Circuit Equilibration Experiment:

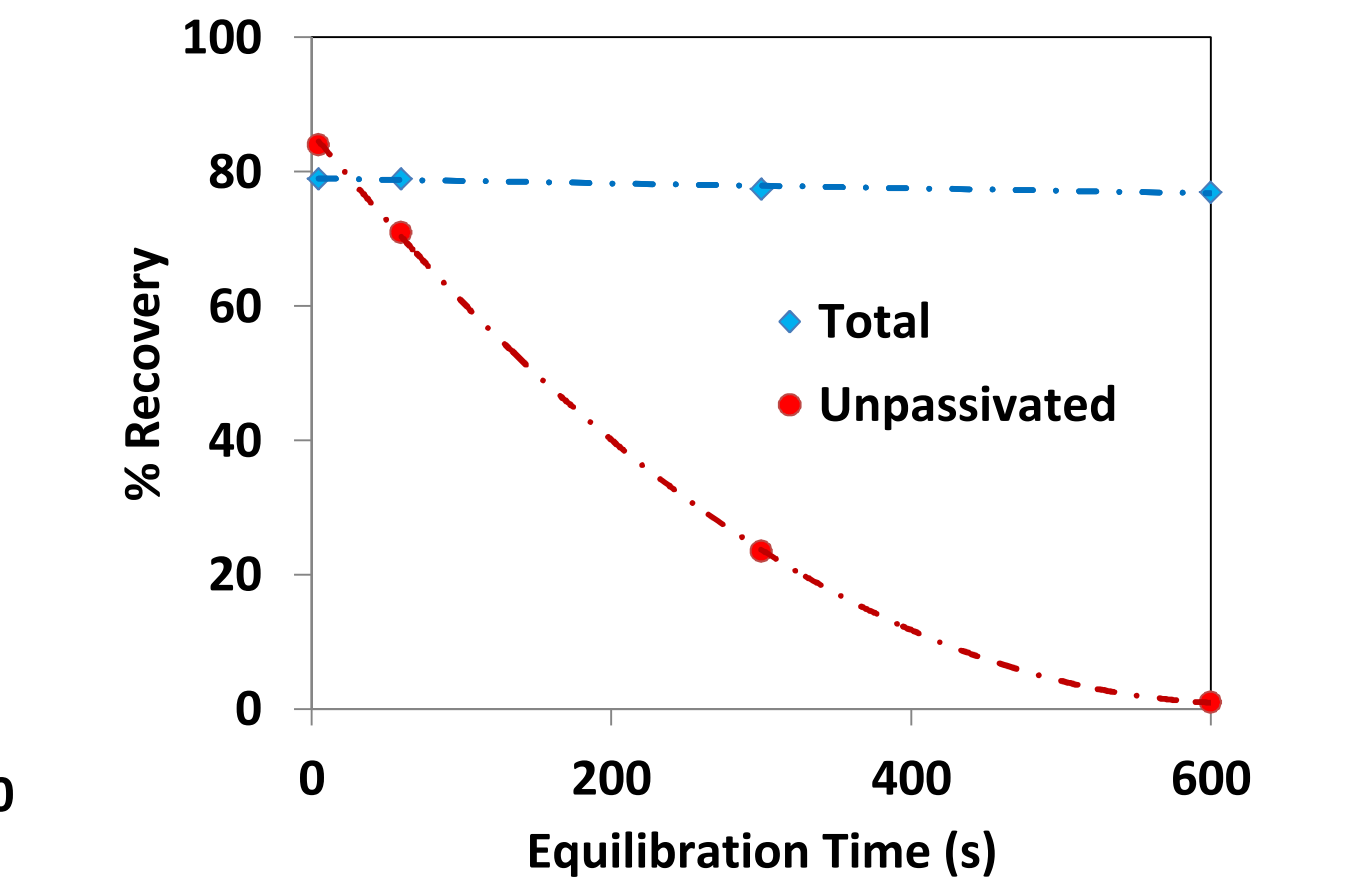


- Trend in passivation does not match coulombic efficiency
- Efficiency loss and passivation are decoupled processes

LSV strip after 500 nm Mg deposition

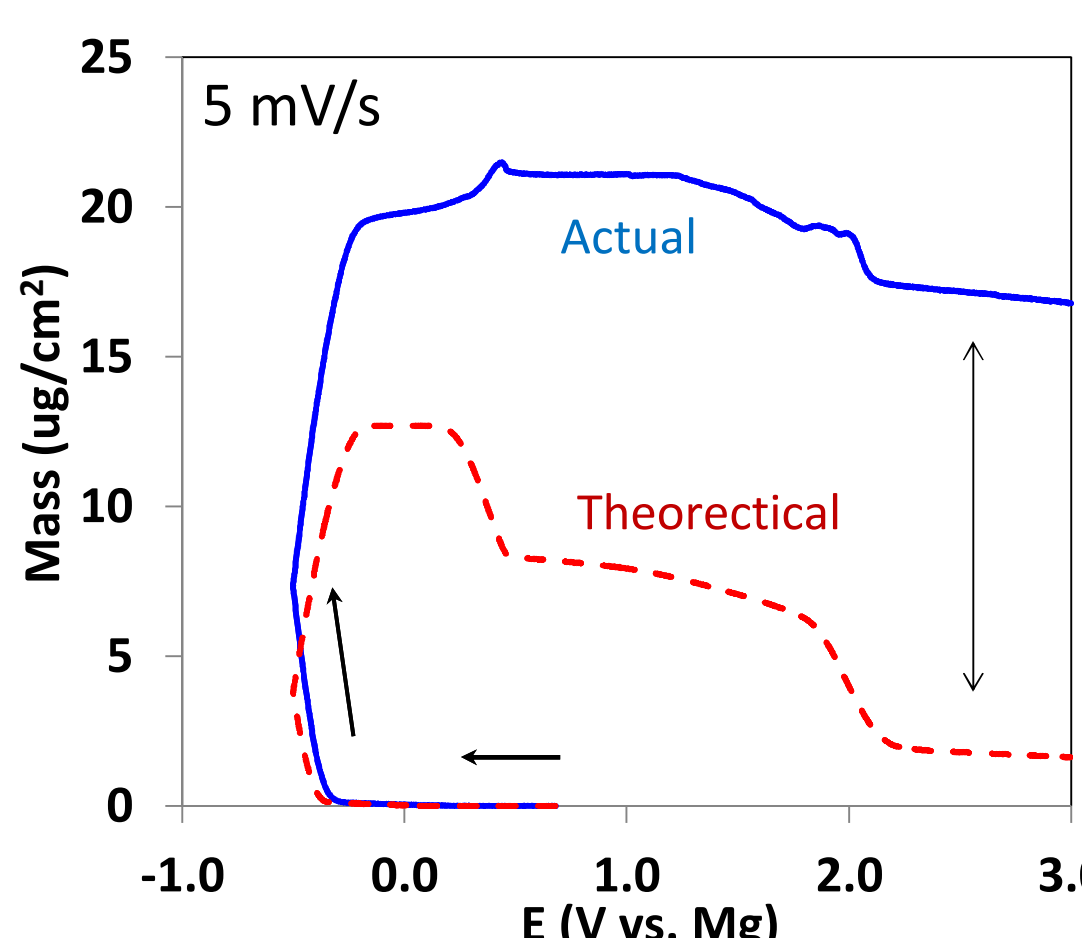


Slight CE loss despite complete passivation

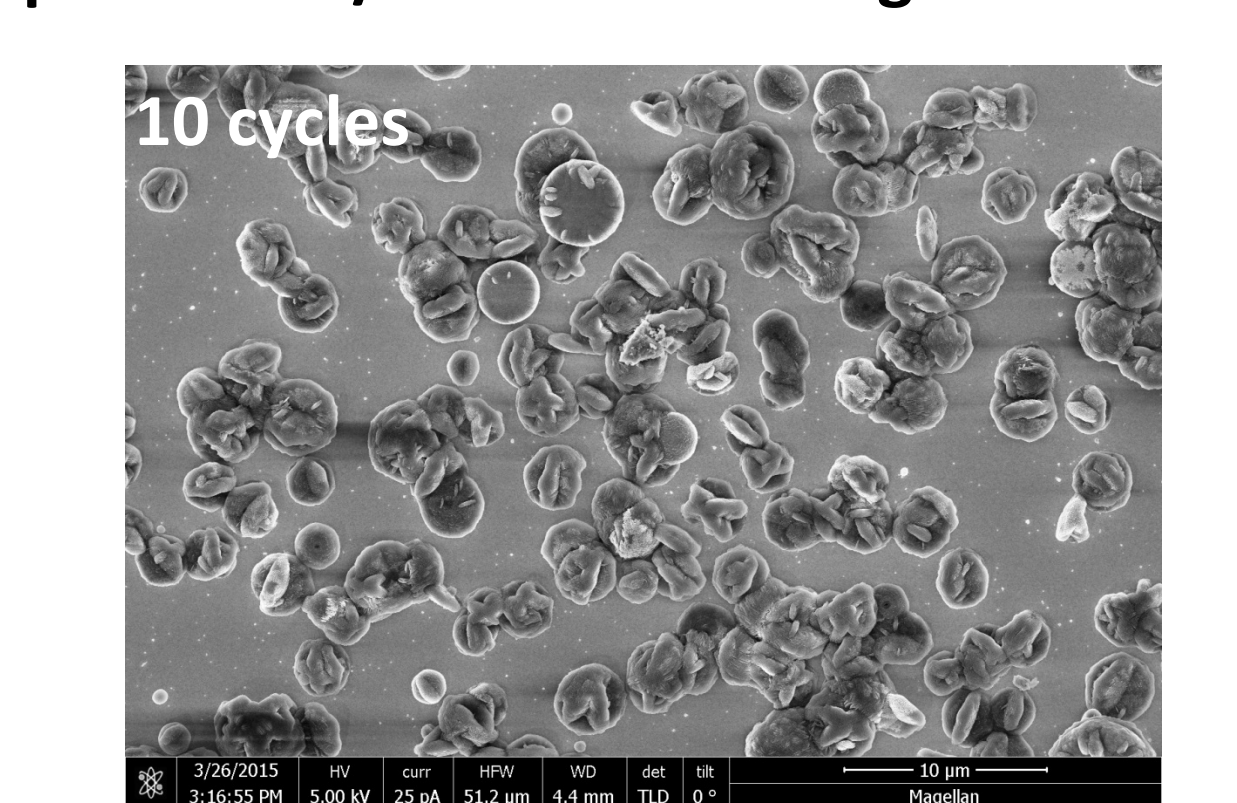


- TFSI decomposition leads to stranded Mg and accumulated material during cycling

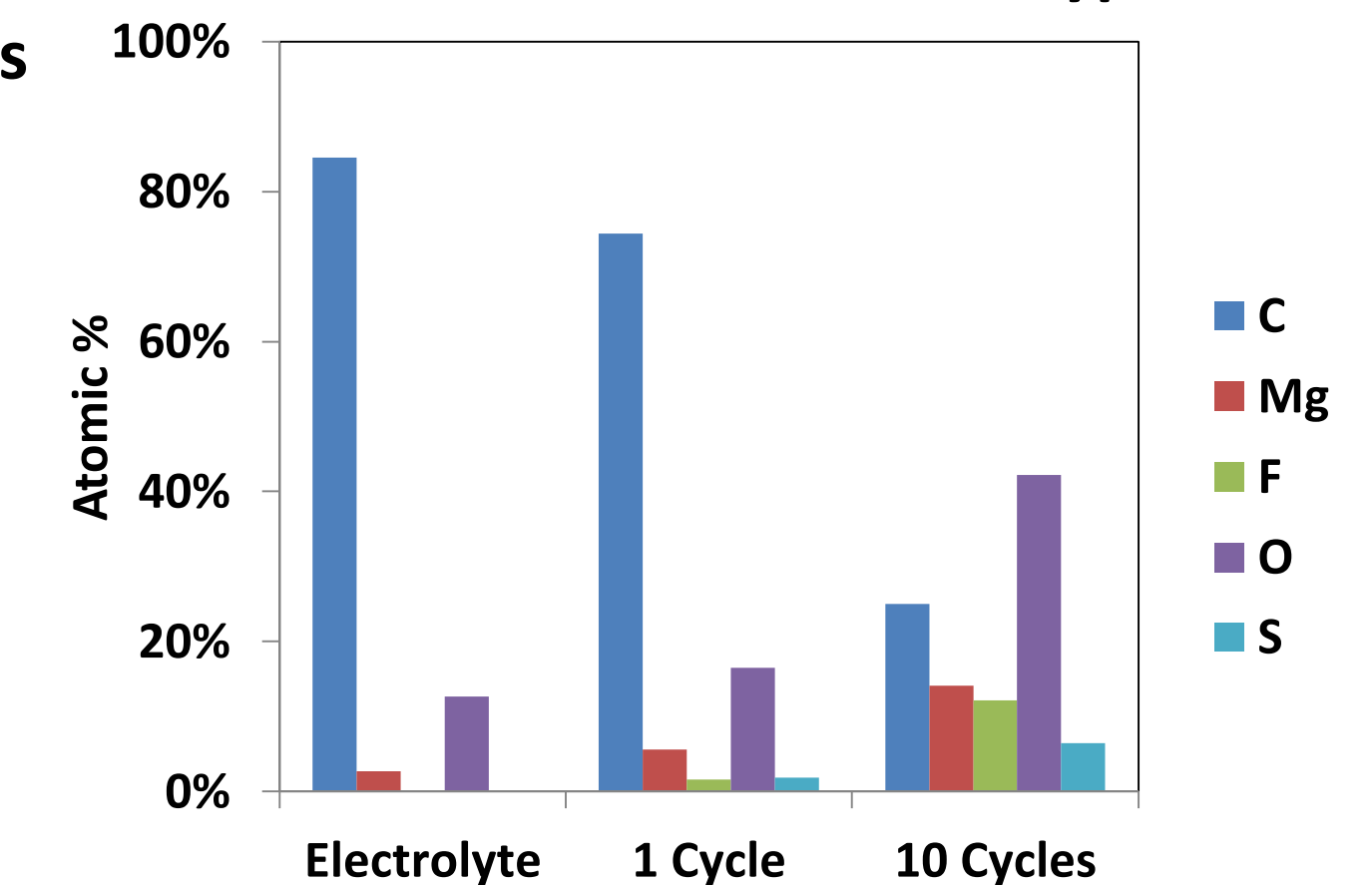
EQCM: Anodic mass accumulation



SEM: Residual passivated/disconnected Mg structures



XPS: Residual film contains TFSI byproducts



Experimental Tools

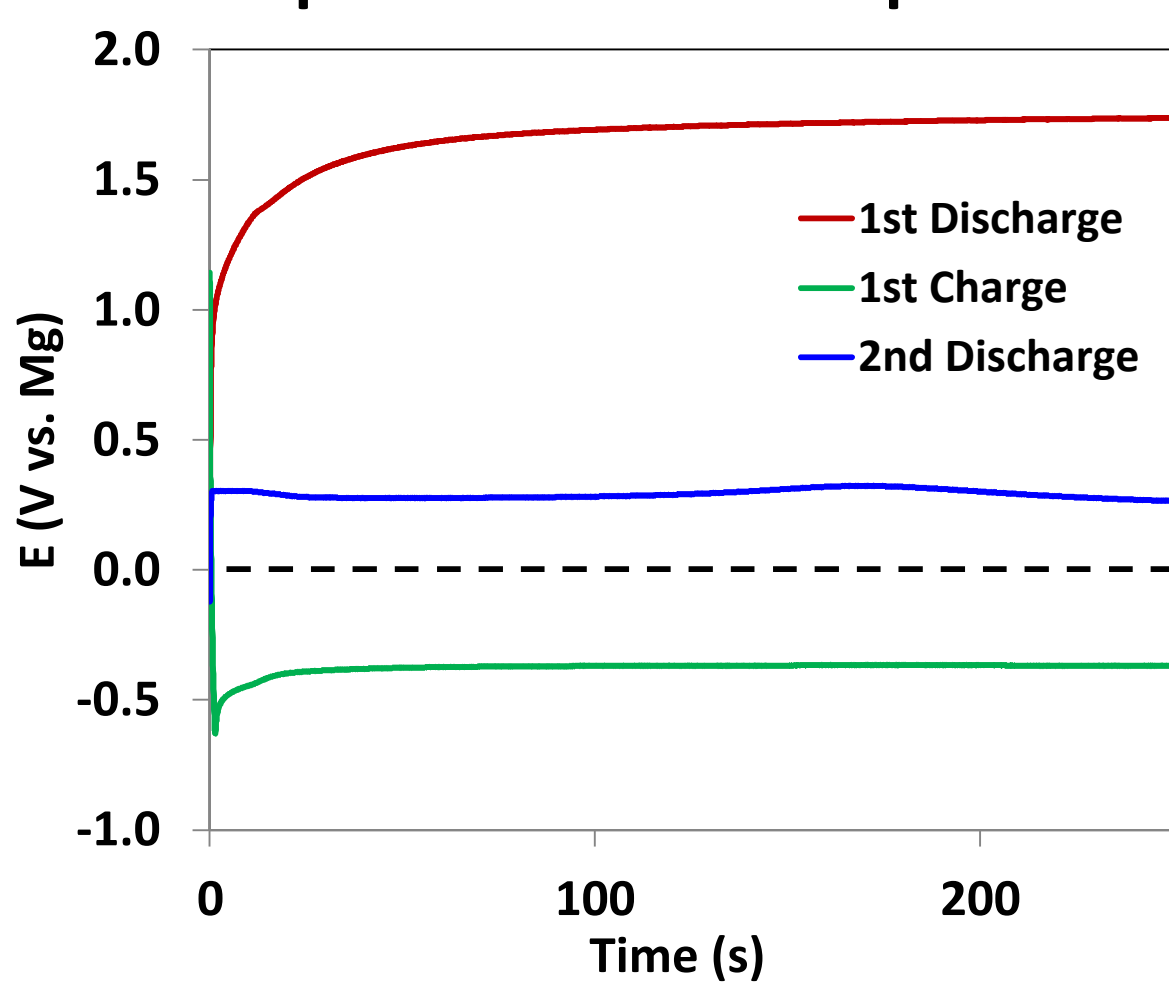


- In-situ tools:
 - AFM, QCM, Raman, FTIR, XAS
- Ex-situ tools:
 - SEM, TEM, XPS, ToF-SIMS, NMR

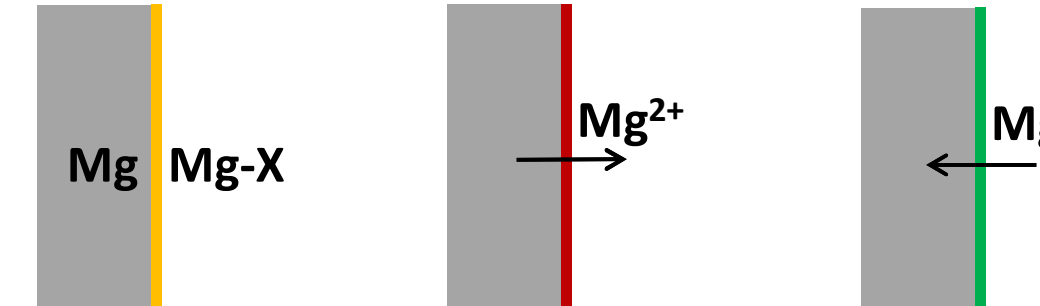
Surface Film Regulation of Electrodeposition/Dissolution

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

Anodic polarization drives passivation

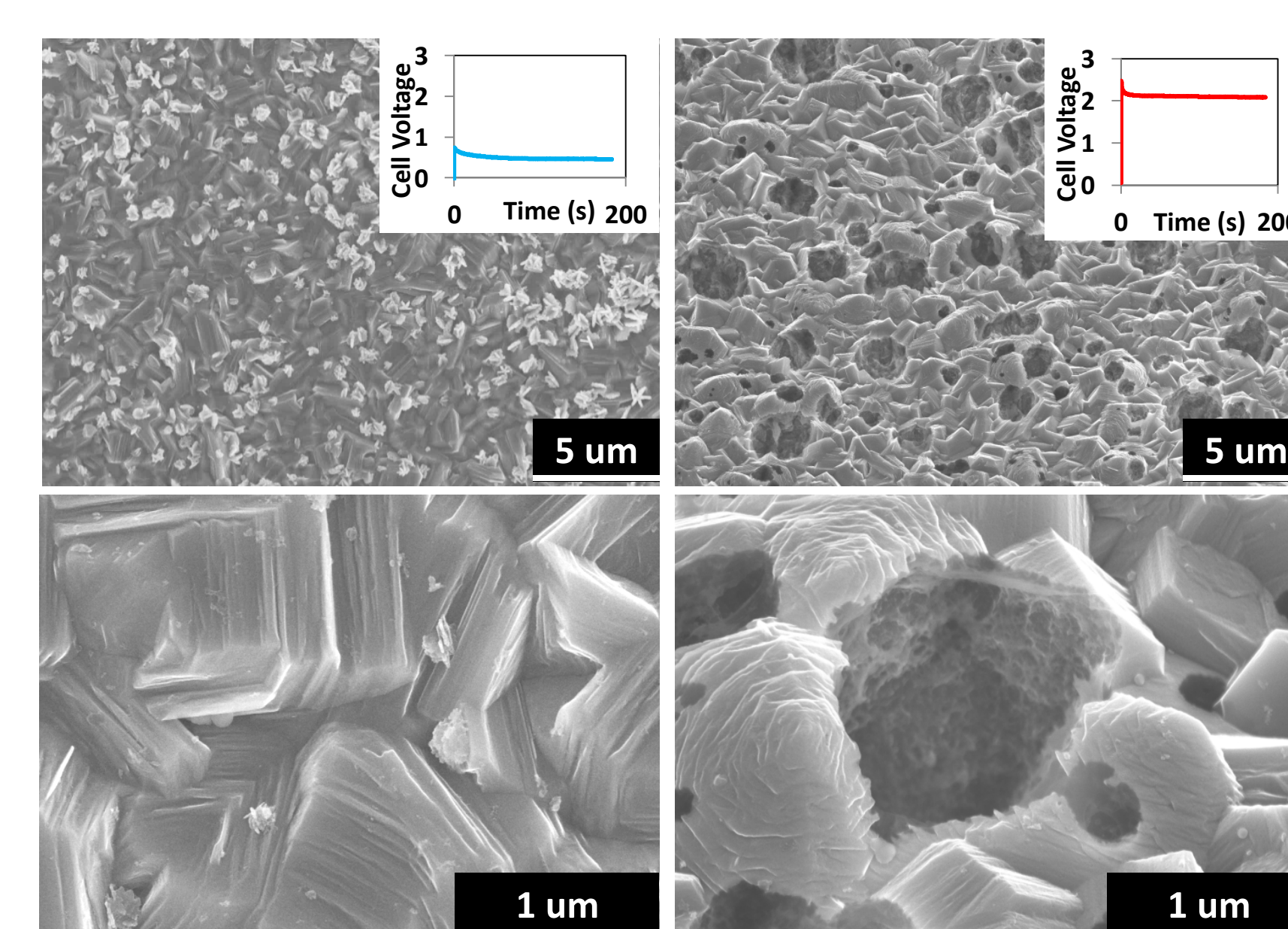


OCV



- Rectifying interface: anodic polarization forms passivating film, cathodic polarization disrupts film to enable deposition.

Active Dissolution vs. Passive Dissolution

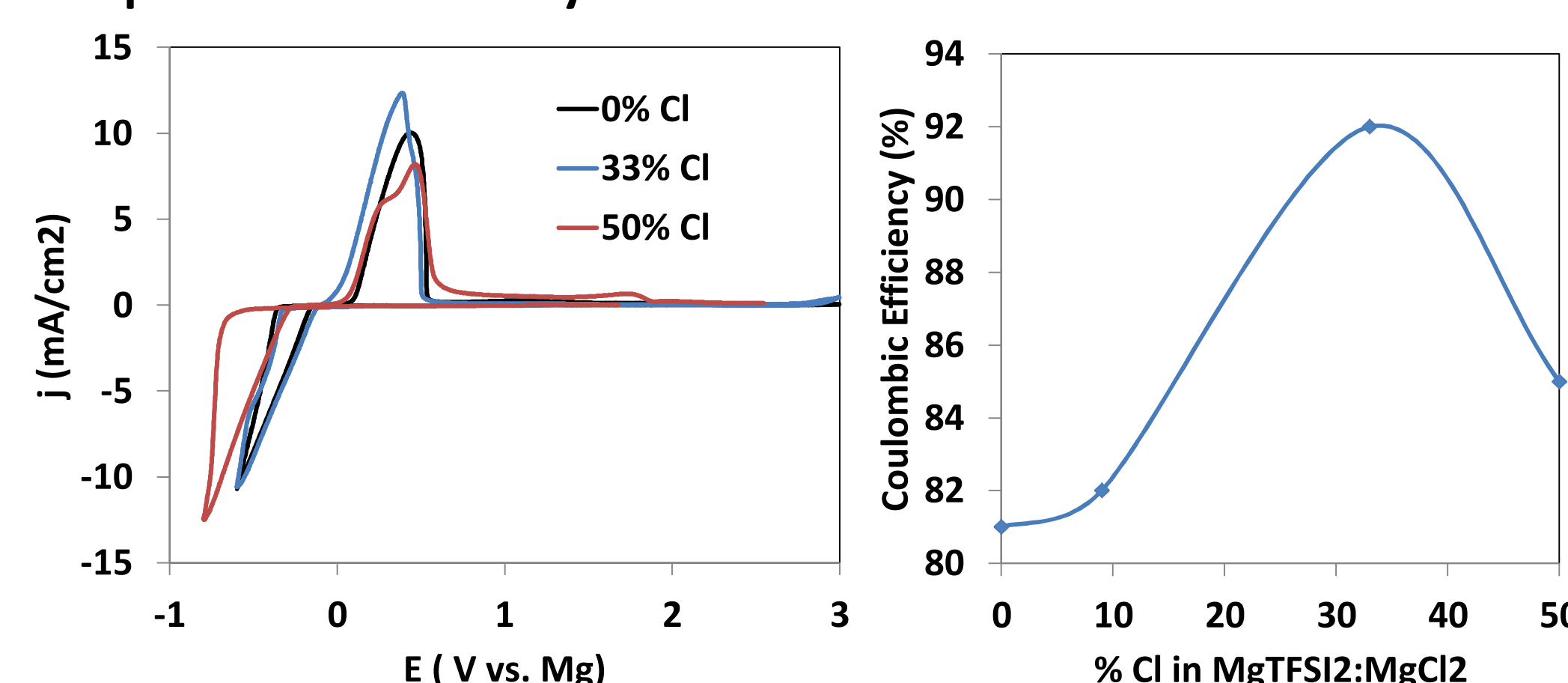


- Corrosion behavior: dissolution in active state (disrupted film) is crystallographic; dissolution in passive state (intact film) proceeds via localized pitting.

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?

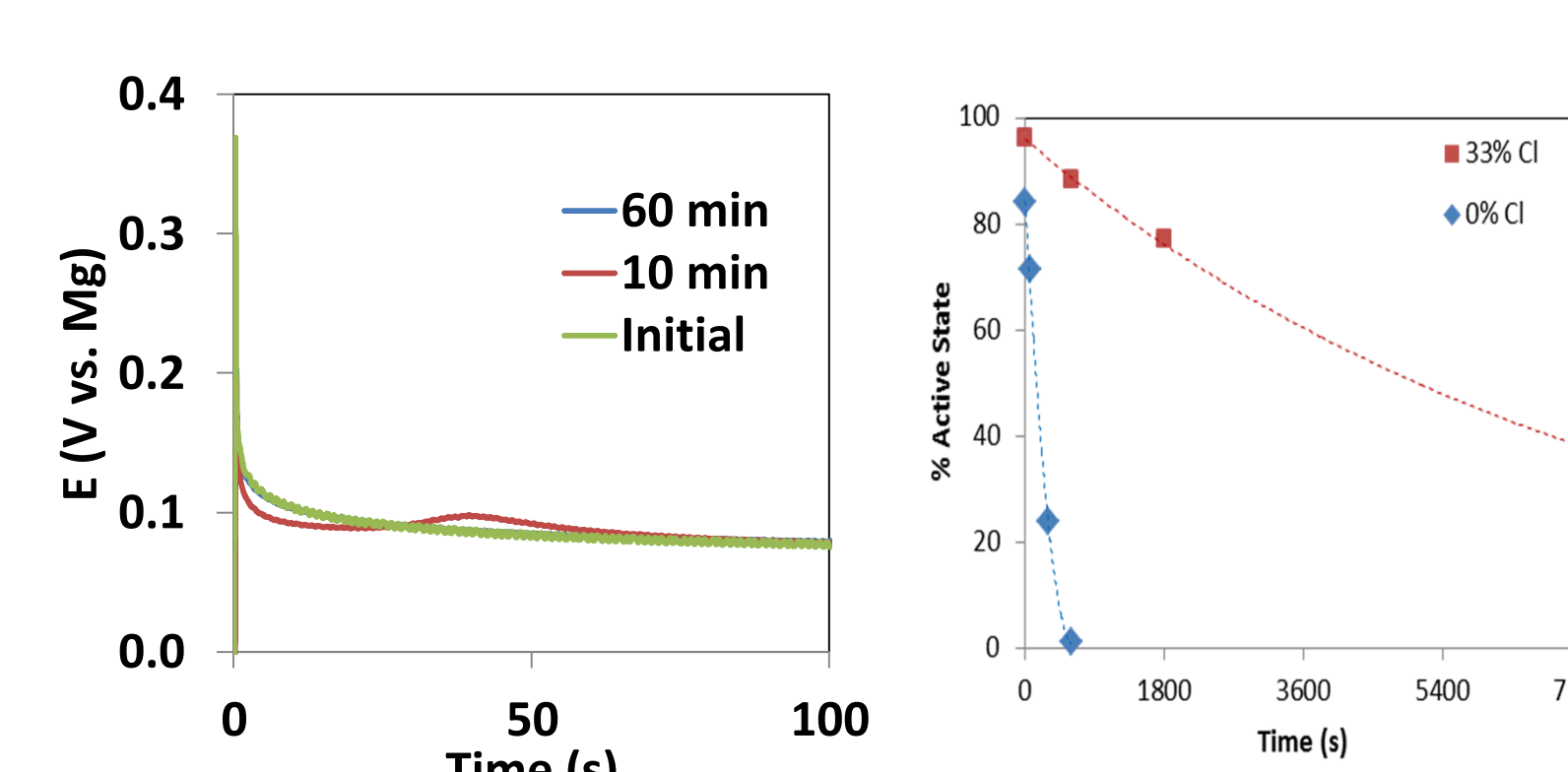
Significant amounts of MgCl_2 are required to improve MgTFSI_2 deposition reversibility



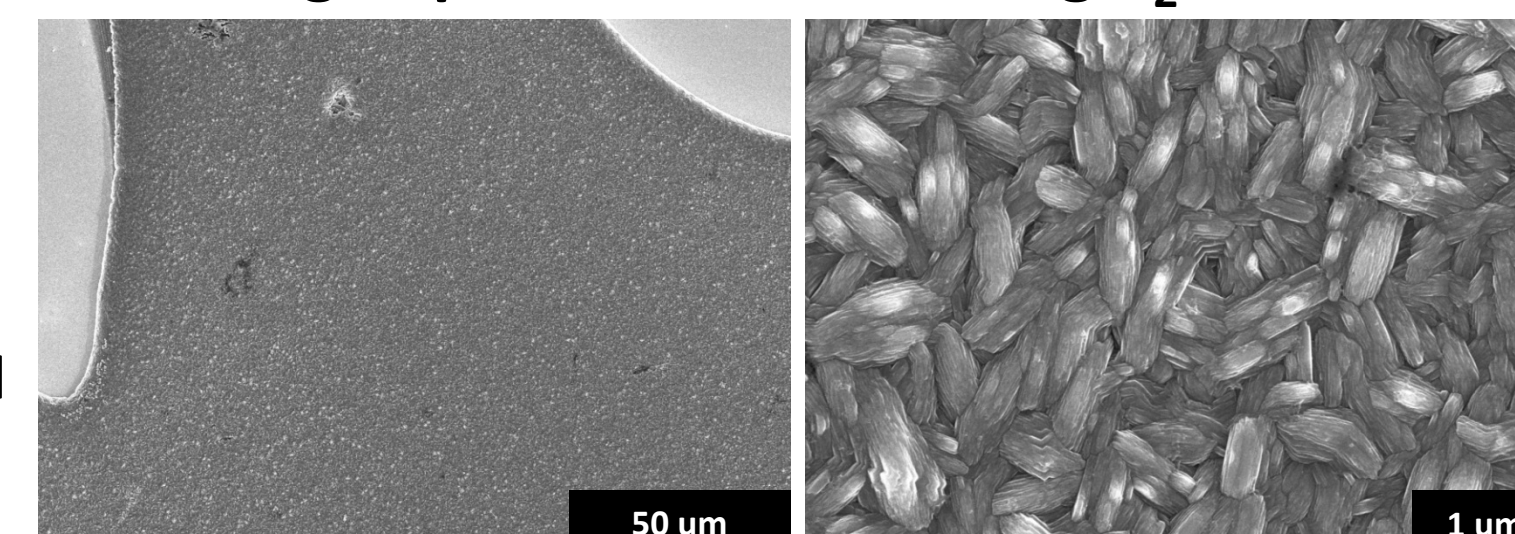
NMR: Mg-Cl species created in bulk solution

Composition	^{25}Mg - δ (ppm)	FWHM (Hz)
1:1 MgTFSI_2 : MgCl_2	+9.7	685
2:1 MgTFSI_2 : MgCl_2	+4.9	669
MgTFSI_2	0.0	294
2:1 MgCl_2 : AlCl_3	+5.7	191

Cl-addition to MgTFSI_2 slows passivation of equilibrating Mg anodes



Mg deposited from 33% MgCl_2 solution



- MgCl_2 improves deposit uniformity, but TFSI influence still apparent

Conclusions

- Facile deposition of Mg is possible in the absence of chloride or reducing agents, i.e. in “conventional” electrolytes
- Mg anode reversibility in MgTFSI_2 :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 MgTFSI_2 and similar systems will provide valuable insight into electrolyte development for Mg batteries

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