

Molecular Foundry Example Proposal #4

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Revealing atomic-scale details of Mg-ion based battery electrolytes through X-ray absorption measurements and simulation

Foundry Facilities

Facility ↕	Description
Theory: (lead)	To accomplish the multiple, complex calculations simulating the Mg K-edge absorption spectra, we require training and consultation with Theory Facility staff and the use of workstations provided by that facility. We will make use of existing computing allocations of Foundry staff at NERSC. In addition, we will iteratively refine our simulated spectra with data obtained from the ALS to clarify and develop our work for Mg battery electrolytes.

Proposal Description

Significance and Impact

For high-mileage electric vehicles (EVs), the energy density demanded of the battery system exceeds that of a typical Li-ion battery. Therefore, a post Li-ion battery system is very important as a future energy source for the EV. A rechargeable magnesium battery, using magnesium metal ($Mg_{(m)}$) as an anode active material is expected to afford a high energy density due to (1) a high specific capacity (3832 mAh cm^{-3}) from Mg^{2+} inherent two-electron transfer and (2) a high cell voltage owing to the low equilibrium electrode potential of magnesium (-2.356 V vs. SHE) compared with other multivalent metal such as zinc (-0.763 V vs. SHE) or aluminum (-1.676 V vs. SHE). Previous results suggest that $Mg_{(m)}$ may also have unique cycle life and safety advantages as an anode for high energy secondary batteries (██████ et al. *Nature*, 2000).

A major challenge in advancing magnesium batteries is the development of electrolytes compatible with the magnesium metal anode. Conventional electrolytes such as $Mg(ClO_4)_2$, $Mg(TFSI)_2$ and $Mg(PF_6)_2$ are not capable of reversible $Mg_{(m)}$ deposition and stripping, and thus the essential electrochemical reactions at the anode/electrolyte interface are blocked and the battery ceases to function. To overcome the challenge, our group has pioneered crystallization of classic Lewis-acid/Lewis-base reactions, such as $[Mg_2(?-Cl)_3?6THF][C_6H_{18}Si_2NAICl_3]$ (██████ et al. *Nature Communications*, 2011), and a new generation of magnesium electrolytes based on $Mg(BH_4)_2$ (██████ et al., *Angew. Chem.* 2012). In addition, we have harnessed the unique, element specific power of soft X-ray absorption at the Advanced Light Source at LBL to investigate the electronic structure of the Mg-ion *in operando* to electrochemical deposition and stripping (██████ et al., *Electrochem. Comm.*, 2012; ██████ et al., *J. Phys. Chem. C*, 2013). Figure 1 shows how we are able to capture a pre-edge feature during in situ measurements for Mg deposition using the capabilities developed at 6.3.1.2.

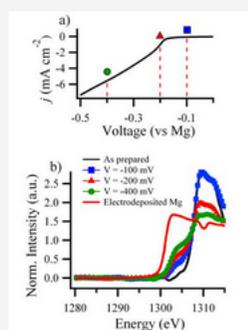


Figure 1. In situ electrochemical/Mg K-edge XAS for Mg deposition.

Our novel technique united the atomistic specificity of X-ray absorption spectroscopy with the electrochemical response of the $Mg_{(m)}$ anode, and the next step is to clarify our observations with theoretical simulations of the absorption spectra. Identifying the magnesium bonding in Mg electrolytes is a critical element to understanding the complex deposition and dissolution of $Mg_{(m)}$ at the anode-electrolyte interface. Furthermore, the research to be completed at the molecular foundry will guide the synthesis of future electrolytes compatible with a $Mg_{(m)}$ anode and with high oxidation potential limits.

The high-voltage electrolytes are crucial to testing and developing high-voltage, high-energy Mg^{2+} intercalation cathodes. We expect the combination of our electrochemical, spectral and theoretical results to produce multiple high-impact publications.

Project Plan

Currently, our group has collected and continues to collect Mg K-edge absorption spectra on beamline 6.3.1.2 ISAACs endstation at the ALS. Based on discussions with the Prendergast Group in the Theory Facility of the Molecular Foundry, we understand that our goals require first-principles electronic structure simulations of the structure and dynamics of proposed electrolyte chemistries using finite temperature molecular dynamics. In addition, interpretation of Mg K-edge absorption spectra (or those of other elements) require additional excited state simulations using the DFT-XCH methodology developed by Prendergast, which take structural snapshots from the simulated thermodynamic ensemble (or proposed hypothetical structures). Such simulations require using available software at the Foundry and access to high-performance computing resources. We recognize that these can be quite expensive simulations, requiring several nodes for days to develop equilibrated trajectories that sample the relevant point in phase space (temperature and concentration). Furthermore, for solutions with ambiguous speciation, we understand that in the full length of possible simulations (which might span 10's of picoseconds) we might never observe rare-events, such as ligand-stripping, and so, different possible species will require additional simulations which explicitly include them.

Our proposed scope-of-work is to begin the collaboration by simulating the Mg K-edge structure of magnesium electrolytes based on $[\text{Mg}_2(\text{?}-\text{Cl})_3?6\text{THF}][\text{R}_x\text{AlCl}_{4-x}]$ (Estimated timeline = 4 months):

- 1) 1) Simulate the Mg K-edge absorption spectra of $[\text{Mg}_2(\text{?}-\text{Cl})_3?6\text{THF}]^+$ as a salt in $[\text{Mg}_2(\text{?}-\text{Cl})_3?6\text{THF}][\text{R}_x\text{AlCl}_{4-x}]$ and in solution. Solid state simulations will have a well-defined structure but will also explore finite-temperature sensitivity, particularly with respect to modification of spectral line shape in Mg K-edge spectra. Solution phase simulations will attempt to model experimental working conditions but will require significant investment in time, requiring significantly large simulation cells to model the complex ions and their full solvation shells. We will rely heavily on available high-performance computing resources accessible to the Prendergast Group within the Foundry and at NERSC.
- 2) 2) Propose and simulate the intermediate species, such as $[\text{MgCl}]^+$ present at the interface of deposition from these electrolytes. These simulations will require simulations with variably charged interfaces to explore the attraction and association of this charged intermediate with the anode surface. In addition, the anode may be modeled initially as a non-reactive metal, such as Pt, to remove additional complications related to Mg metal anode passivation.
- 3) Compare the simulations with the absorption spectra taken at the ALS and analyzed at the [REDACTED] to complement our previous electrochemical and spectral analysis of $\text{Mg}_{(m)}$ deposition/dissolution from $[\text{Mg}_2(\text{?}-\text{Cl})_3?6\text{THF}][\text{R}_x\text{AlCl}_{4-x}]$.
- 4) 3) Publish the results as an impactful strategy to study magnesium electrolytes.

Second, we propose to continue our work by simulating the absorption spectra of electrolytes based on $\text{Mg}(\text{BH}_4)_2$ and LiBH_4 . As a complement to our current results, we propose that understanding the solvation of electrolyte solutions that are *not* active for $\text{Mg}_{(m)}$ deposition and dissolution is a crucial comparison for the active electrolytes (Estimated timeline = 8 months):

- 1) 1) Simulate the Mg K-edge and B K-edge absorption spectra of $\text{Mg}(\text{BH}_4)_2$ and LiBH_4 in dimethyl ether (DME). In addition, we will simulate the absorption spectra of $\text{Mg}(\text{TFSI})_2$ and $\text{Mg}(\text{ClO}_4)$ in DME.
- 2) 2) Propose and simulate the effect of LiBH_4 addition to $\text{Mg}(\text{BH}_4)_2$ electrolytes and compare the simulations to current spectra. Figure 2 shows the XAS spectra collected by [REDACTED] at BL 6.3.1.2. We recognize the complex edge and pre-edge features represent changes in the electronic structure of the magnesium, however we lack the capability to finger-print these spectra accurately due to complex speciation of the electrolyte. Theoretical calculations of the absorption spectra becomes paramount.

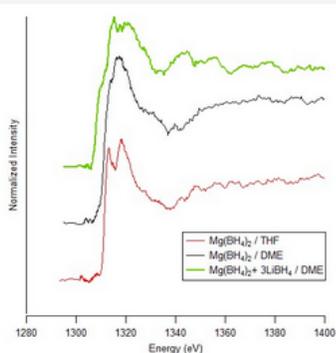


Figure 2. Mg K-edge spectra of $\text{Mg}(\text{BH}_4)_2$ electrolytes

- 3) 3) Propose and publish the active species for $\text{Mg}_{(m)}$ deposition and dissolution from $\text{Mg}(\text{BH}_4)_2$ electrolytes as a synthetic guide for future magnesium electrolytes.

In each of the cases above, the isolation (and validation) of stable/probable solvation shells or coordination complexes is key to interpreting measured spectra as well as determining the active species which might arrive at the anode surface prior to electron transfer during the charging process. Clearly, knowledge and control of these specific species will reveal bottlenecks in battery performance and point to strategies for developing optimal electrolyte formulations.

Molecular Foundry Utilization Timeline

The initial learning and developing of the skills needed to simulate absorption spectra requires constant communication with the experts at the Molecular Foundry. If approved, [REDACTED] will dedicate at least 2 weeks located at the Molecular Foundry solely to learn and develop the requisite skills. From that point, monthly visits of 2-3 days will be dedicated for personal communication and advanced technique learning, to discuss results, and to outline publications obtained from the results. In total, for the 1-year length of the proposal, we expect 10-12 visits to the Molecular Foundry. In parallel, [REDACTED], [REDACTED] and [REDACTED] will consistently communicate to design experiments to be performed at the ALS to supplement and enforce the calculations performed under this proposal at the Molecular Foundry.

In addition, [REDACTED] will dedicate time during ALS beam-time experiments to discuss results with the experts at the Molecular Foundry and to plan future experiments for simulated and experimental absorption spectroscopy. Therefore, by combining the expertise of Mg K-edge spectroscopy on BL6.3.1.2 at the ALS and a dedicated scientist, [REDACTED], we expect a low impact on the operation of the facility.

Relevant Experience

[REDACTED] has been working on Mg batteries since 2010 and has been developing X-ray absorption cells, collecting Mg K-edge spectra at BL 6.3.1.2 ISAACs of Mg electrolytes from 2011. [REDACTED] also holds several publications and patents for research into Mg batteries and has pioneered *in operando* electrochemical/XAS studies for Mg electrolytes.

[REDACTED] is a world-leading researcher in the field of soft-X-ray spectroscopy of liquids. He holds multiple, high-impact publications and is currently the beamline scientist for 6.3.1.2 ISAACs. Xin Li is student working in Dr. [REDACTED]'s group specializing the theoretical simulations of XAS spectra. Dr. [REDACTED]'s group has been in collaboration with [REDACTED] since 2010.

Need for the Molecular Foundry

Recently, Kortright *et al.* in collaboration with David Prendergast of the *Theory of Nanostructured Materials Facility* at the Molecular Foundry illustrated the power of Mg K-edge absorption simulation for CO₂ absorption in Mg-based metal-organic frameworks. In addition, Prendergast *et al.* have published impactful work on the B K-edge of borohydrides. Therefore, the Molecular Foundry has the expertise needed to understand and accelerate our work performed at the Advanced Light Source and [REDACTED].

The simulations performed at the Molecular Foundry are based on an excited-electron and Core Hole (XCH) approach. The XCH approach has been successfully employed to study soft X-ray K-edge spectra of isolated molecules, molecular crystals, surfaces, and various condensed phases. The approach has also been successfully translated for the development of battery materials and is coupled with an efficient, user-friendly interface. Additionally, accelerated simulations and calculations are possible through access to super-computing clusters at the Molecular Foundry. Finally, the Molecular Foundry has developed Web-based access for spectral simulations, which allows for further (remote) refinement at [REDACTED].