Mapping Mechanisms and Growth Regimes of Magnesium Electrodeposition at High Current Densities


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**Figure S1.** A) XPS survey scan measured for detached Mg fractal deposits formed at a current density of 0.921 mA/cm$^2$ from a 0.5M solution of MeMgCl in THF; High-resolution XPS spectra measured at B) Mg 2p; C) O 1s; D) C 1s regions; and E) high-resolution Cl 2p XPS spectrum. Spectral assignments are indicated for each of the deconvoluted lines.

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**Figure S2.** Projections of 3D tomographic maps from soft-X-ray microscopy at the Mg K-edge acquired at tilt angles of A) 40°, B) 80°, and C) 120°.
Figure S3. Plots of voltage versus time for the electrodeposition of Mg from MeMgCl as a function of applied current density for electrodeposition reactions at A) 0.307, B) 0.921, and C) 1.54 mA/cm² constant current applied for 8 h in 0.5 M MeMgCl solutions in THF.

Figure S4. Plots of voltage versus time for the electrodeposition of Mg from MeMgCl as a function of concentration of electrolyte showing plots for reactions run with A) 0.25, B) 0.5, C) 1.0, D) 1.5, E) 2.0 M MeMgCl electrolyte solutions under a constant current of 0.921 mA/cm² applied for 24
Figure S5. Digital image of a dendrite deposited under 0.921 mA/cm² applied current density in a 1.5 M MeMgCl solution for 24 h.

Figure S6. A) XPS survey scan measured for detached Mg fractal deposits formed at a current density of 0.921 mA/cm² from a 0.5M solution of MeMgCl in THF with the addition of oleylamine; High-resolution XPS spectra measured at B) Mg 2p; C) O 1s; D) C 1s regions; E) high-resolution Cl 2p XPS spectrum; and F) N 1s. Spectral assignments are indicated for each of the deconvoluted lines.
Figure S7. Optical image acquired for a set of indents in the cross-section of a polished Mg dendrite grown in 0.5 M MeMgCl solutions under 0.921 mA/cm$^2$ applied constant current for 24 h, displaying insignificant indentation pile-up.

Figure S8. Powder XRD patterns for Mg deposits electrodeposited at a current density of 0.921 mA/cm$^2$ from 0.5M MeMgCl electrolyte solutions with the addition of dodecanethiol and oleylamine. The reflections can be indexed to metallic Mg with hexagonal close packing of atoms (PDF 35-0821).
Figure S9. A) XPS survey scan measured for detached Mg fractal deposits formed at a current density of 0.921 mA/cm$^2$ from a 0.5M solution of MeMgCl in THF with the addition of dodecanethiol; High-resolution XPS spectra measured at B) Mg 2p; C) O 1s; D) C 1s regions; E) high-resolution Cl 2p XPS spectrum; and F) S 2p. Spectral assignments are indicated for each of the deconvoluted lines.

Figure S10. Digital images of an Mg ribbon and disk electrode as a function of time upon electrodeposition from a 0.5 M MeMgCl solution in THF under a 0.921 mA/cm$^2$ applied current density held constant for 24 h.
Figure S11. A) Hypothetical phase diagram and charge-neutral plane for Mg(M)-MeMgCl-THF. B) Dendrite formed following initial seeding at the bottom center of the domain. C) Phase-field order parameters extracted along the blue line in (B). D) Comparison of the nonlinear phase-field model with a Butler-Volmer symmetric coefficient of $\alpha=0.5$ used in this study and Butler-Volmer coefficients reported by Viestfrid and co. workers$^1$ for (0.25 M complex in THF) and for (0.25 M complex in (0.25 M Bu$_2$Mg + THF) solutions.

Phase-field modeling of dendritic growth. The model described here was developed based on the earlier work of Guyer et. al$^2$, Bazant$^3$, Chen et al$^4$, and Yurkiv et al$^5$. Primary deposition occurs through the reaction of $M^{n+}$ cations in the electrolyte solution ($M^{n+} + e^-$) with electrons $e^-$ at the surface of the electrode. In an isothermal and isobaric state, the total free energy of a heterogeneous system with constant volume $V$ is given by:

$$ F^{tot}(\zeta, c_i, \nabla c_i, \psi) = \int_V \left[ f^{chem} + f^{int} + f^{elec} + f^{noise} \right] dV $$

(S1)
where $f_{\text{chem}}$, $f_{\text{int}}$, $f_{\text{elec}}$ and $f_{\text{noise}}$ are the chemical, interfacial, electrical, and Langevin noise contributions respectively, given as:

$$f_{\text{chem}} = g(\bar{c}) + RT[\bar{c}_+ \ln(\bar{c}_+) + \bar{c}_- \ln(\bar{c}_-)]$$  \hspace{1cm} (S2)

$$f_{\text{int}} = \frac{1}{2} \nabla \kappa \cdot \nabla c$$  \hspace{1cm} (S3)

$$f_{\text{elec}} = \mathcal{F} \sum_i z_i c_i \psi$$  \hspace{1cm} (S4)

$$f_{\text{noise}} = A h'(\zeta) \chi$$  \hspace{1cm} (S5)

where $g(\bar{c}) = W \bar{c}^2(1 - \bar{c}^2) = W^2(1 - \bar{c}^2)$ is a double well potential function with $W$ being the barrier height of transformation in between the equilibrium states of the electrode and electrolyte. The second term in Eq. (S2) is the entropic contribution of mixing ions where $R$ is the ideal gas constant, and $T$ is the operating temperature. $f_{\text{int}}$ describes the interfacial contributions due to heterogeneous nature of the electrode-electrolyte interface where the anisotropic characteristics of this interface was taken into account by:

$$\kappa(\theta) = \kappa_0(1 + \delta \cos[j \theta - \theta_0])$$  \hspace{1cm} (S6)

where $\delta$ and $j$ are the strength and mode of anisotropy, respectively; $\kappa_0$ is the interface energy gradient, $\theta$ and $\theta_0$ are related to the angle between the normal vector of the surface and the reference axis. $f_{\text{elec}}$ is the electrostatic energy density, where $\mathcal{F}$ and $z_i$ are the Faraday's constant and valence of species $i$, respectively. An additional phase-field variable was used to distinguish the states of the electrolyte ($\zeta = 0$) and electrode ($\zeta = 1$), which continuously changes in the interface region. $f_{\text{noise}}$ denotes the Langevin noise, which was applied to the interface region by using $\chi$, which is a quasi-random number between [-1,1], and $A$ is the amplitude of the fluctuation. The evolution of the non-conserved, conserved, and electrostatic fields were prescribed by the following equations, respectively:

$$\frac{\partial \zeta}{\partial t} = -L_\sigma (g'(\zeta) - \kappa(\theta) \nabla^2 \zeta) - \Gamma$$  \hspace{1cm} (S7)

$$\frac{\partial c_+}{\partial t} = \nabla \left[ D_{\text{eff}} \nabla c_+ + \frac{D_{\text{eff}} c_+}{RT} \mathcal{F} \nabla \psi \right] - \frac{c_+}{c_0} \frac{\partial \zeta}{\partial t}$$  \hspace{1cm} (S8)

$$\nabla [\sigma_{\text{eff}} \nabla \psi] = n \mathcal{F} c_s \frac{\partial \zeta}{\partial t}$$  \hspace{1cm} (S9)
where $L_\alpha$ is the interface mobility, and $\Gamma$ is the electrodeposition rate defined by:

$$\Gamma = L_\eta i_0 h'(\zeta) \left\{ e^{\frac{(1-\alpha)nF\eta_a}{RT}} - c_+ e^{\frac{(\alpha)nF\eta_a}{RT}} \right\}$$  

where $L_\eta$ is the reaction related kinetic coefficient, $i_0$ is the exchange current density, $h'$ is the derivative of the interpolation function $h(\zeta) = \zeta^3(10 - 15\zeta + 6\zeta^2)$, $\alpha$ is the anodic/cathodic symmetric charge-transfer coefficient (assumed to be 0.5 in this study ($0 < \alpha < 1$)), and $\eta_a$ is the overpotential. $D_{\text{eff}}$ and $\sigma_{\text{eff}}$ are the interdiffusion and conductivity, respectively defined over the domain by means of the interpolation function $h(\zeta)$. The source term in Eq. (S9) is related to reaction rate.

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<tr>
<th>Table S1. List of boundary conditions used for equations 7-9</th>
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References: