**Supporting Information** 

## **Elucidating Zn and Mg Electrodeposition Mechanisms in Nonaqueous Electrolytes for Next-Generation Metal Batteries**

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**Voltammetric Simulations.** The voltammograms obtained with the Pt UME working electrode were simulated with the COMSOL Multiphysics 5.2a platform. Two geometric rectangles represented the solution in the electrochemical cell and a disc with  $r = 12.5 \mu m$  represented the working UME. When rotated around the 2D axis-symmetry, the rectangles formed cylinders in 3D symmetry. Inside the rectangles, diffusion under Fick's law of the oxidizing species was described using the Diffusion within the Transport of Dilute Species (TDS) module. Diffusion of active species in electrolyte is governed by Fick's first and second laws of diffusion, which describe the flux of species and its concentration as functions of distance and time:

$$J = -D\nabla C \tag{1}$$

where *J* is the molar flux of the area normal to axis of diffusion, *D* is the diffusion coefficient, and  $\nabla C = \frac{\partial C(x,t)}{\partial x}$  is the concentration gradient.

$$\frac{\partial C}{\partial t} = D\nabla^2 C \tag{2}$$

for an inlaid disk UME,  $\nabla^2 = \frac{\partial^2}{\partial r^2} + \left(\frac{1}{r}\right)\left(\frac{\partial}{\partial r}\right) + \frac{\partial^2}{\partial z^2}$  where *r* is the radius of electrode and *z* is the

distance normal to the disk surface. The first boundary condition (Type 1, Figure S1) was assigned to the area of the UME under Flux condition in the TDS module and Reactions condition in Surface Reaction (SR) module. Within the TDS module, the Flux boundary was described using Butler-Volmer kinetics, simulating the adsorption of the oxidized species as negative flux with appropriate rate constants, while the same amount was added onto the surface in Reactions boundary under SR module. Type 2 (Figure S1) boundary conditions illustrated the glass insulator surrounding the UME and were simulated using the No Flux condition in TDS module. The bulk solution was simulated as a semi-infinite liquid with the concentration of the oxidized species, set to the nominal concentration of the as-prepared electrolytes, under Open Boundary condition in the last boundary conditions (Type 3, Figure S1). Chemicalelectrochemical (CE) type mechanism was simulated using Bulk Reaction condition in the TDS module. The reaction rates of the two species in solution prior to electrochemical step were described using rate equations with associated rate constants.



**Figure S1.** Boundary conditions assigned to specific domains in simulated electrochemical system in COMSOL Multiphysics. Boundary lengths are not to scale.



**Figure S2.** Overlay experimental and simulated CVs of Zn electrodeposition/stripping at a 25– um Pt UME in 0.5 mM Zn(TFSI)<sub>2</sub> + 0.5 mM ZnCl<sub>2</sub> in MeCN. Errors in the fit are estimated to be  $\leq 10\%$ .



**Figure S3.** (a), (b), and (c) show CVs of Mg deposition/stripping at a Pt macroelectrode (2.5-mm radius) in 0.5 M, 0.1 M, and 25 mM (DTBP)MgCl-AlCl<sub>3</sub> electrolyte solution at 5 mV/s, respectively.