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

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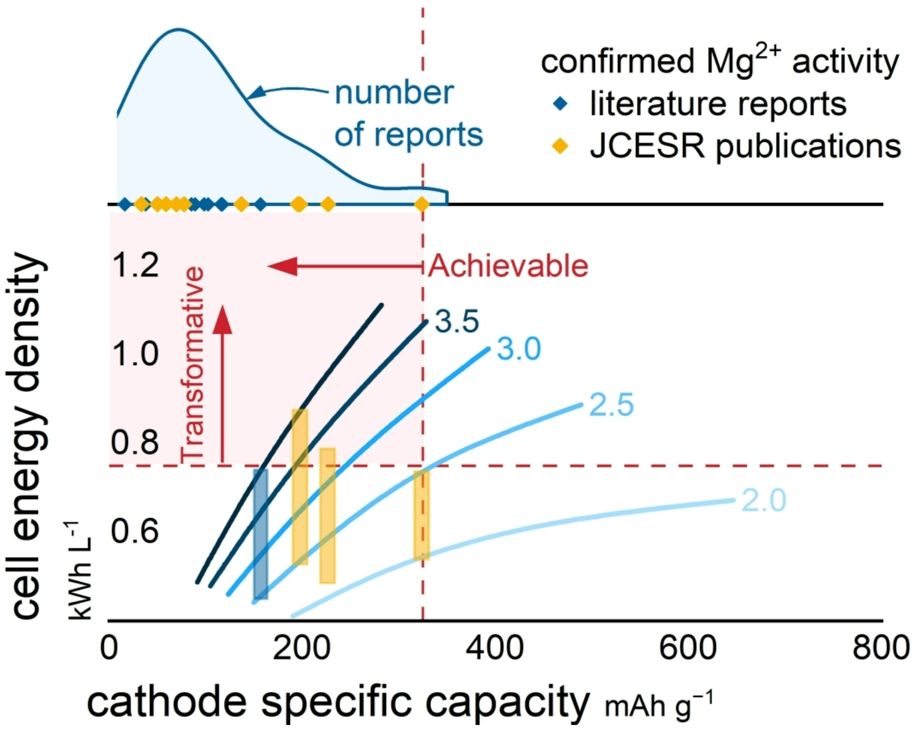
Multivalent metal ion batteries could provide transformative energy densities

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



<u>Current materials challenges</u>

metal coulombic efficiency

electrolyte redox stability

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 deposition

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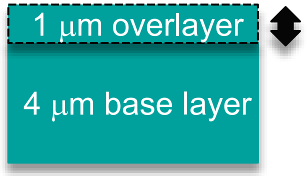
Free Cl^- as an ideal interphase former for Mg deposition

MACC: $MgCl_2 + AlCl_3 + nTHF \rightarrow$ **$Mg_2Cl_3^+THF_n$** $+ AlCl_4^-$

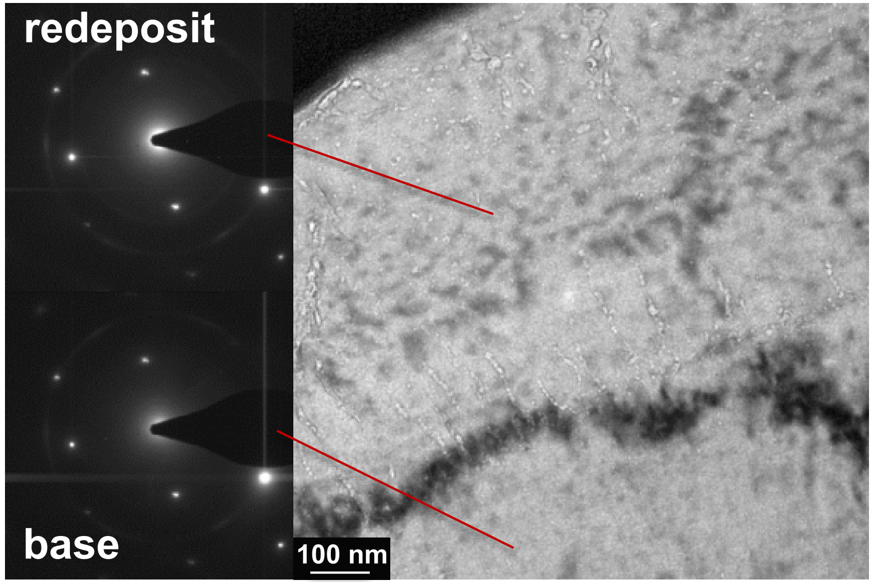


50 cycles @ 2 mA/cm^2

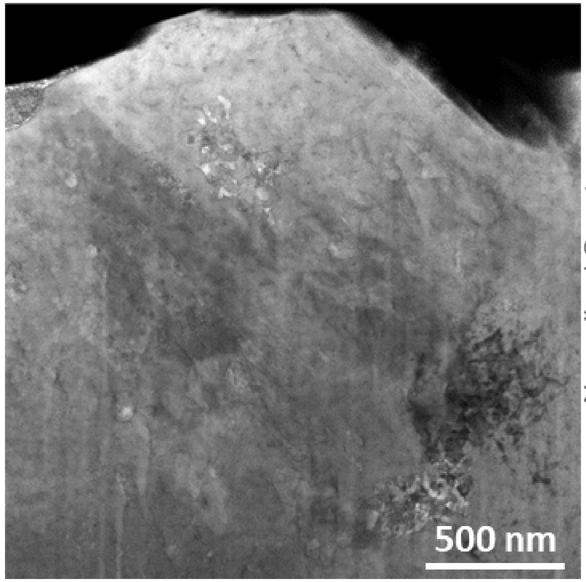
Equilibrate between cycles
Interrupt 0 to 1800 s

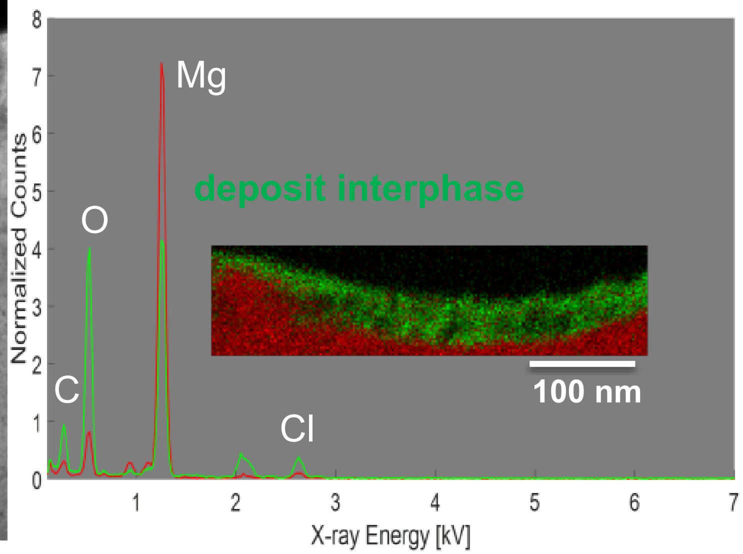
APC: $2PhMgCl + AlCl_3 + nTHF \rightarrow$ **$Mg_2Cl_3^+THF_n$** $+ Ph_2AlCl_2^-$

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





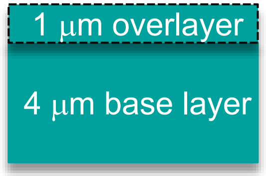
Epitaxial Mg deposition – same orientation within a grain from substrate to electrolyte interface

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

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

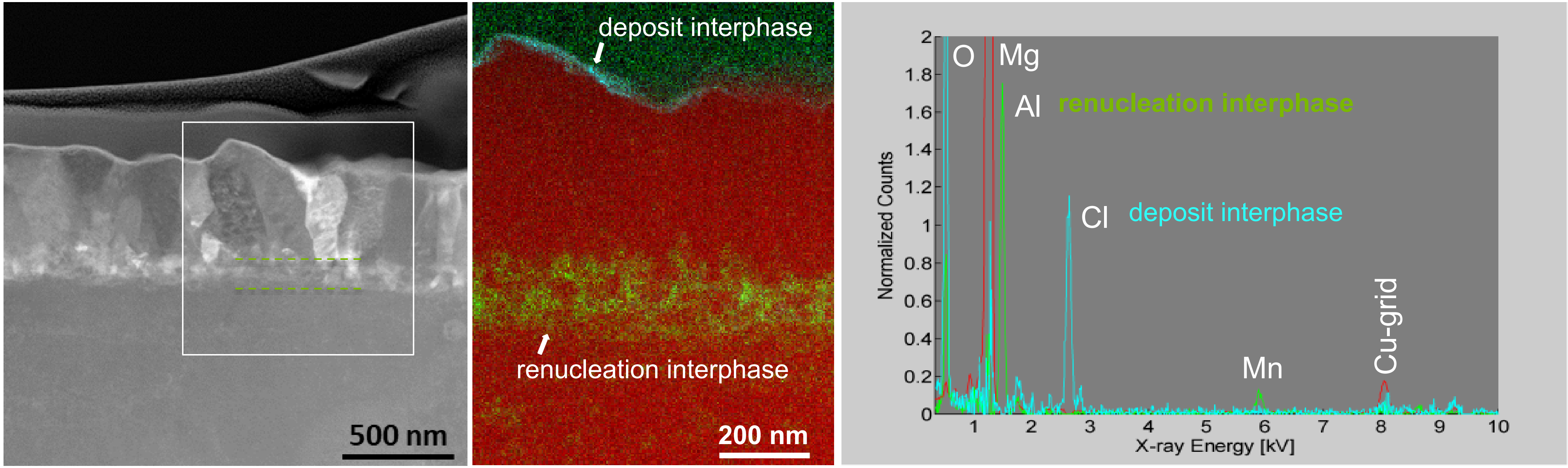


50 cycles @ 2 mA/cm^2

Interrupt 0 to 7200 s

Electrolyte does not support 100% CE

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



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

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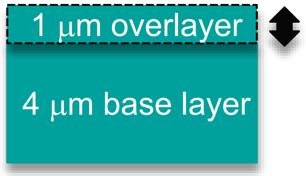
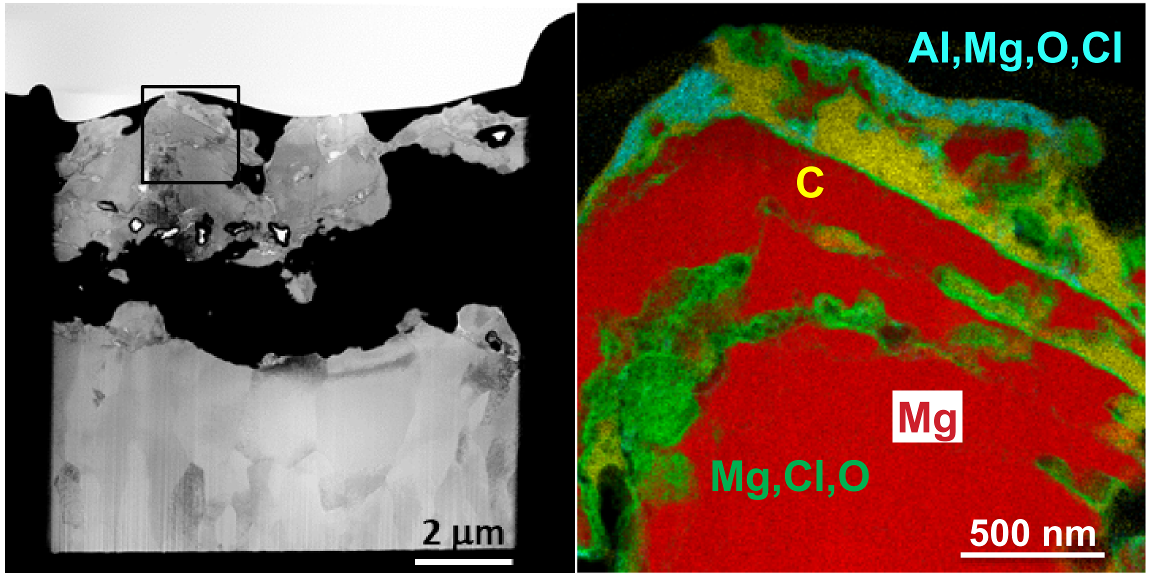
Free Cl^- protection of the Mg surface is short-lived



50 cycles @ 2 mA/cm^2

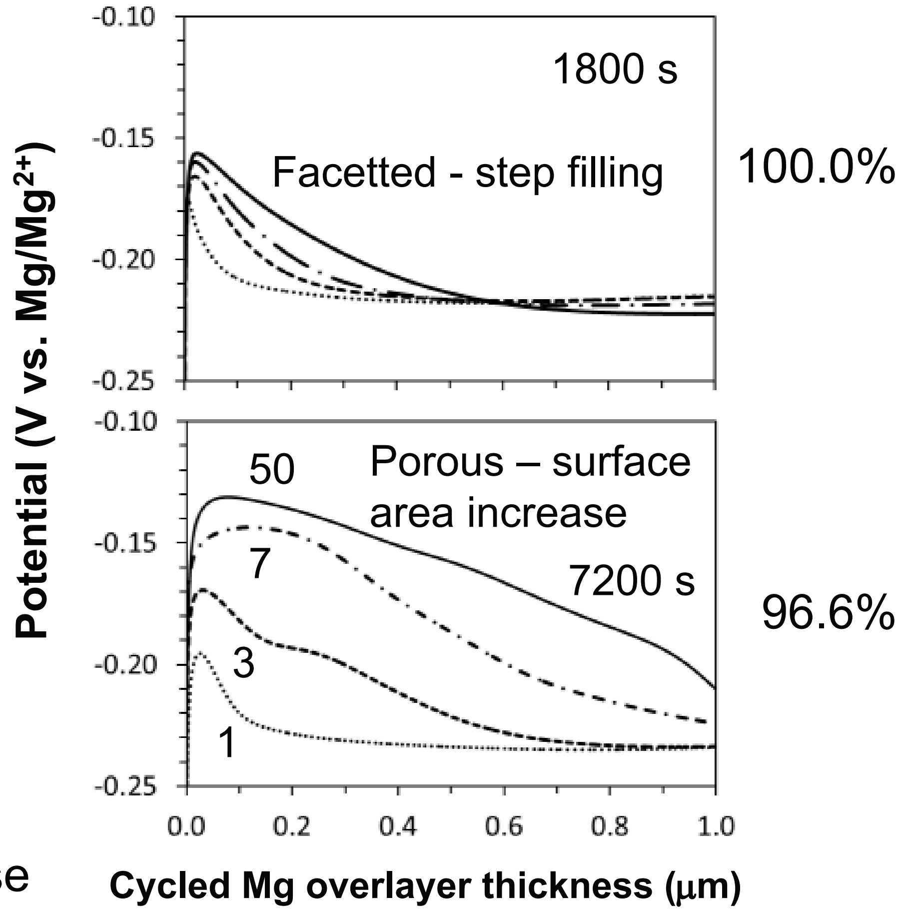
Interrupt 7200 s

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



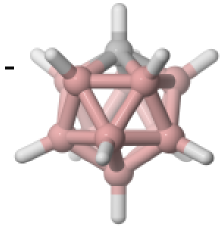
Accumulation of Al, O, Cl in a highly heterogeneous interphase

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



Mg deposit structure/orientation change dramatically without Cl^-

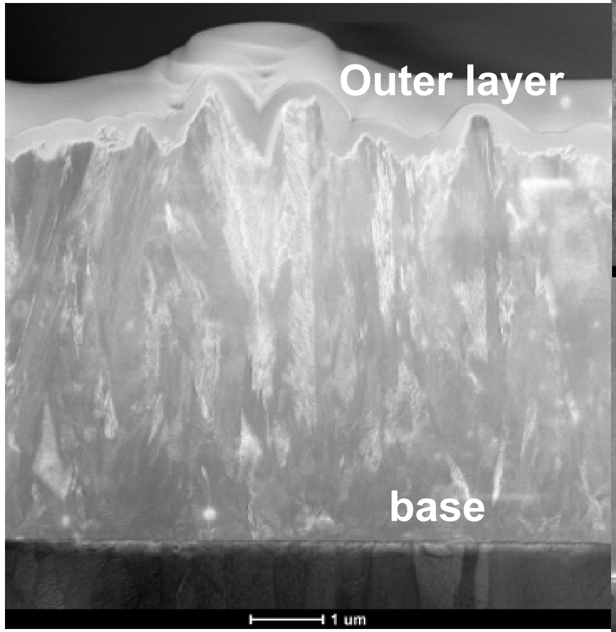
$Mg(CB_{11}H_{11})_2 \rightarrow Mg^{2+}G3_n + 2CB_{11}H_{11}^-$

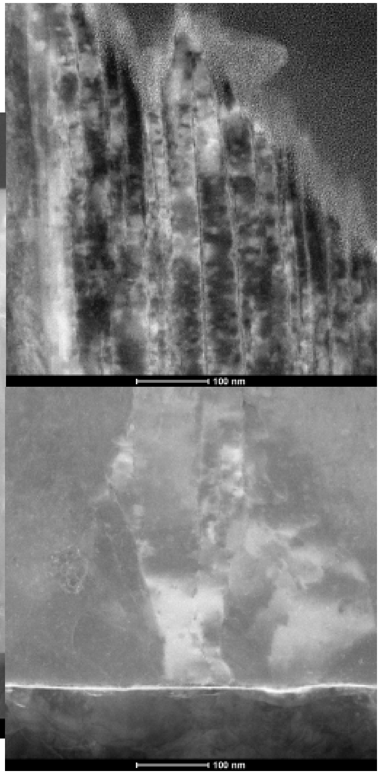


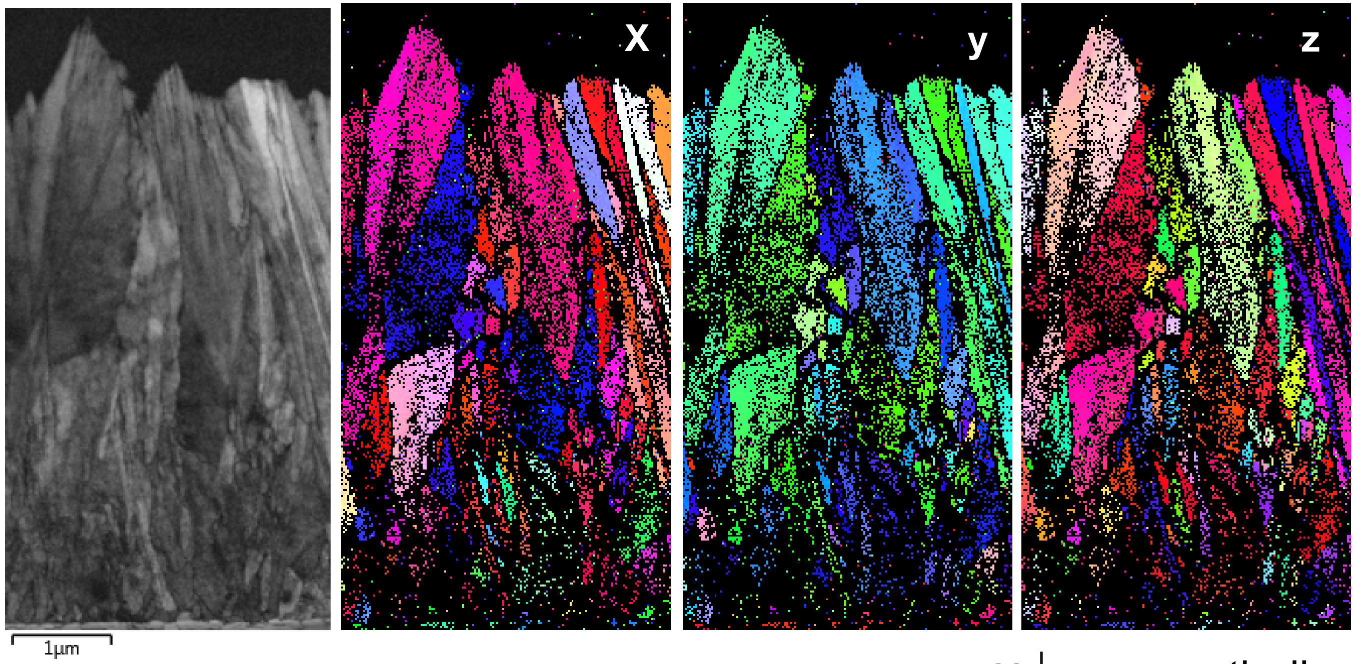
G3 is stabilized to reductive decomposition

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

99.3 ± 0.2% CE, 2 mA/cm^2



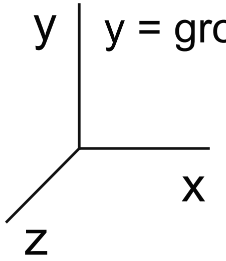




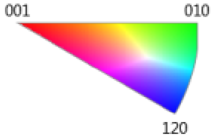
Growth of dense continuous films – absent a TEM discernable interphase at the Pt:Mg interface, XPS shows O, C at surface

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

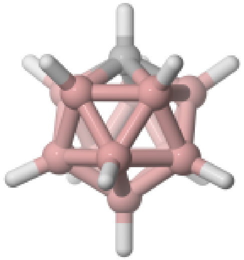


N. Hahn et al. JACS, 2018, 140 (35), 11076

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

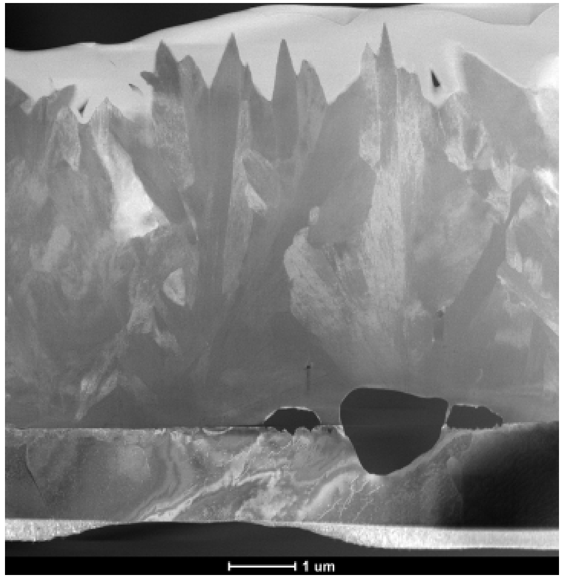
Impurities play a key role in dictating microstructure

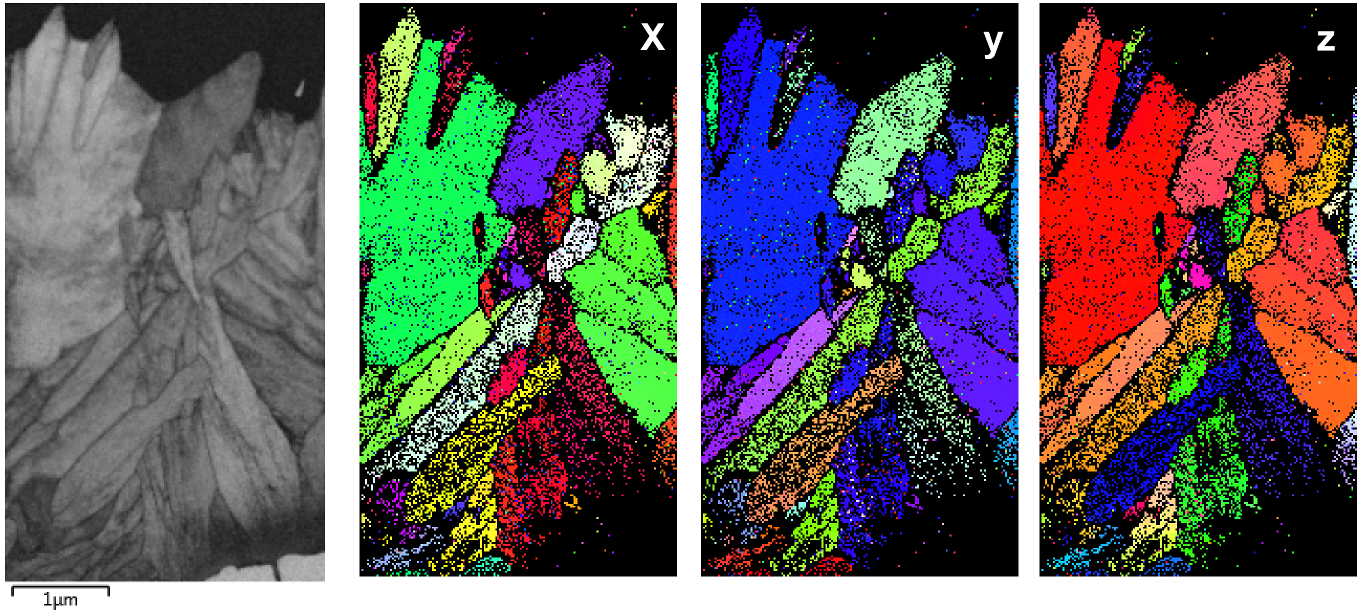
Spike electrolyte with 50 ppm H_2O



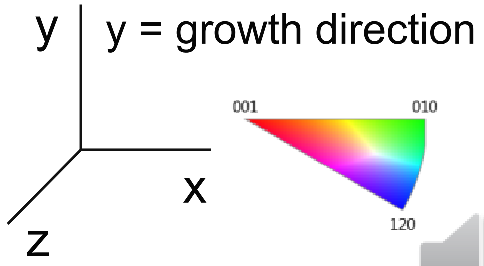
$Mg(CB_{11}H_{11})_2 + nG3 + 50\ ppm\ H_2O \rightarrow Mg^{2+}G3_n \cdot H_2O + 2CB_{11}H_{11}^-$

90% CE, 2 mA/cm^2

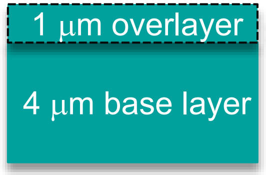




Trace H_2O directs greater degree of isotropic grain growth – water will be tied up in coordination with Mg^{2+} and this is the complex that is altering surface energetics.

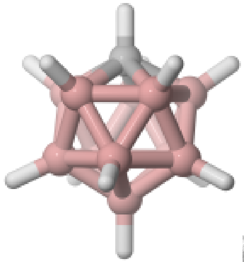


Carborate formed microstructure yields anisotropic dissolution

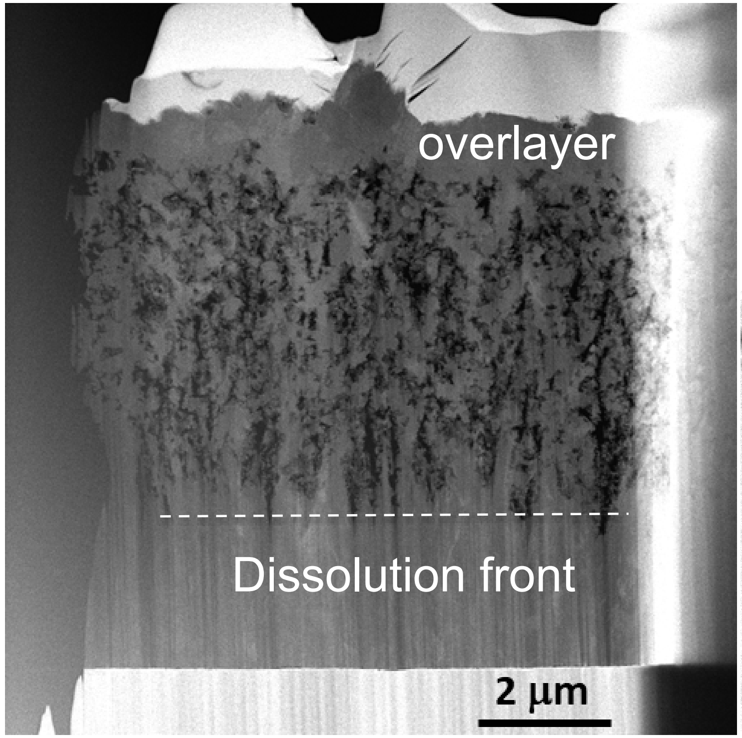


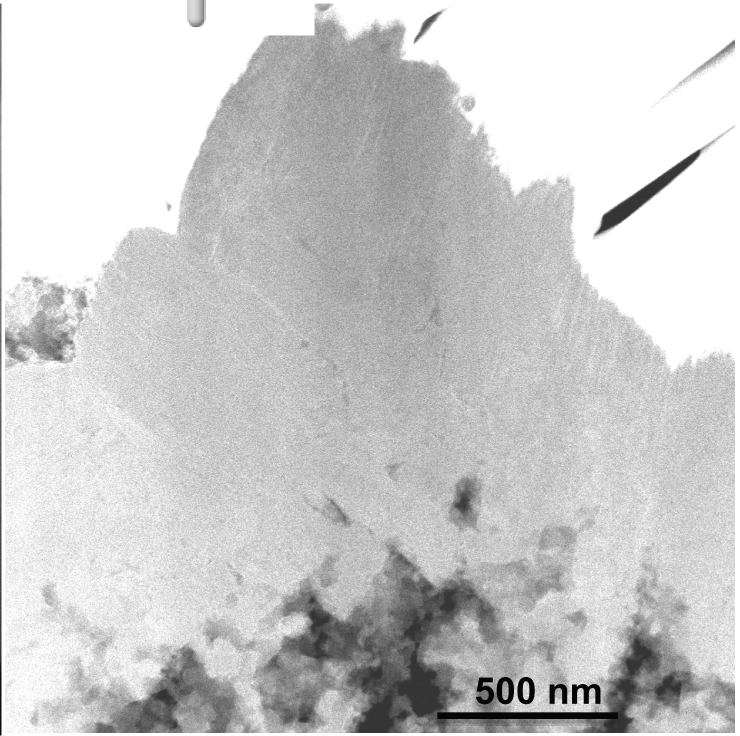
50 cycles @ 2 mA/cm^2

Interrupt 0 to 1800 s

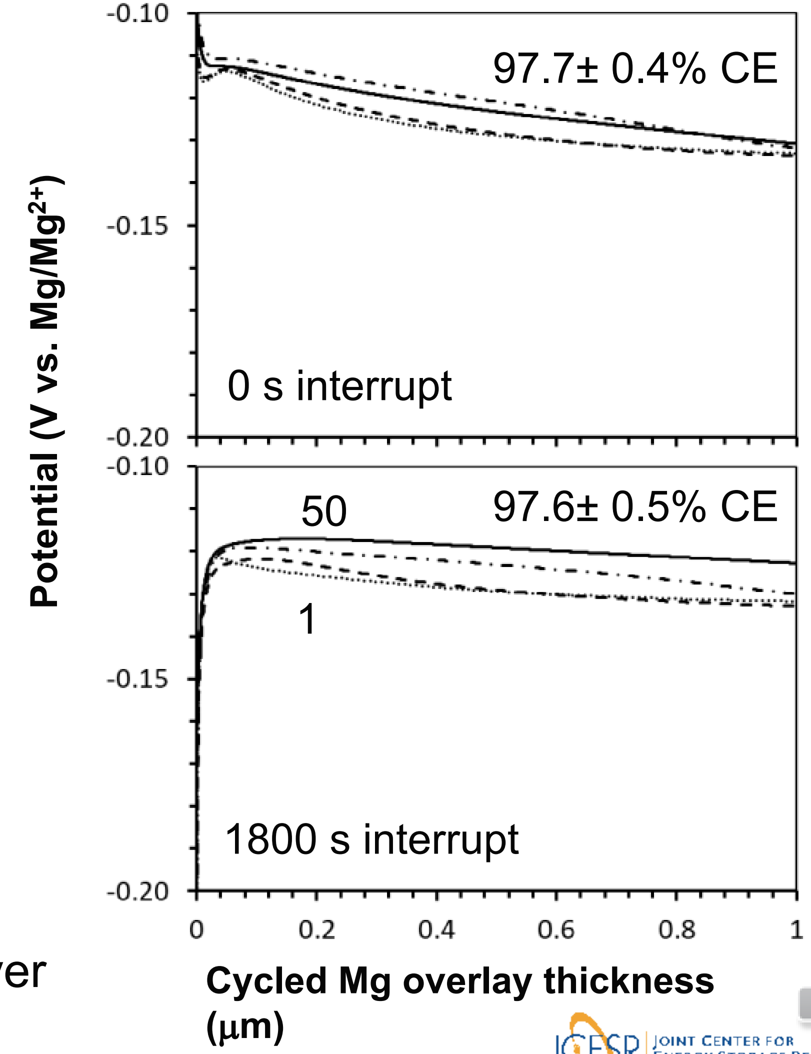


Dry: $Mg(CB_{11}H_{11})_2 \rightarrow Mg^{2+}G3_n + 2CB_{11}H_{11}^-$





Single cycle 99.3 ± 0.2% CE, 2 mA/cm^2



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

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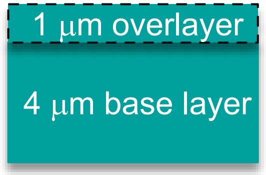
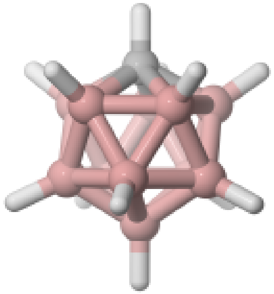
Carborate formed interphase is a discontinuous oxide



50 cycles @ 2 mA/cm^2

Interrupt 0 to 1800 s



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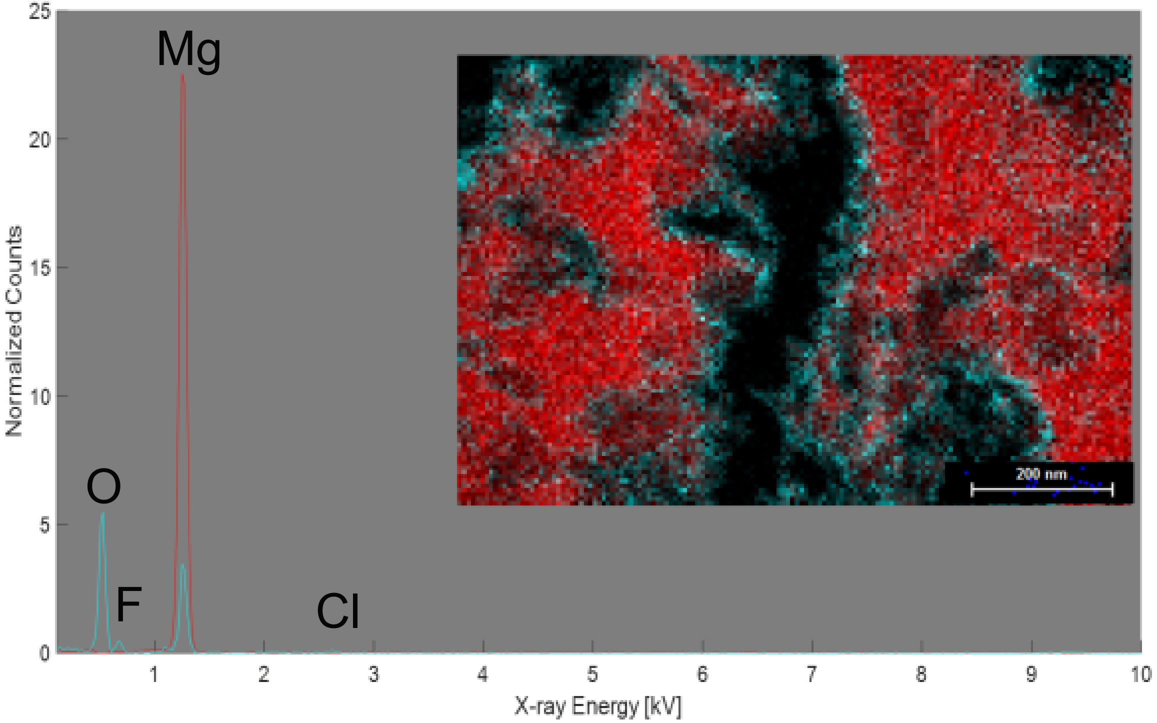
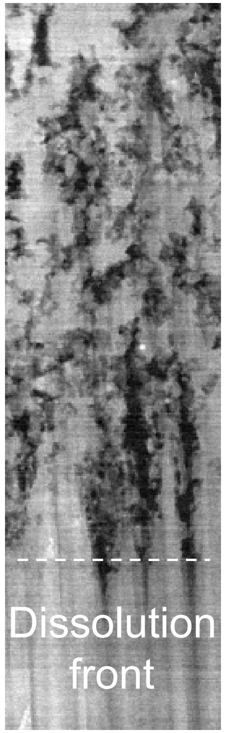
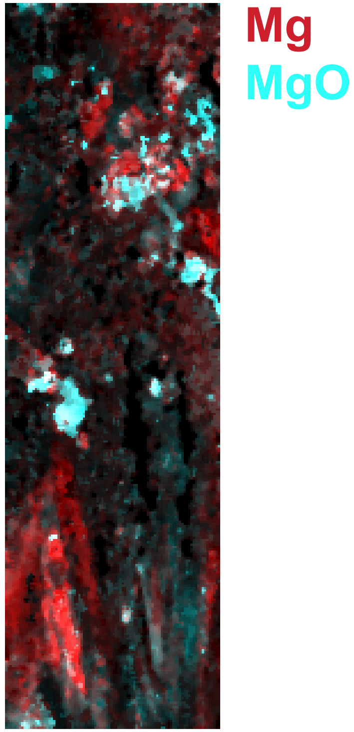


HAADF



CBD



Dissolution pore walls are oxide capped

Basic crystallinity and orientation are unchanged

Capping oxide is crystalline, heterogeneous

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 decreased efficiency, 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.

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

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