

# ND ENERGY STUDENT RESEARCH FELLOWSHIP FINAL REPORT

<b>STUDENT NAME:</b>	Laura Merrill
<b>FACULTY ADVISOR:</b>	Jennifer Schaefer
<b>REPORT PERIOD:</b>	2019
<b>PROJECT TITLE:</b>	The Role of Morphology and Electrochemical Interface on the Electrodeposition/Dissolution Efficiency of Magnesium Batteries
<b>CONNECTION TO ND ENERGY'S RESEARCH AREAS (CHECK ALL THAT APPLY):</b>	<input type="checkbox"/> Energy Conversion and Efficiency <input type="checkbox"/> Sustainable and Secure Nuclear <input checked="" type="checkbox"/> Smart Storage and Distribution <input type="checkbox"/> Transformation Solar <input type="checkbox"/> Sustainable Bio/Fossil Fuels <input type="checkbox"/> Transformative Wind

## MAJOR GOALS AND ACCOMPLISHMENTS:

List your major research goals and provide a brief description of your accomplishments (1-2 sentences). Indicate the percentage completed for each goal. Please use a separate sheet to share additional details, technical results, charts, and graphics.

MAJOR RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
<b>Study Effect of Deposition Morphology on Efficiency</b>	<p>Through this study I found that the use of the highly thermally stable solvents cause the magnesium deposits to be globular and lead to short circuiting. This is caused by a boundary layer that alters the surface energies at the interface. This then leads to short circuiting over time suggesting that the sulfones will not be effective practically in a battery.</p> <p>The results from this work are published in a peer reviewed journal.</p>	100
<b>Artificial Solid Electrolyte Interphase Using an Ionic Polymer</b>	<p>We developed thin film coatings of ionomeric materials to be used as an artificial SEI on a commercial separator. And via aging tests, they did prove to be effective in preventing decomposition on the magnesium surface. However, the presence of the coating did not alter the electrochemical performance of the battery as anticipated.</p> <p>I did, however, go on to do an in depth study of the ionomer materials for use as a bulk electrolyte material but it was found that these materials are intrinsically limited due to low conductivities and high resistances. This secondary study is published in a peer reviewed journal.</p>	40

## RESEARCH OUTPUT:

Please provide detailed information below regarding any output resulting from your research project.

CATEGORY	INFORMATION
<b>EXTERNAL PROPOSALS</b>	(Sponsor, Project Title, PIs, Submission Date, Proposal Amount) N/A
<b>EXTERNAL AWARDS</b>	(Sponsor, Project Title, PIs, Award Date, Award Amount) N/A
<b>JOURNAL ARTICLES</b>	<p>(Journal Name, Title, Authors, Submission Date, Publication Date, Volume #, Page #s) Frontiers in Chemistry; The influence of interfacial chemistry on magnesium electrodeposition in non-nucleophilic electrolytes using sulfone-ether mixtures; Laura Merrill and Jennifer Schaefer; 01/2019; 04/2019; vol 7; 194</p> <p>ACS Applied Energy Materials; Application of Single-Ion Conducting Gel Polymer Electrolytes in Magnesium Batteries; Laura Merrill, Hunter Ford, and Jennifer Schaefer; 05/2019; 08/2019; vol 2; 6355-6363</p>

<b>BOOKS AND CHAPTERS</b>	(Book Title, Chapter Title, Authors, Submission Date, Publication Date, Volume #, Page #s) N/A
<b>PUBLIC PRESENTATIONS, SEMINARS, LECTURES</b>	(Event, Presentation Title, Presentation Date, Location) N/A
<b>AWARDS, PRIZES, RECOGNITIONS</b>	(Purpose, Title, Date Received) N/A
<b>INTERNAL COLLABORATIONS FOSTERED</b>	(Collaborator Name, Organization, Purpose of Affiliation) N/A
<b>EXTERNAL COLLABORATIONS FOSTERED</b>	(Collaborator Name, Organization, Purpose of Affiliation) Xi Chen, Oak Ridge National Laboratory, ASTRO Participant  I went to ORNL through their Advanced Short Term Research Opportunity (ASTRO) to study the ionomer materials we study in the Schaefer lab in composite (ceramic/polymer blend) form at ORNL.
<b>WEBSITE(S) FEATURING RESEARCH PROJECT</b>	(URL) N/A
<b>OTHER PRODUCTS AND SERVICES</b> (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	(Please describe each item in detail)

### **MAJOR GOALS AND ACCOMPLISHMENTS** (Additional Details, Technical Results, Charts and Graphics)

From the first objective, I was able to determine that the solvent composition dramatically impacts the deposition morphology, as observed in Figure 1. This is due to a large interfacial impedance, observed in Figure 2, which is attributed to a boundary layer. Therefore, the magnesium deposition morphology in the case of a sulfone containing electrolyte is driven by surface energies. This preferred deposition morphology in the case of the butyl sulfone containing electrolyte led to electronically isolated deposits and soft short circuiting (cell failure) after extended cycling.

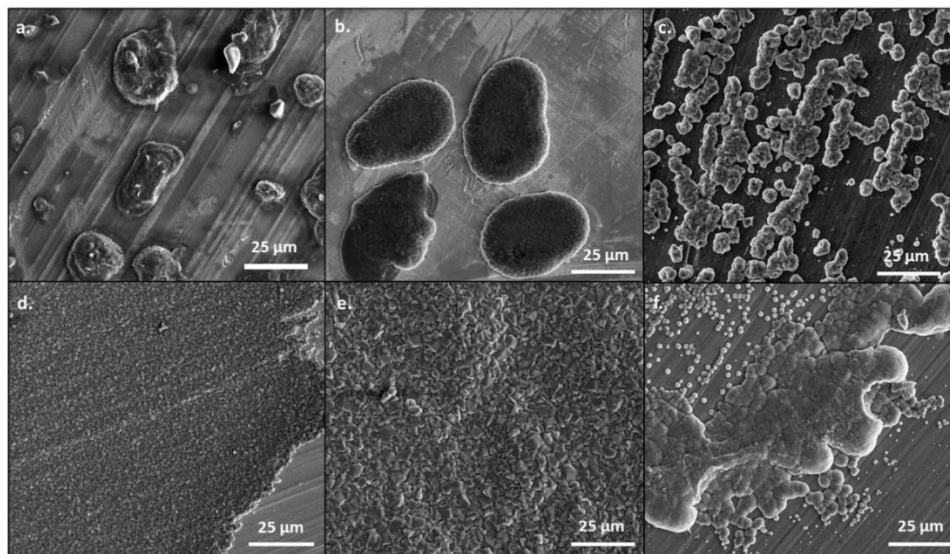


Figure 1: Magnesium deposits from  $Mg(HMDS)_2 - 4 MgCl_2$  in (a), (b), (c) 50 Butyl Sulfone/50 THF and (d), (e), (f) THF. (a) and (d) are on a Cu substrate, (b) and (e) are a Pt substrate, and (c) and (f) are on Mg

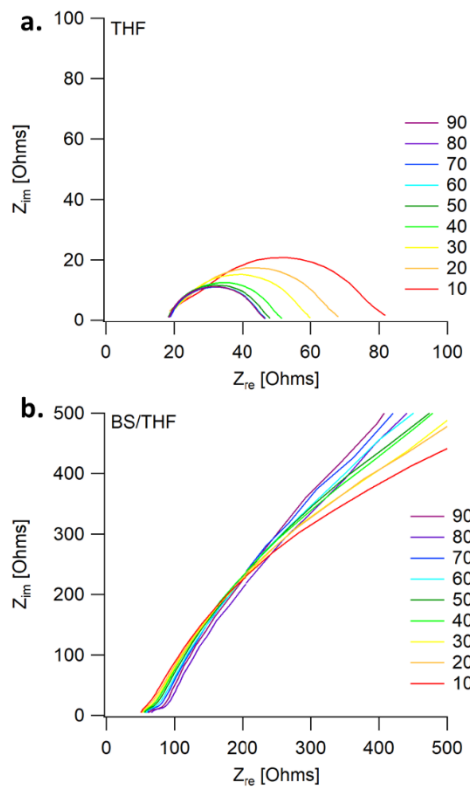


Figure 2: Impedance spectra of  $Mg(HMDS)_2 - 4 MgCl_2$  electrolyte in (a) THF and (b) 50 Butyl Sulfone/50 THF in an Mg/Mg cell.

As mentioned above, the ionomer coatings did not change the electrochemical performance of the cell. This is attributed to the ability of the polymer to, at least partly, swell the electrolyte which does contain parasitic species. However, after extended cycling in the cell with the ionomer coating the magnesium remained shiny whereas the control case turned black. This is evident of a chemical instability between the electrolyte and the magnesium. Although this project did not achieve the intended performance, it does show that there are two obstacles facing certain magnesium electrolytes: chemical stability and electrodeposition reversibility, and that these are not coupled.

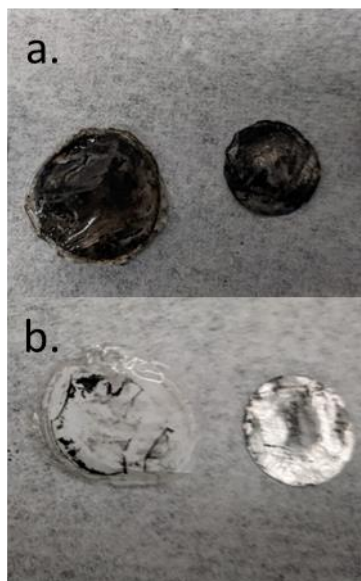


Figure 3:  $Mg(TFSI)_2$  electrolyte after cycling in an Mg/SS cell (a) without ionomer coated Celgard and (b) with ionomer coated Celgard.

These ionomer materials were studied in depth in their bulk phase to determine if magnesium ions could be both conducted through the polymer phase and then electrodeposited to form magnesium metal. From Figure 4, it is shown that the dry ionomers do not enable facile magnesium ion transport. However, the addition of solvent increases magnesium ion

dissociation and therefore increases magnesium ion transport. The highest ionic conductivity is observed when the film is swelled in DMSO, reaching  $10^{-3}$  S/cm (approximately that of a liquid electrolyte), suggesting complete ion dissociation. This was confirmed via SAXS measurements (not shown). The effect of DMSO was maintained in solvent mixtures of 10 % DMSO 90 % ether (THF or DME). Therefore, the ability of magnesium to deposit was studied in the 90 DME/10 DMSO system, as the  $[\text{Mg}(\text{3DME})]^{2+}$  solvated cation is hypothesized to be the electrochemically active species in some electrolyte formulations.

Large interfacial impedances prevented the deposition of magnesium from a galvanostatic (constant current) hold, so Figure 5 shows deposits from a potentiostatic (constant voltage) hold. The large interfacial impedance is hypothesized to be due to the large resistance that comes from the phase between the polymer and the metal, making it unfavorable for magnesium ions to transport through due to the lack of a counter anion. Nevertheless, a small amount of magnesium deposits did occur from the potential hold.

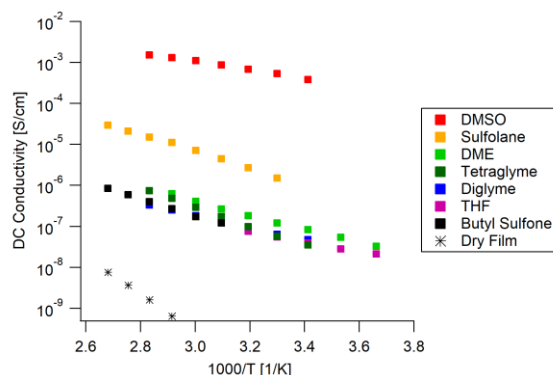


Figure 4: Temperature dependence of PEGDMA1000-Mg(STFSI)<sub>2</sub> polymers at a 20 EO:Ch ratio swelled in different solvents.

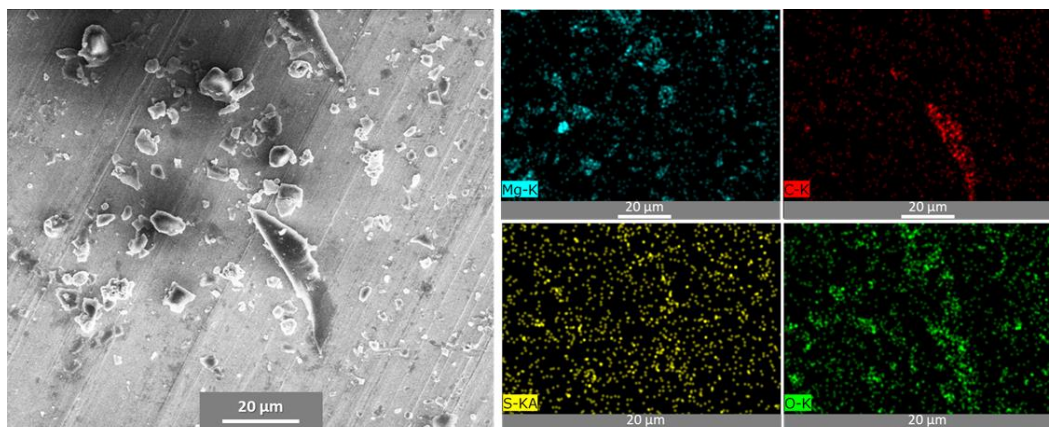


Figure 5: Magnesium deposits on copper after constant potential hold at  $-700$  mV vs. Mg for 10 hours. Left, SEM image. Right, individual elemental maps from EDS measurement.