THE SEE GROUP

Multielectron and Multivalent Chemistry for Energy Storage

Caltech

Join Us!

We are an interdisciplinary group interested in:

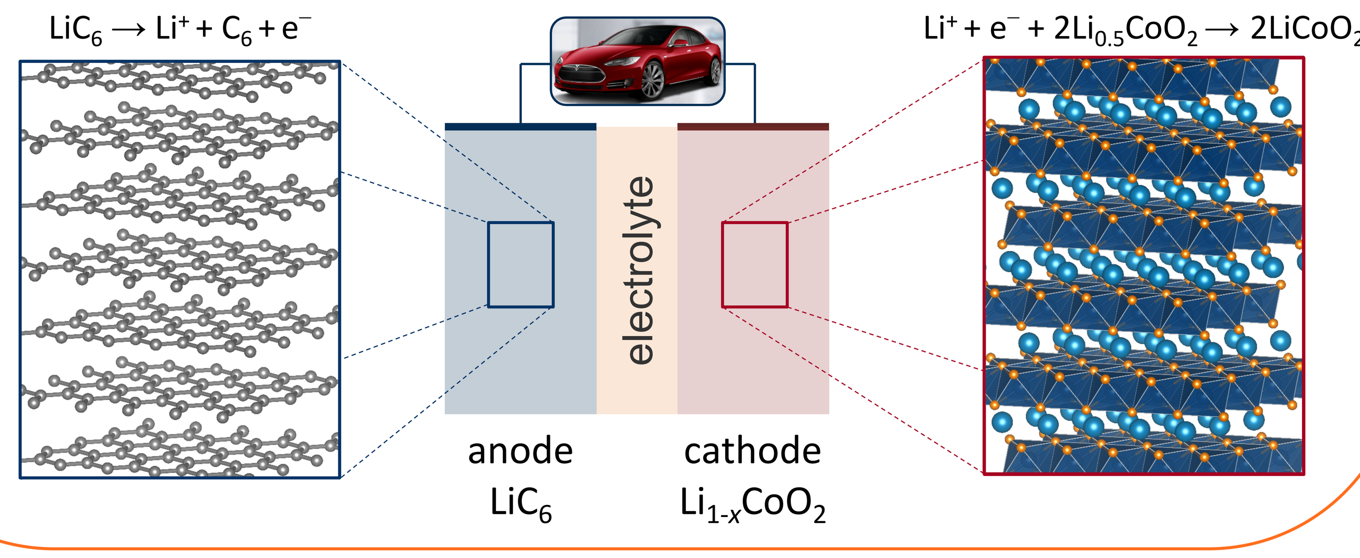
- inorganic chemistry
- analytical chemistry
- materials chemistry
- solid state chemistry
- physical chemistry

Contact Me!
Kimberly See
Assistant Professor of Chemistry
Email: ksee@caltech.edu
Labs: 329 Noyes

Why Batteries?

Energy storage is an enabling technology:
Renewable energy technologies, such as wind and solar, require efficient and inexpensive energy storage. Furthermore, the increasing computing power of portable electronic devices requires higher energy density energy storage solutions.

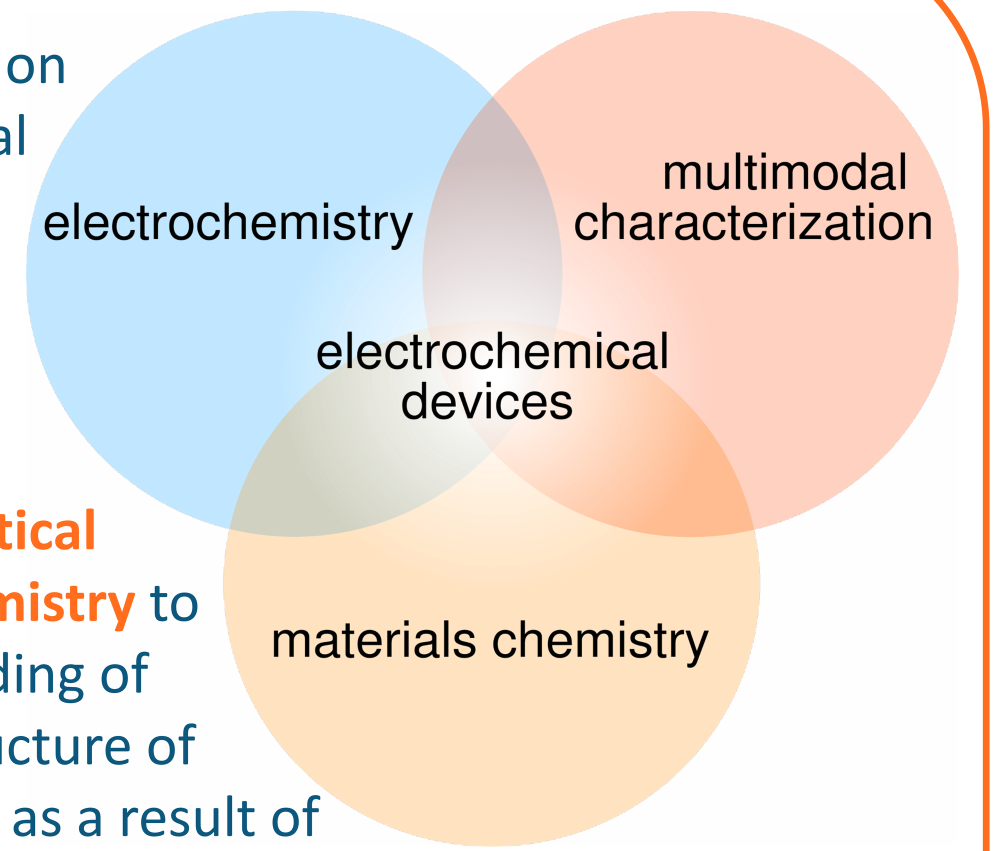
The ubiquitous Li-ion battery:
Although conventional rechargeable Li-ion batteries are able to deliver high power and long lifetimes, Li-ion batteries are composed of a graphite anode and a oxide cathode that usually contains scarce and toxic components.



The Group

The See Group focuses on understanding fundamental processes governing performance in relevant electrochemical devices.

We combine expertise in **materials chemistry**, **analytical chemistry**, and **electrochemistry** to gain a thorough understanding of the bulk and interfacial structure of active materials during and as a result of charge transfer processes in electrochemical devices.



materials of interest

alkali earth metal sulfides
complex transition metal oxides
alkaline earth metal complexes
battery materials
electrochromic materials

characterization techniques

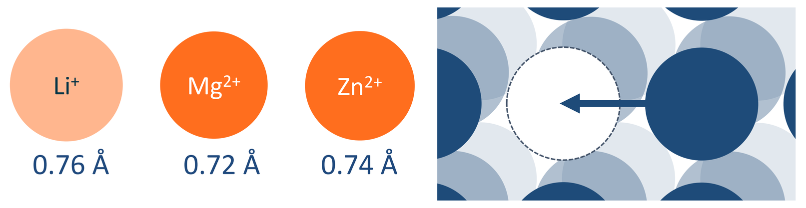
electrochemistry
operando spectroscopy
diffraction
synchrotron techniques
•••

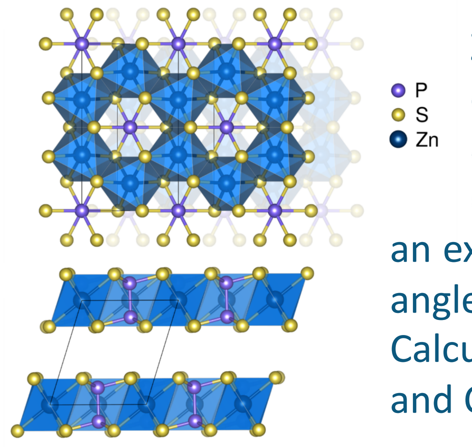
Functional Materials Design

Divalent cation conduction in the solid state is rare and not well understood. We seek to prepare electronically insulating materials that can conduct divalent cations such as Mg^{2+} and Zn^{2+} to broaden the understanding of divalent solid state ionics and enable next generation, all solid-state batteries.

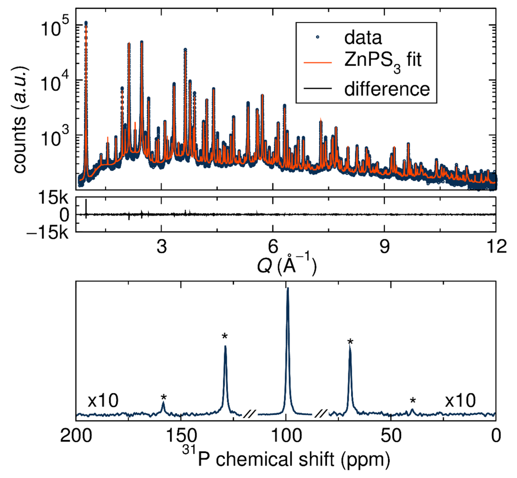
Projects

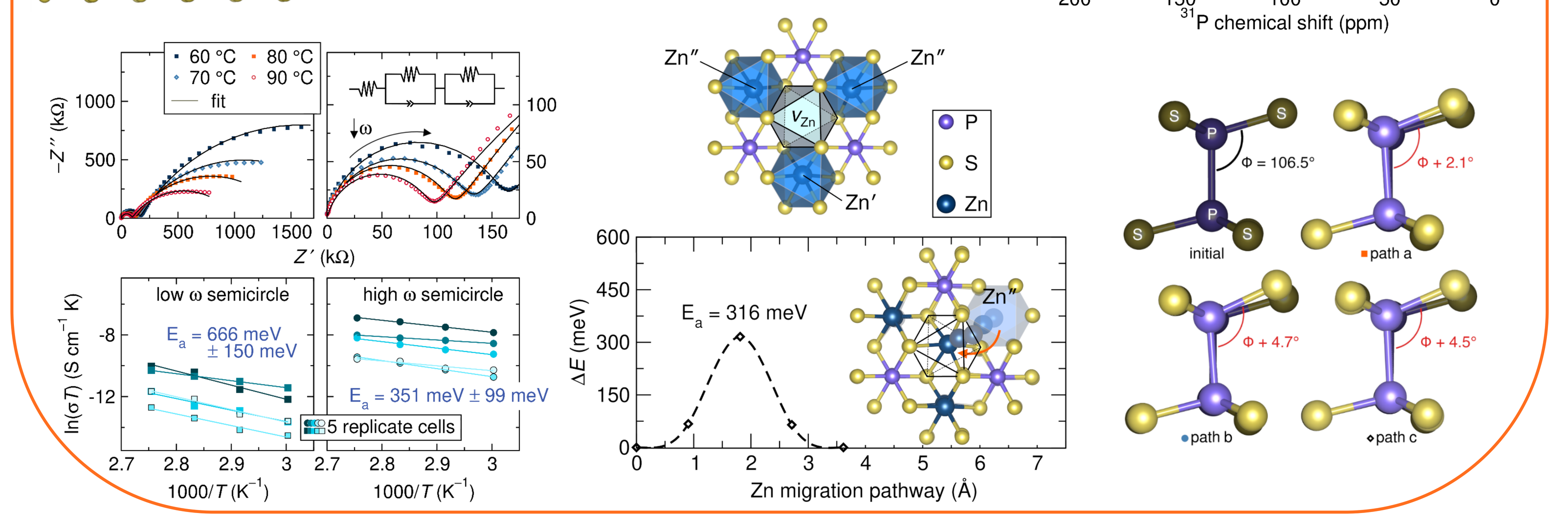
- Probe divalent ion diffusion in solid-solutions of $ZnPS_3$
- Prepare solid-solutions of MPS_3 materials with redox active metals
- Evaluate the redox activity of $[P_2S_6]^{4-}$
- Probe phonon-assisted ionic conductivity





$ZnPS_3$ supports Zn^{2+} conductivity with low activation energies. The diffusion is facilitated by an expansion of the P-P-S bond angle it the transition state. Calculations by André Schleife and Cheng-Wei Lee at UIUC.

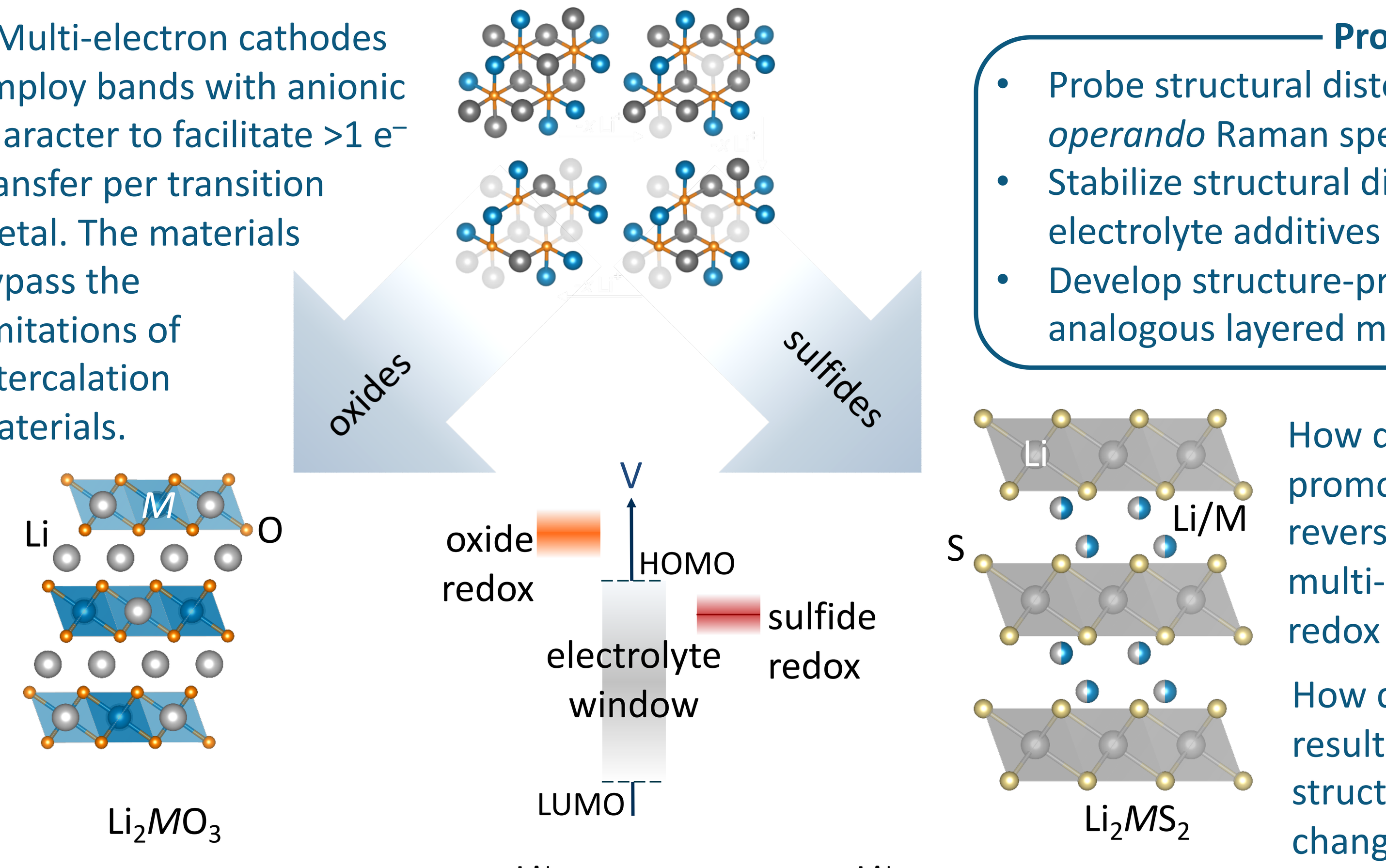




Next Generation Battery Chemistry

Multi-electron redox to push the boundary between intercalation and conversion

Multi-electron cathodes employ bands with anionic character to facilitate >1 e⁻ transfer per transition metal. The materials bypass the limitations of intercalation materials.

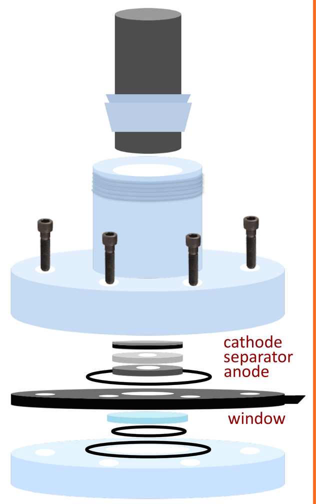


Projects

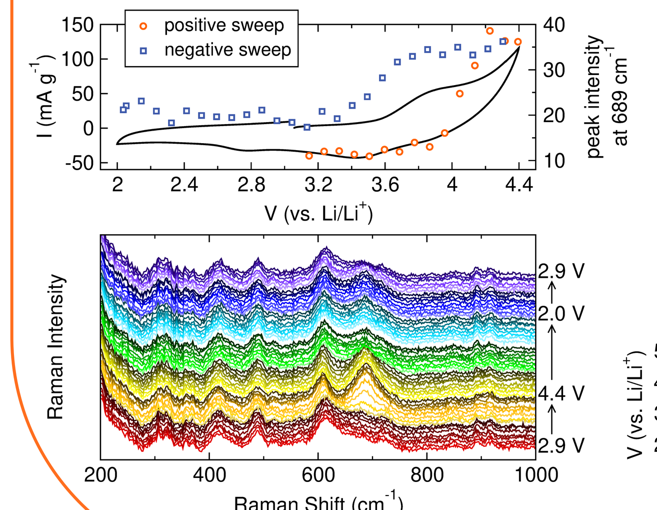
- Probe structural distortions in oxides with *operando* Raman spectroscopy
- Stabilize structural distortions in oxides with electrolyte additives
- Develop structure-property relationships with analogous layered metal sulfides

How do we promote reversibility of multi-electron redox processes?

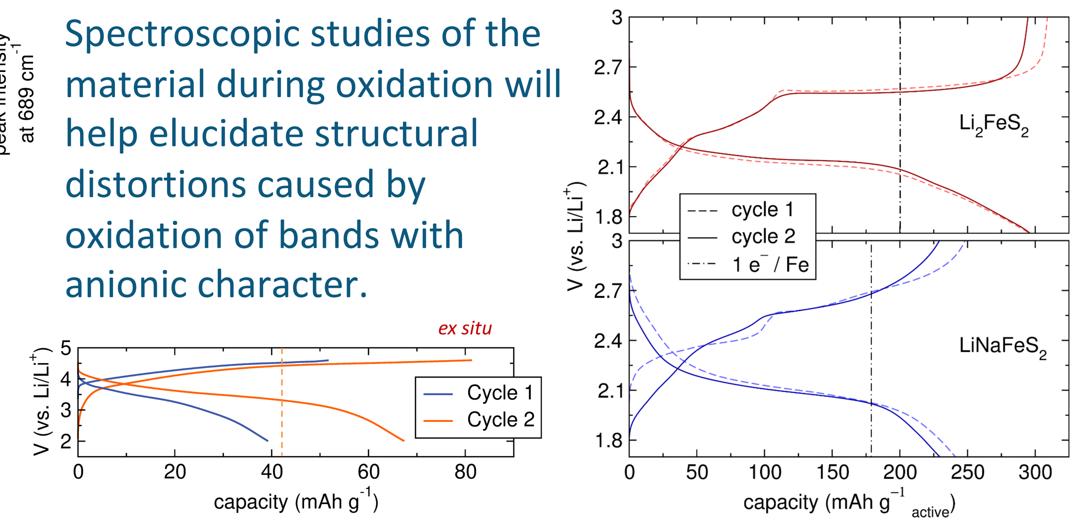
How do resulting structural changes affect reversibility?



e.g.: $Li_2Ru^{(4+)}O^{(2-)}_3 \underset{-e^-}{\xrightarrow{-Li^+}} LiRu^{(5+)}O^{(2-)}_3 \underset{-x\,e^-}{\xrightarrow{-x\,Li^+}} Li_{1-x}Ru^{??}O^{??}_3$



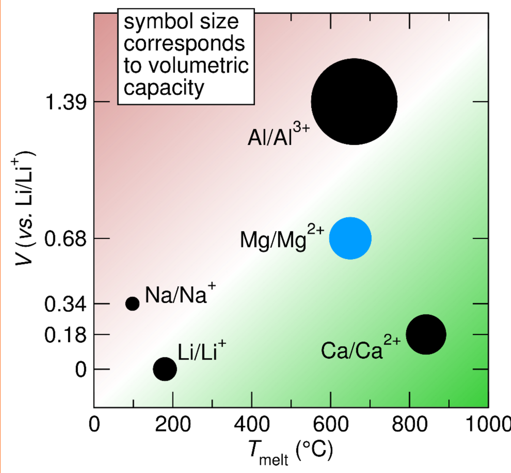
Spectroscopic studies of the material during oxidation will help elucidate structural distortions caused by oxidation of bands with anionic character.

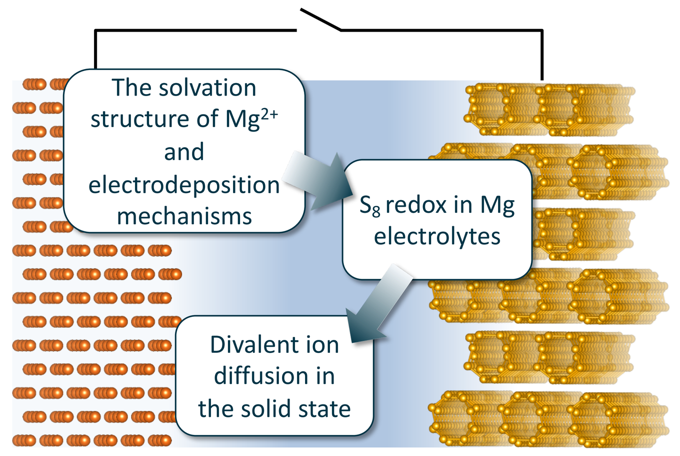


Li_2FeS_2 demonstrates reversible electrochemistry involving $S^{2-}/(S_2)^{2-}$ redox, while isostructural $LiNaFeS_2$ shows irreversible capacity loss on first oxidation.

Mg-S energy storage

The natural abundance and electrochemical performance of Mg metal makes it an excellent choice as an alternative anode to Li. S-based batteries afford very high capacities, up to 1672 mAh g^{-1} which is 5 times that of theoretical capacity of intercalation materials. The high capacity translates into a lighter battery.



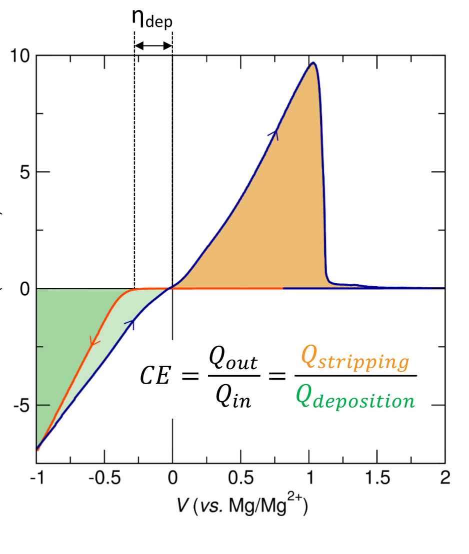


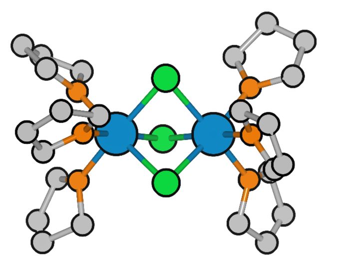
$Mg \rightarrow Mg^{2+} + 2\,e^-$ $\qquad$ $S + 2e^- \rightarrow S^{2-}$

Projects

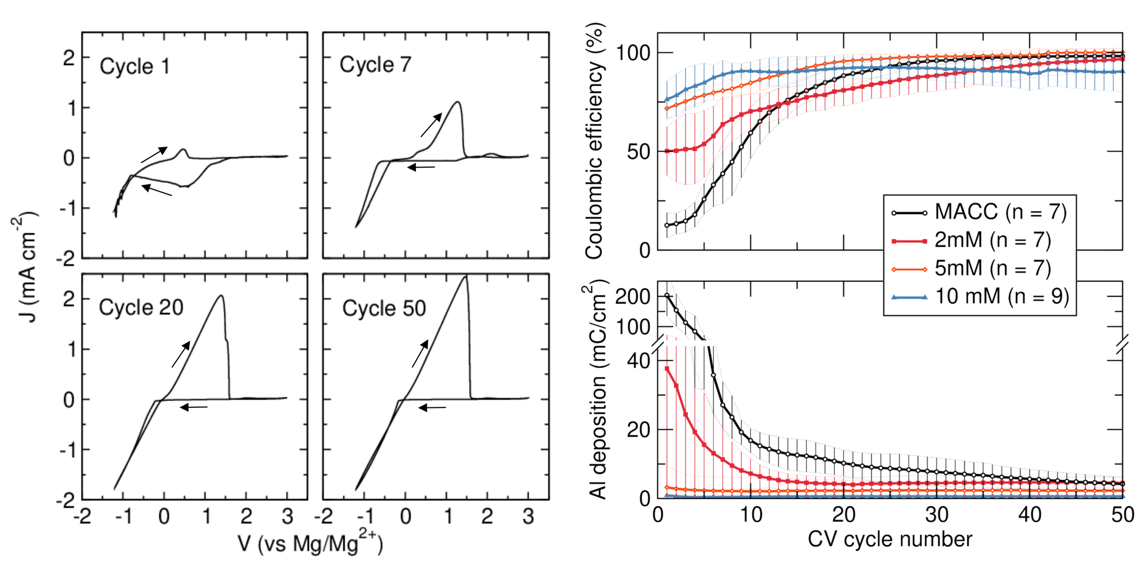
- Develop new electrolytes that support both Mg deposition and stripping and S_8 electrochemistry.
- Reduce unwanted side reactions like corrosion by protecting electrode-electrolyte interfaces
- Assess long-term cyclability by comparing dendrite formation on Li and Mg anodes
- Enhance the performance of MACC by preventing initial Al deposition with additives

Mg electrodeposition and stripping metrics are dependent on the electrolyte. Changing the solvent causes changes in the electrodeposition and stripping behavior as the solvent plays an active role in solvating the Mg complexes.





The magnesium aluminum chloride complex (MACC) is composed of 2:1 $MgCl_2$:$AlCl_3$. When prepared in THF, the active Mg species is $[Mg_2(\mu\text{-}Cl)_3\cdot 6THF]^+$.



MACC undergoes electrolytic conditioning to reach high Coulombic efficiency. The addition of small concentrations of magnesium bis(hexamethyldisilazane) shortens the conditioning process by inhibiting initial aluminum deposition.

MACC supports reversible Mg electrodeposition and stripping in various solvents. S_8 reduction is observed in Mg-S cells with the MACC electrolyte and the reductive wave is tuned by changing the solvent. The position of the S_8 reduction wave is affected by solvent, suggesting a solvent-mediated reduction pathway.