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The Identity and Role of Interphases in Regulating Mg Anode Morphology Evolution

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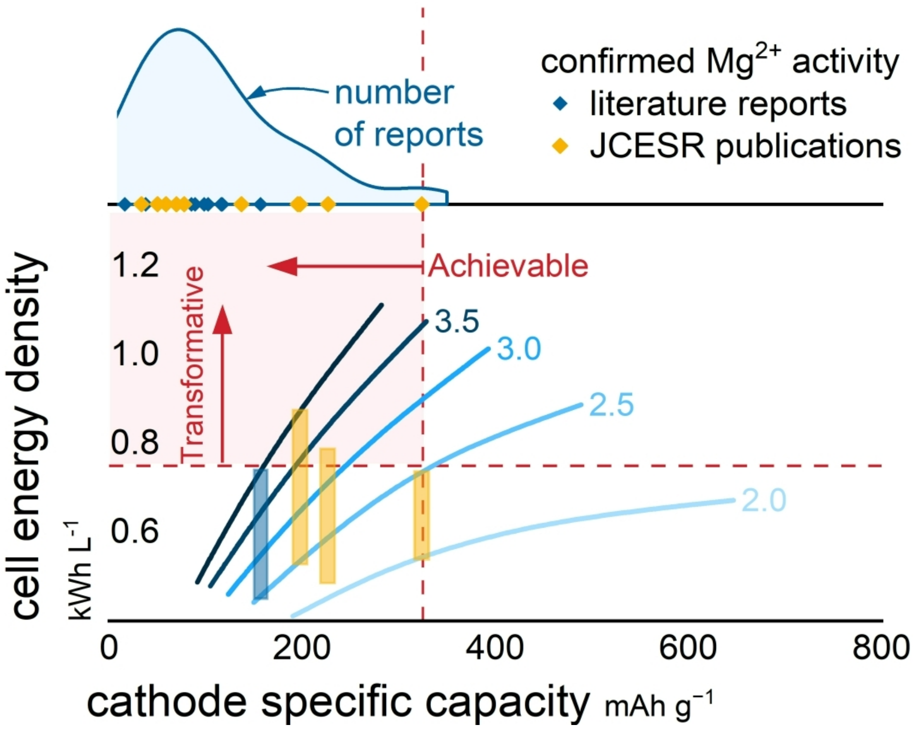
Multivalent metal ion batteries could provide transformative energy densities

Mg^{2+} 3,833 mAh ml^{-1} -2.37 V vs. SHE



<u>Current materials challenges</u>

low metal coulombic efficiency

low electrolyte redox stability

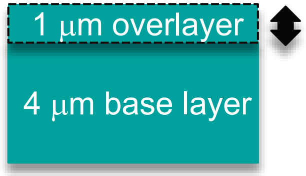
low cathode capacity/stability

- Interphases form at electrodes impacting ion and electron transport
- Limited knowledge exists of interphase identity and attributes, key to designing stable battery electrodes

Our goal is to determine the identity of and understand how interphases regulate Mg^{2+} deposition

Free Cl^- as an ideal interphase former for Mg deposition

MACC: $MgCl_2 + AlCl_3 + nTHF \rightarrow$ $\mathbf{Mg_2Cl_3^+THF_n} + AlCl_4^-$

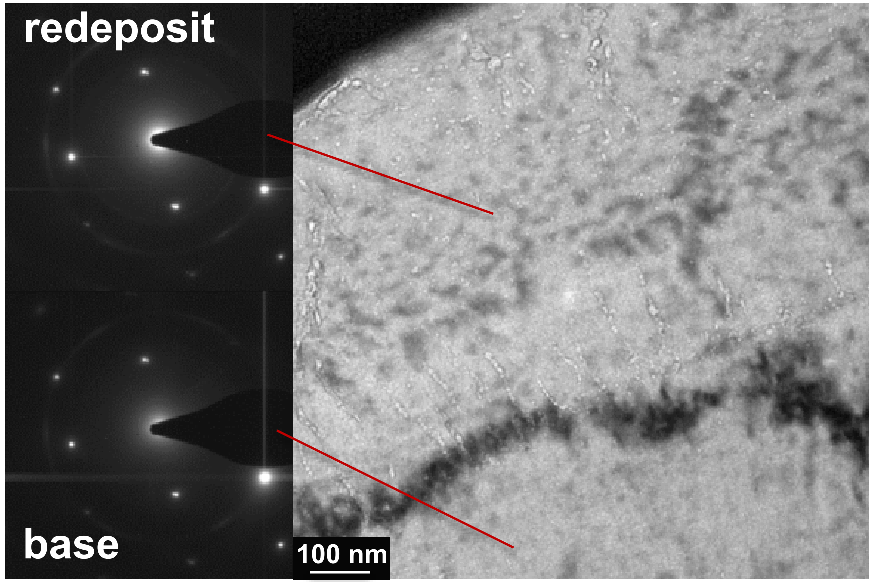


50 cycles @ 2 mA/cm^2

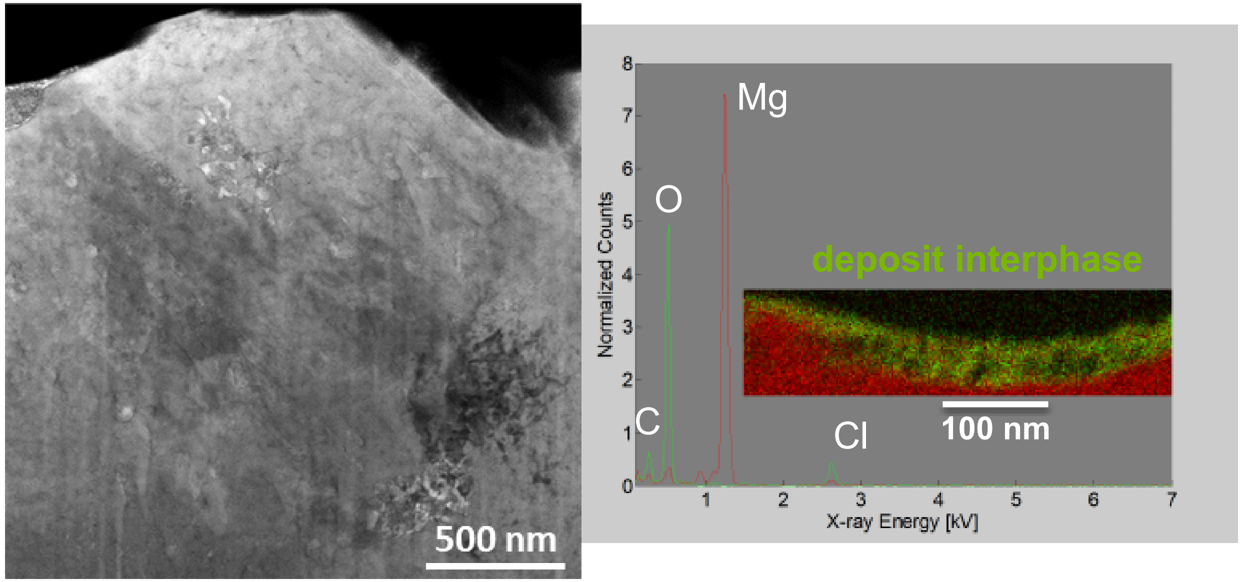
Equilibrate between cycles
Interrupt 0 to 1800 s

APC: $2PhMgCl + AlCl_3 + nTHF \rightarrow$ $\mathbf{Mg_2Cl_3^+THF_n} + Ph_2AlCl_2^-$

MACC: Single cycle epitaxial growth, 99.9 ± 0.1% CE, 0 s interrupt



APC: 50 cycle epitaxial growth, 100.0 ± 0.1% CE, 1800 s interrupt



Epitaxial Mg deposition – no new interface, same orientation within a grain from substrate to electrolyte interface

The interphase formed facilitates Mg^{2+} transport – Mg, O, Cl

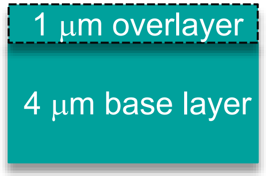
MACC: R. Doe et al. Chem Comm, 2014, 50, 243
K. See at al. JACS, 2016, 138 (1), 328

APC: Mizarahi et al. JECS 2008, 155 (2), A103

Reduced electrolyte efficiency drives renucleation not epitaxy

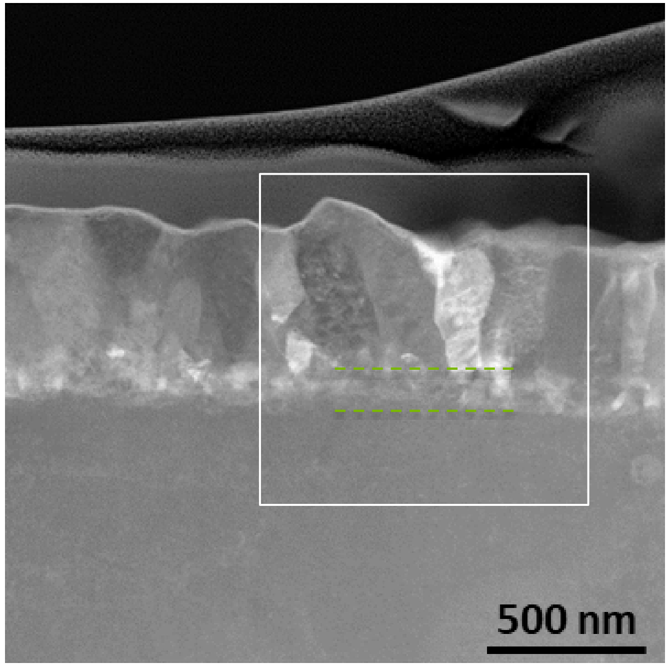
Electrolyte does not support 100% CE

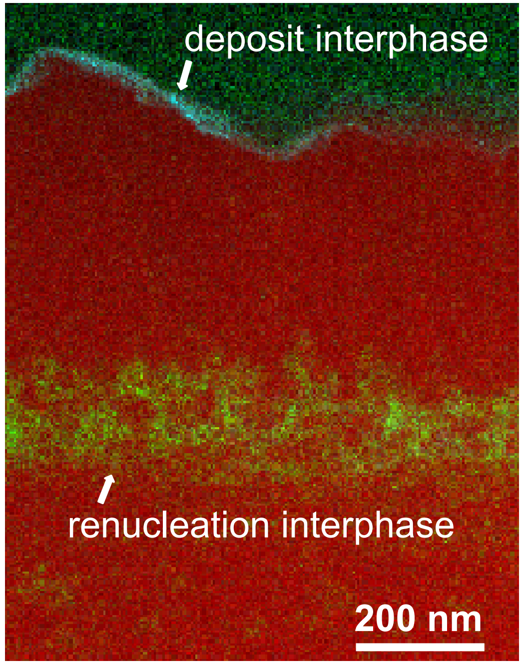
99.3 ± 0.1% CE, 50 cycles (APC), 1800 s interrupt

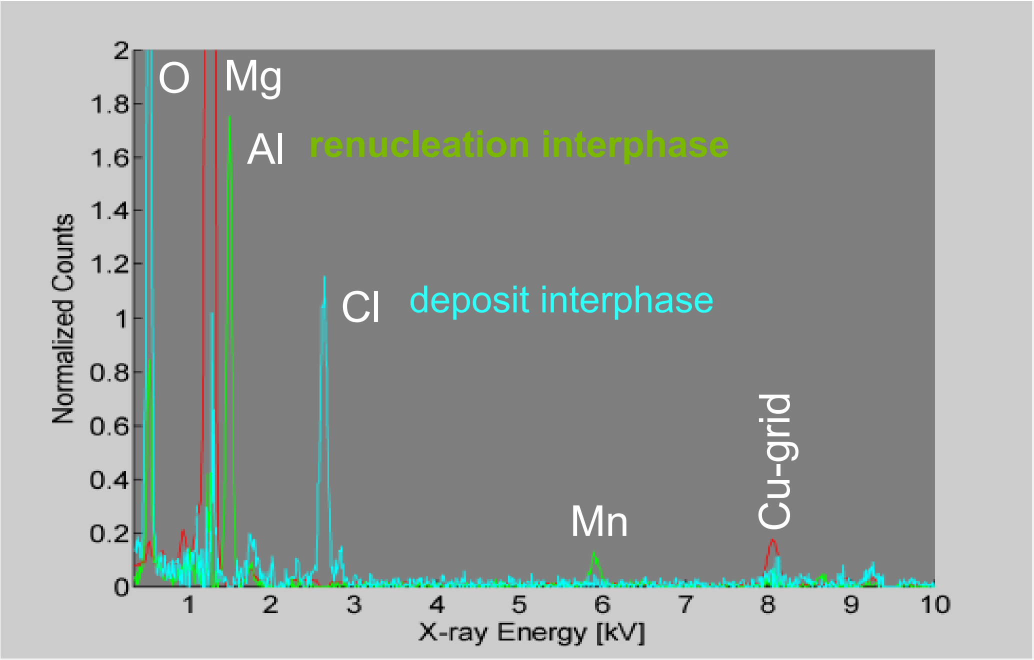


50 cycles @ 2 mA/cm^2

Interrupt 0 to 7200 s





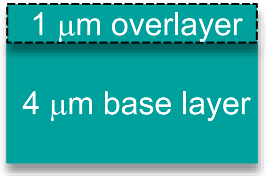


A sub-unity coulombic efficiency electrolyte drives Mg renucleation

Renucleation layer – accumulation of Al and O, low in Cl – adsorbed Cl^- loss with equilibration

Newly formed interphase is O and Cl enriched

Free Cl⁻ protection of the Mg surface is short-lived

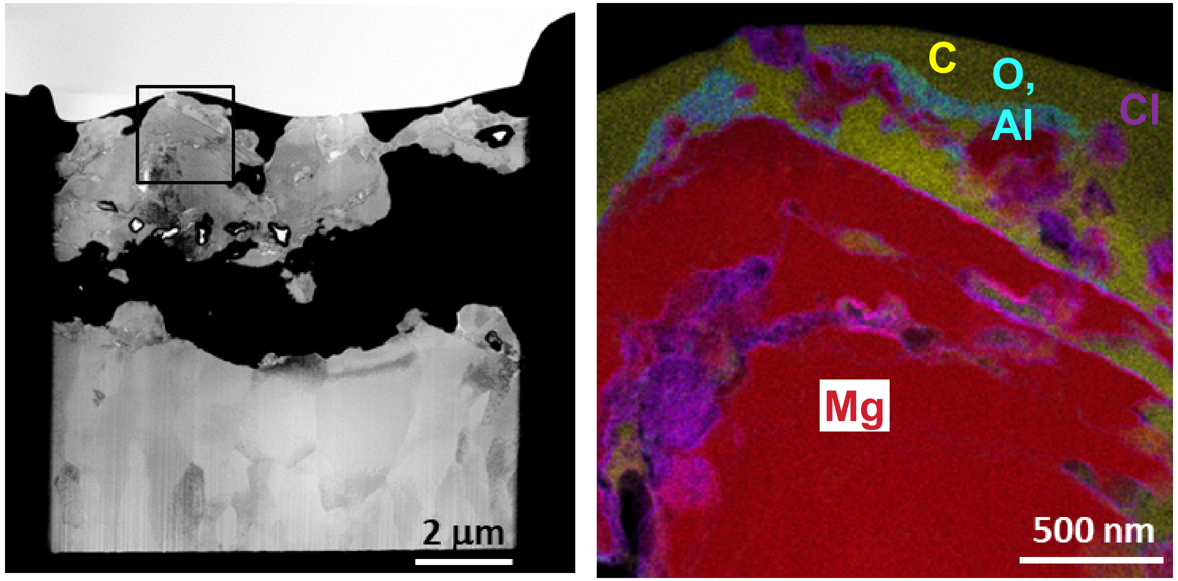


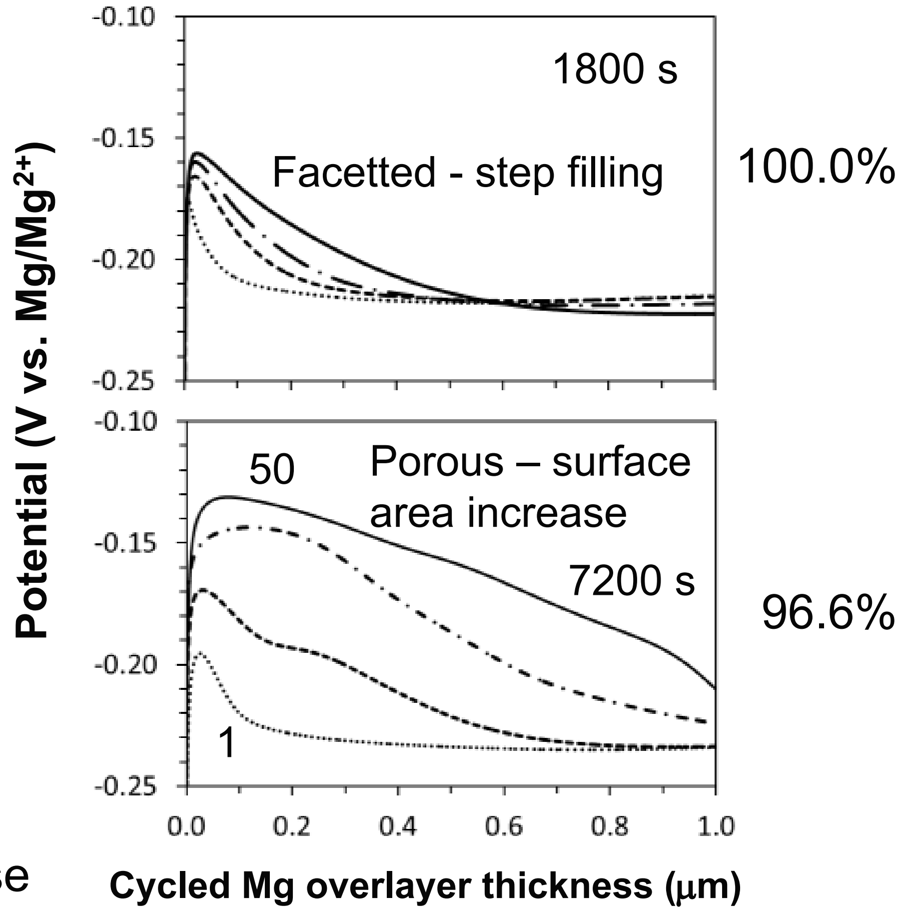
50 cycles @ 2 mA/cm²

Interrupt 7200 s

Interrupt extended from 1800 to 7200 s, CE decreases, shift from facetted to porous response

Cycling leads to porosity evolution and Mg particle separation, possible disconnection





Accumulation of Al, O, Cl in a highly heterogeneous interphase

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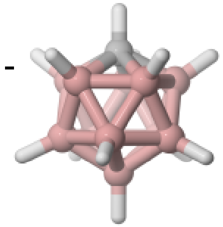
JCESR Joint Center for Energy Storage Research

Mg deposit structure/orientation change dramatically without Cl^-

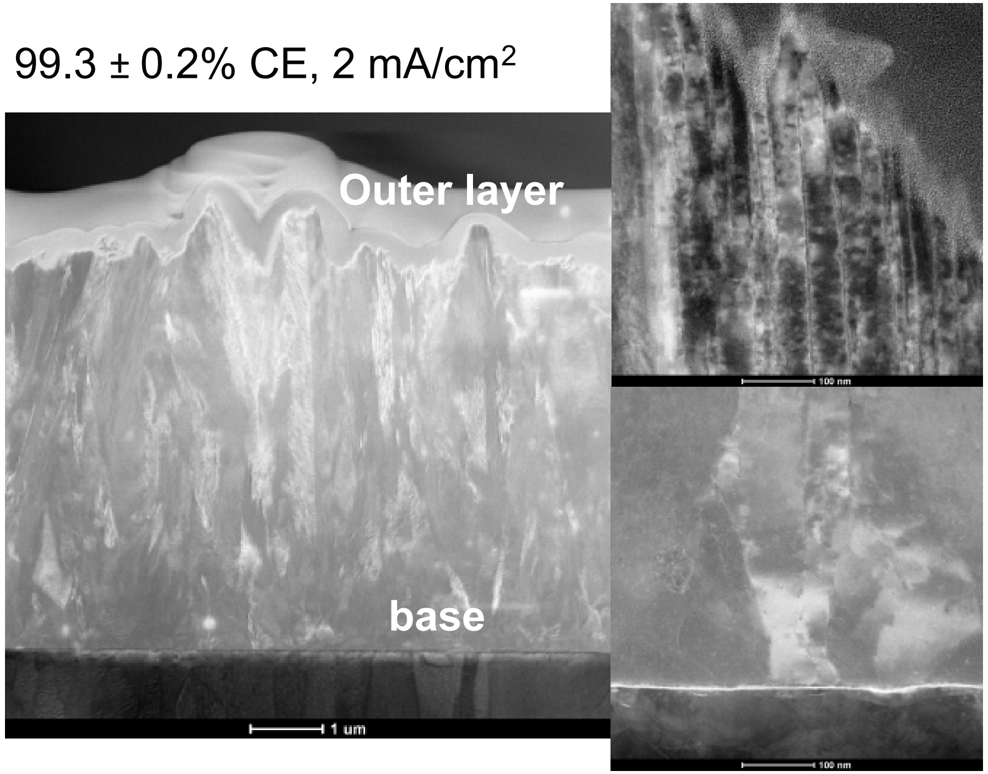
$Mg(CB_{11}H_{11})_2 \rightarrow Mg^{2+}G3_n + 2CB_{11}H_{11}^-$

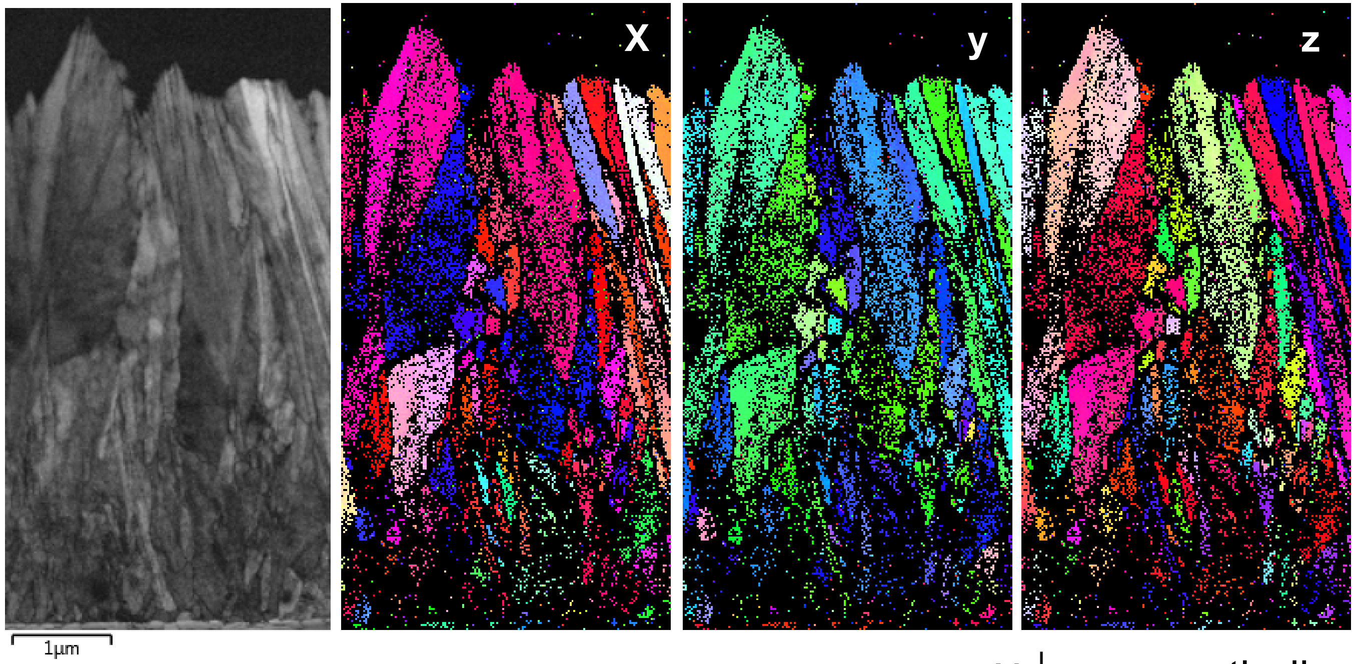


G3 is stabilized to reductive decomposition

T. Seguin et al. Front Chem, 2019, 10.3389/fchem.2019.00175

99.3 ± 0.2% CE, 2 mA/cm^2



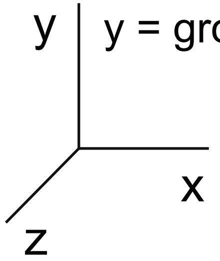


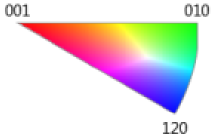
Growth of dense continuous films – absent a TEM discernable interphase at the Pt:Mg interface, XPS O well into deposit

Growth occurs at the higher energy prismatic planes not the lower energy basal plane*

Facet	*E (kJmol^{-1})
001	15.4
010	30.4
120	29.9

y = growth direction





U.S. DEPARTMENT OF ENERGY

N. Hahn et al. JACS, 2018, 140 (35), 11076

*B.-Q. Fu et al. Appl Surf Sci, 2009, 255, 9348

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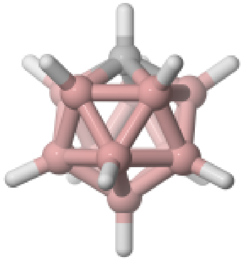
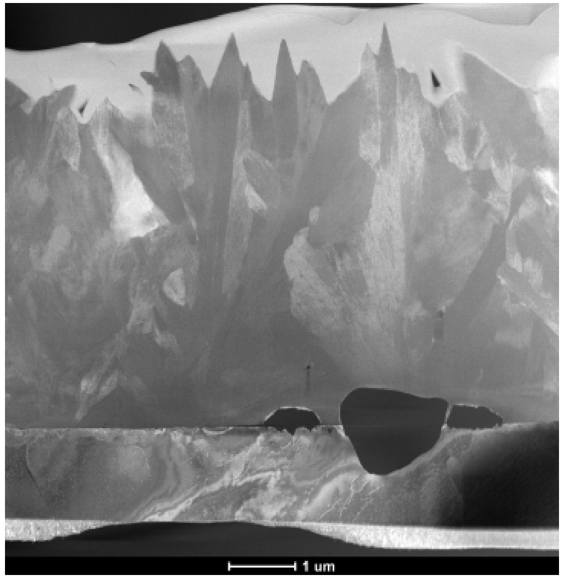
Impurities play a key role in dictating microstructure

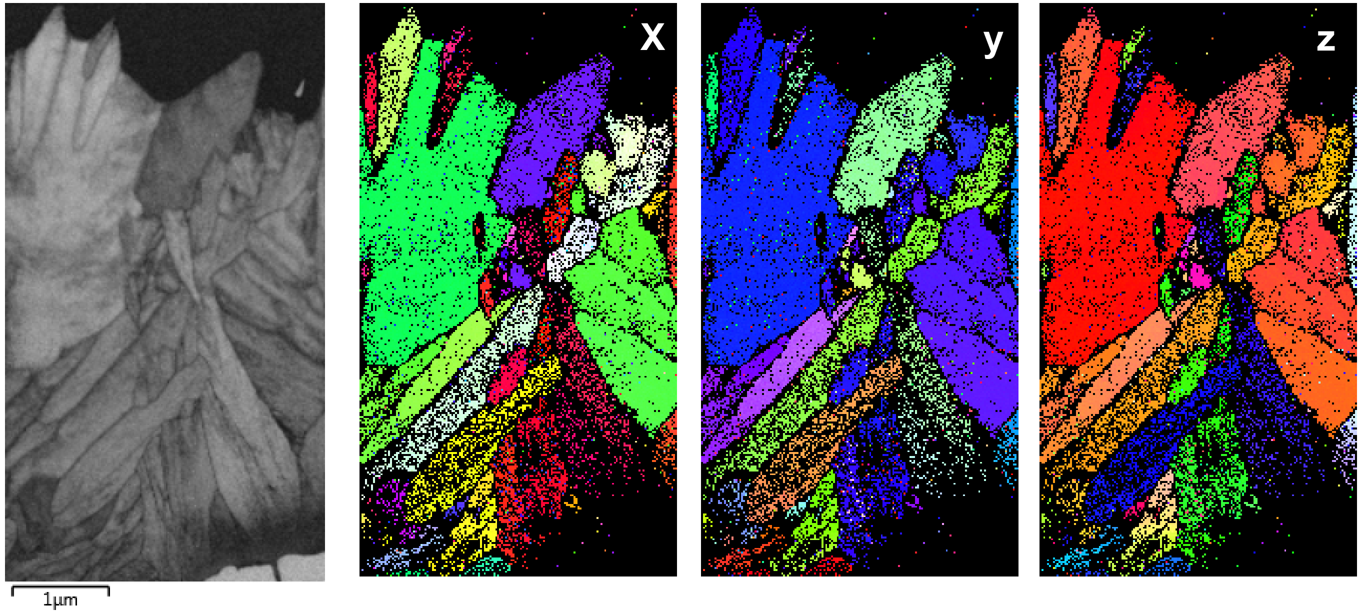
Spike electrolyte with 50 ppm H_2O



$Mg(CB_{11}H_{11})_2 + nG3 + 50\ ppm\ H_2O \rightarrow Mg^{2+}G3_n \cdot H_2O + 2CB_{11}H_{11}^-$

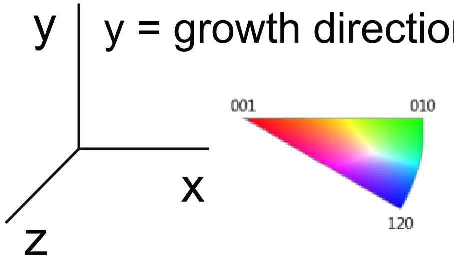
90% CE, 2 mA/cm^2



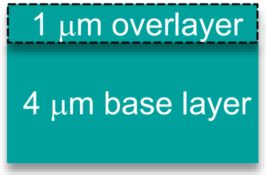


Trace H_2O directs greater degree of isotropic grain growth – displaced the stabilizing .

y = growth direction

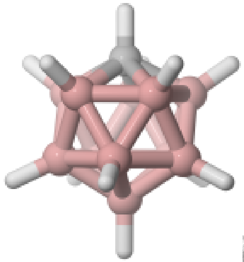


Carborate formed microstructure yields anisotropic dissolution

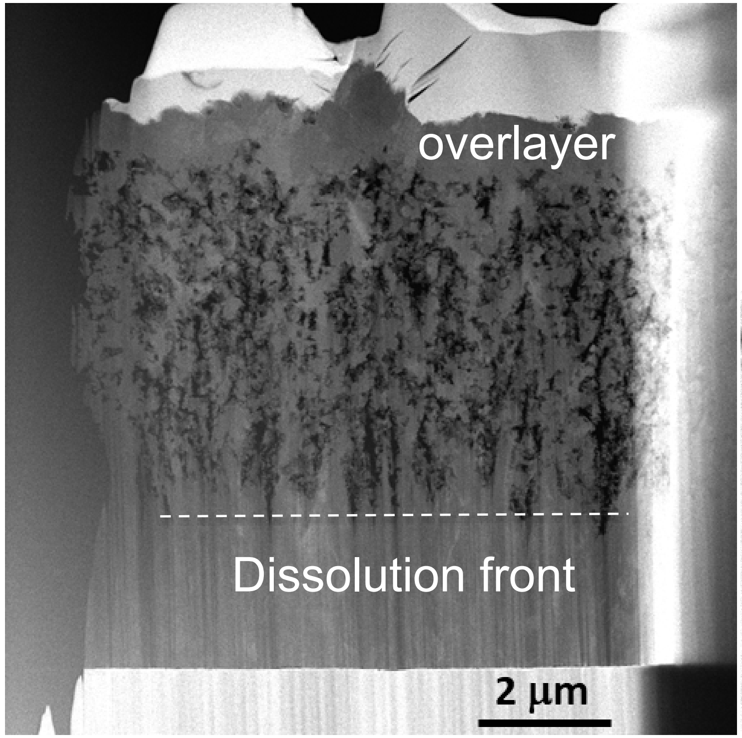


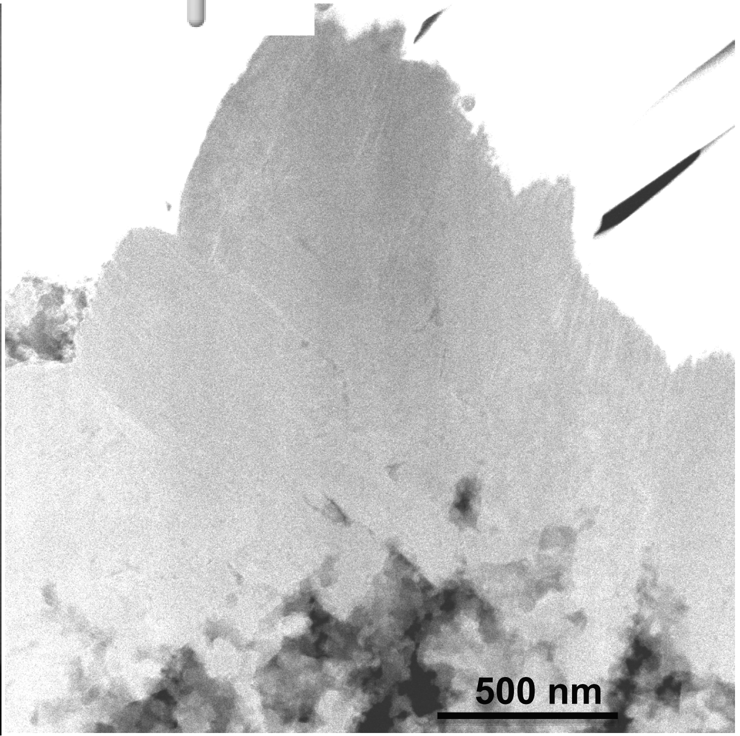
50 cycles @ 2 mA/cm^2

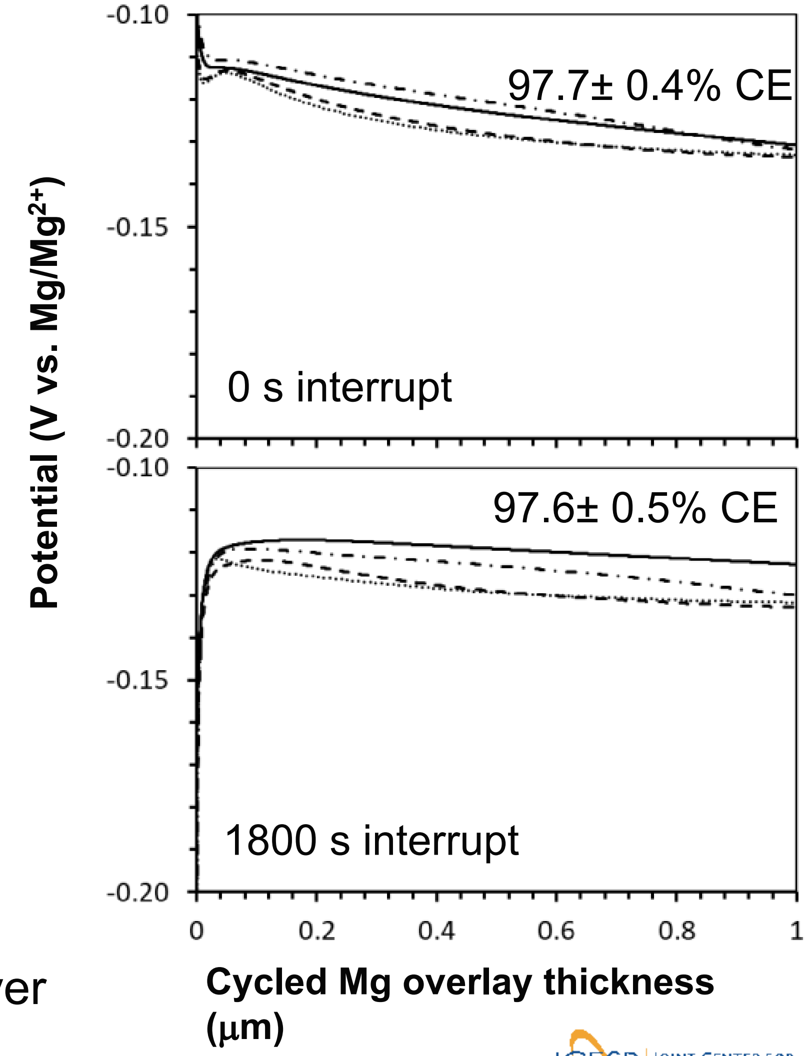
Interrupt 0 to 1800 s



Dry: $Mg(CB_{11}H_{11})_2 \rightarrow Mg^{2+}THF_6 + 2CB_{11}H_{11}^-$







Dissolution occurs along grain boundaries – independent of hold time

Mg redeposits on top of the porous layer

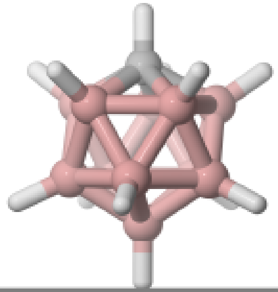
Redeposited layer has a similar microstructure as the original base layer

Carborate formed interphase is a discontinuous oxide

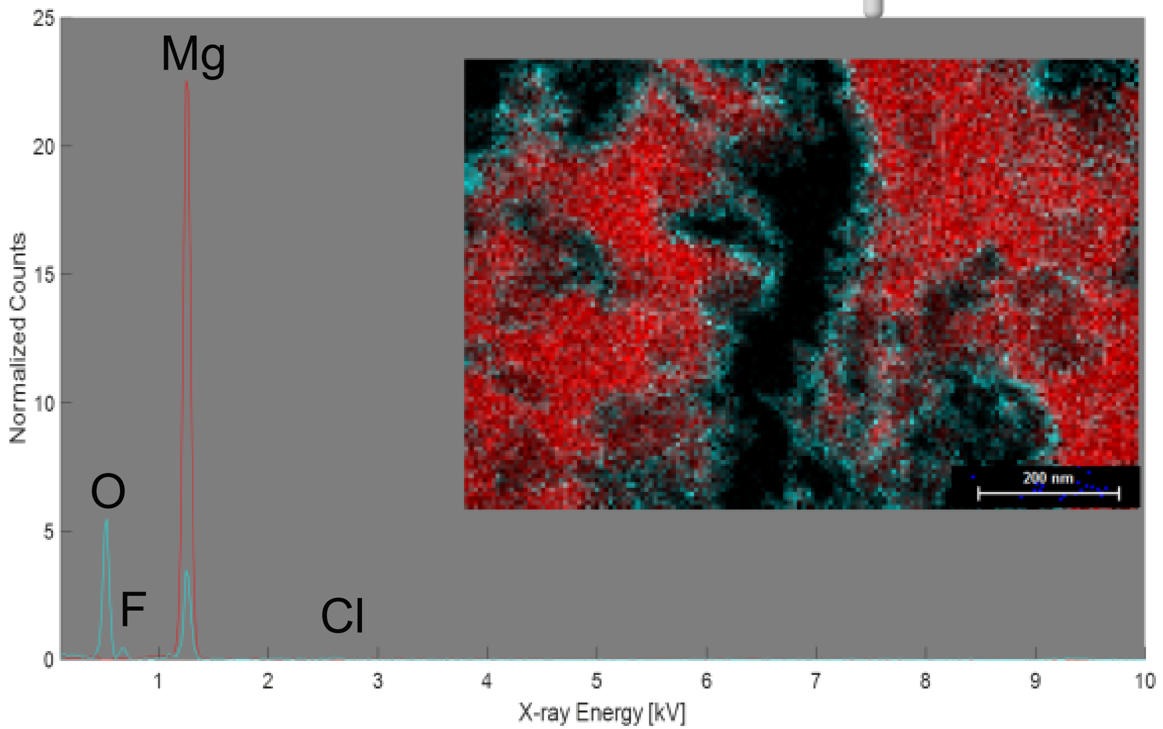
1 μm overlayer
4 μm base layer

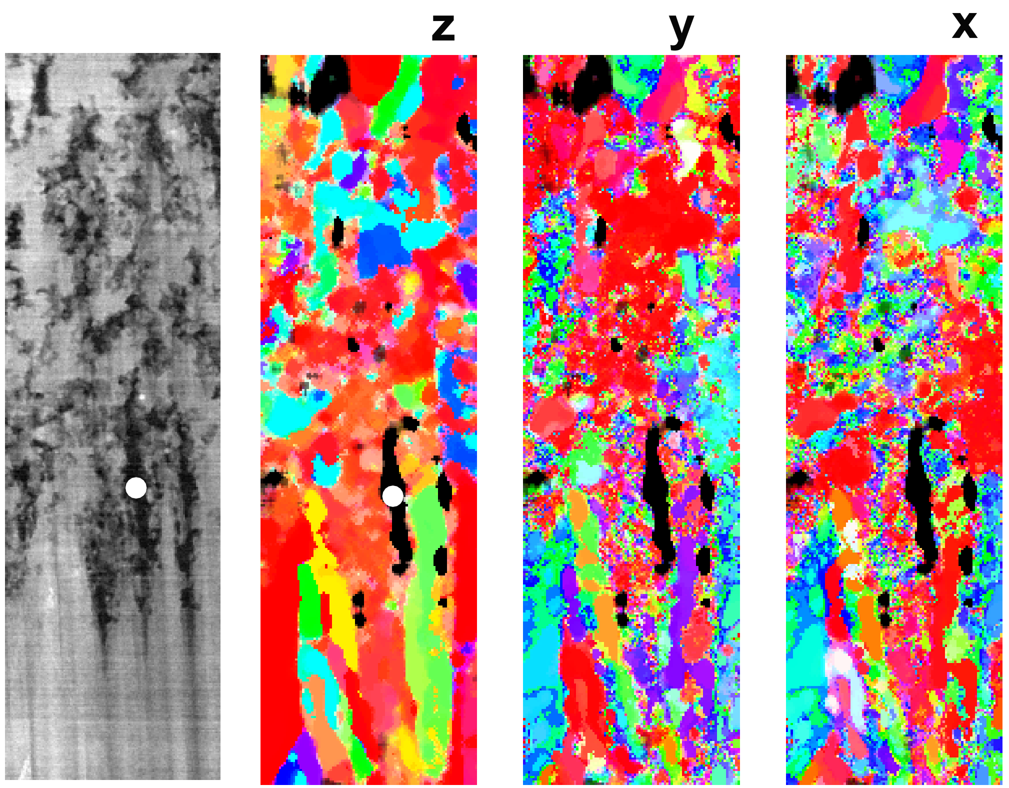
50 cycles @ 2 mA/cm^2

Interrupt 0 to 1800 s



$Mg(CB_{11}H_{11})_2 \rightarrow Mg^{2+}THF_6 + 2CB_{11}H_{11}^-$





Coordinates [0001]; [10-10]; [2-1-10]

y = growth direction

Dissolution pore walls are oxide capped - crystalline?

Change in crystallinity and orientation?

Message?

Conclusions

- Epitaxial electrodeposition of Mg is possible in Mg chloroaluminate electrolytes. We believe that epitaxy is possible in a range of chloro-Mg complex forming electrolytes.
- The effect of free chloride is short lived as re-equilibration of the stripped interface results in Cl^- loss and O, Al accumulation. Continued cycling drives localized activity, parasitic losses, and porosity.
- Mg can be deposited as fully solvated dication $Mg^{2+}G3_n$ using the carba-closo-dodecaborate anion yielding continuous, crystalline films with growth occurring along the prismatic axes.
- Cycling produces anisotropic dissolution propagating vertically through the film with redeposition on top, resulting in a thickening of the porous body.

Acknowledgements

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- Timothy Ruggles (SNL) TKD
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- Colin Ophus (LBNL) ACOM

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