Self-assembling rechargeable Li batteries from alkali and alkaline-earth halides (Project ES326)

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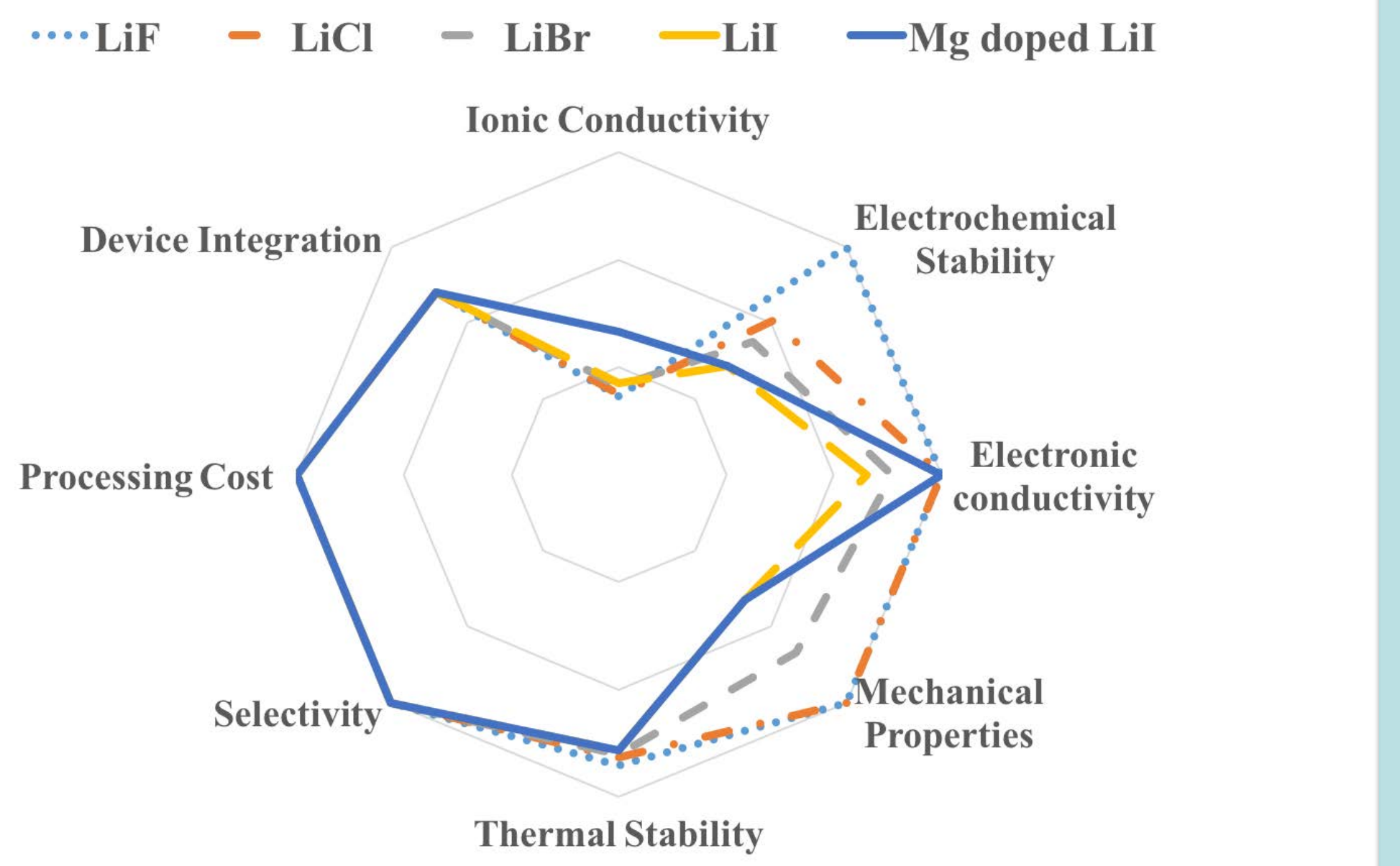
Abstract

This project investigates electrochemical formation of lithium halide based solid electrolytes, with the goal of enabling and demonstrating self-assembling and self-healing batteries using lithium metal negative electrodes. The ability to repair damage spontaneously is highly desirable for rechargeable batteries because electrochemical reactions in battery materials normally result in structural changes, which may cause degradation and damage, and ultimately cause the battery to become non-functional with cycling.

Introduction

The spontaneous reaction between Li metal and iodine, historically used in lithium iodine primary battery technology to self-form a solid electrolyte/separator during electrochemical use, offers a starting paradigm for self-assembling and potentially self-healing rechargeable batteries using Li metal anodes. Based on preliminary analysis, we believe that mixed halides Li(I,Br,Cl,F) compositions, including graded solid electrolytes, can be produced by appropriate control of the reaction pathway. Strategies for doping of the **self-assembling** lithium halide solid electrolytes will be evaluated through combined computation and experiment. **Self-healing** functionality will be introduced by tuning the metal halide and the liquid electrolyte compositions to provide limited solubility of the halide in the liquid electrolyte. Any lithium metal that is exposed during battery cycling, for instance through cracking of the solid electrolyte film, will be able to passivate upon exposure to the liquid. The solubility of lithium halides in nonaqueous solvents varies very widely, from high solubilities in ethereal solvents that have enabled use of dissolved LiI as catholytes[2], to low solubility as witnessed by stable LiF forming in the SEI on graphite anodes in Li-ion cells. The wide range of formation potentials suggests that the choice of solvent and halogen will allow a wide range of tuning to accomplish partial solubility. This area is especially amenable to thermodynamics-based computational search in order to guide experiments.

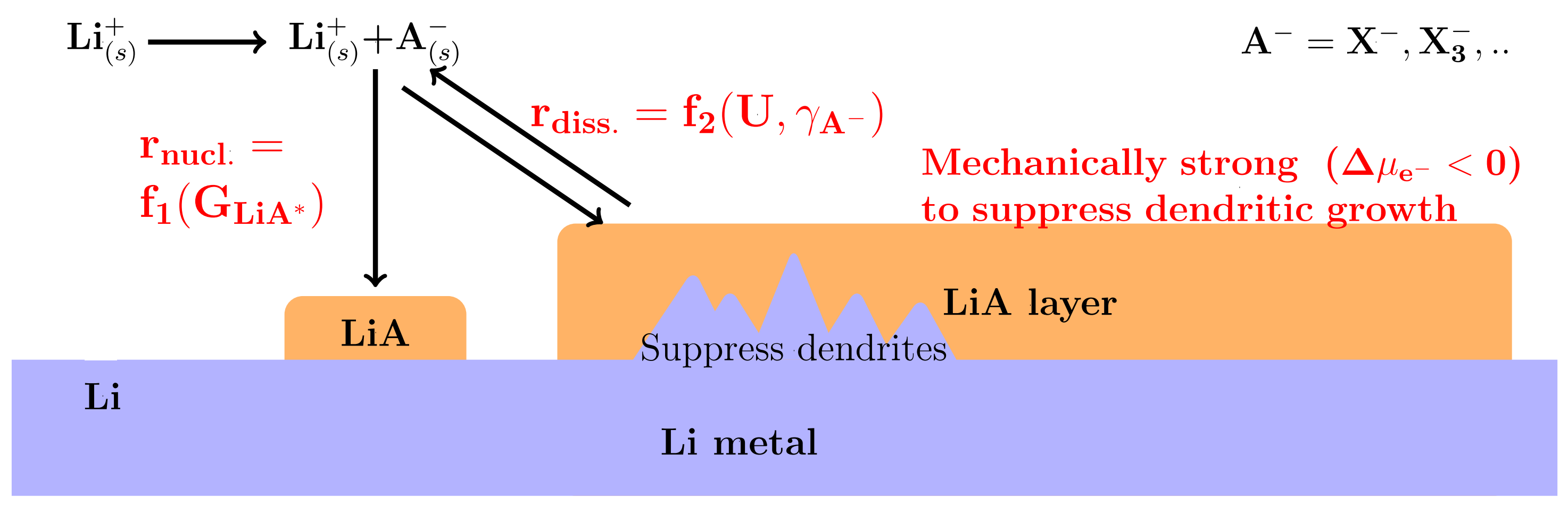


Radar chart for proposed self-forming electrolyte

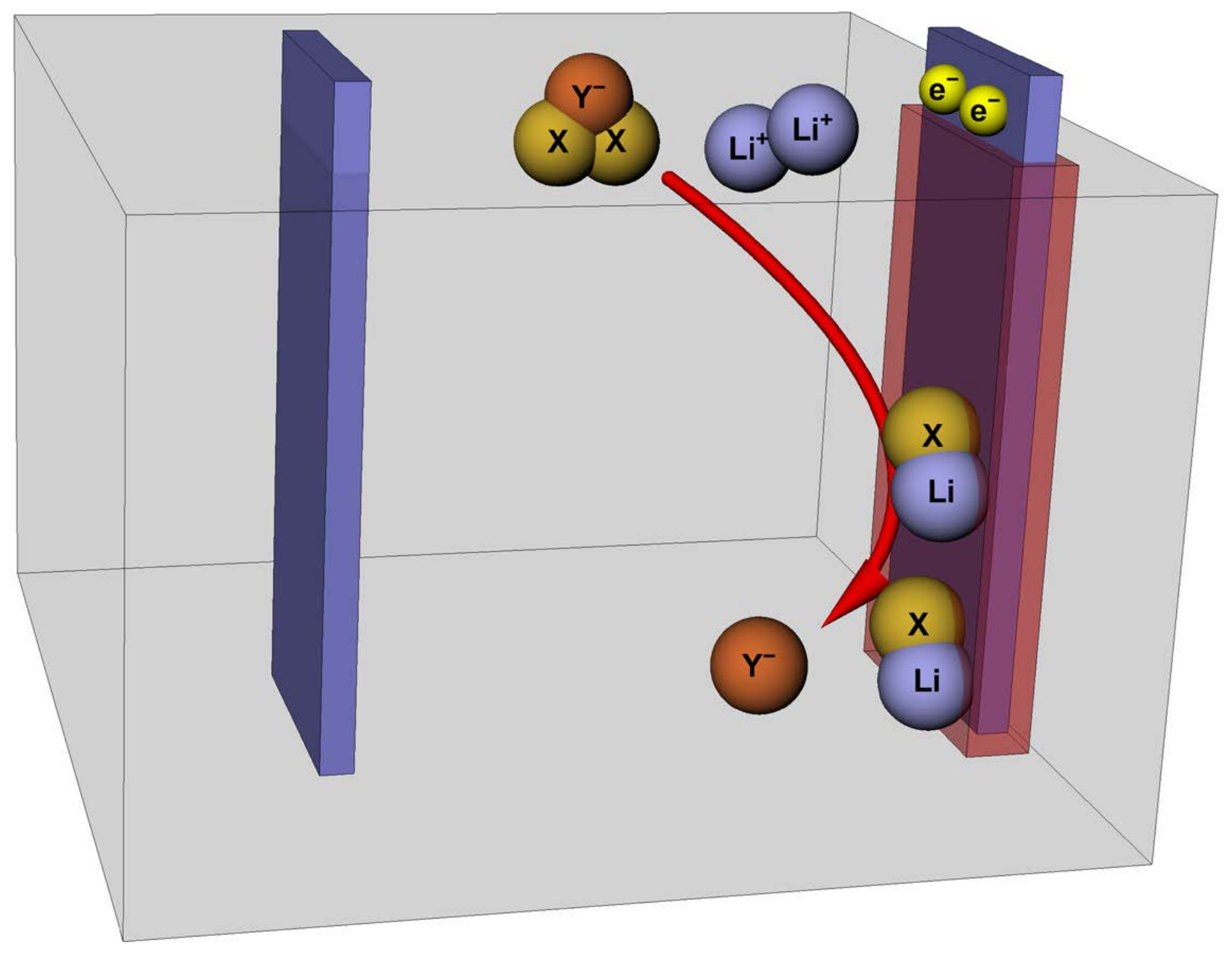
Objectives

A combined experimental/computational collaboration between MIT and CMU will investigate electrochemical formation of lithium halide based solid electrolytes, with the goal of enabling and demonstrating self-assembling/self-healing batteries using lithium metal negative electrodes. The computational research will compute the thermodynamics of polyhalide speciation to determine the stability range for these various polyhalide species under the operating potential. Polyhalides have complex chemistry and we will calculate the free energies using first-principles density functional theory calculations within an implicit solvation framework. The thermodynamics of polyhalides show dramatic changes depending on the solvent and our prior work has been successful in capturing trends in solvation thermodynamics for anionic species, for e.g. O_2^-. This analysis will provide a clear understanding of the active polyhalide species that will enable the self-assembling and self-healing processes and will tie in closely to the half-cell and full cell testing.

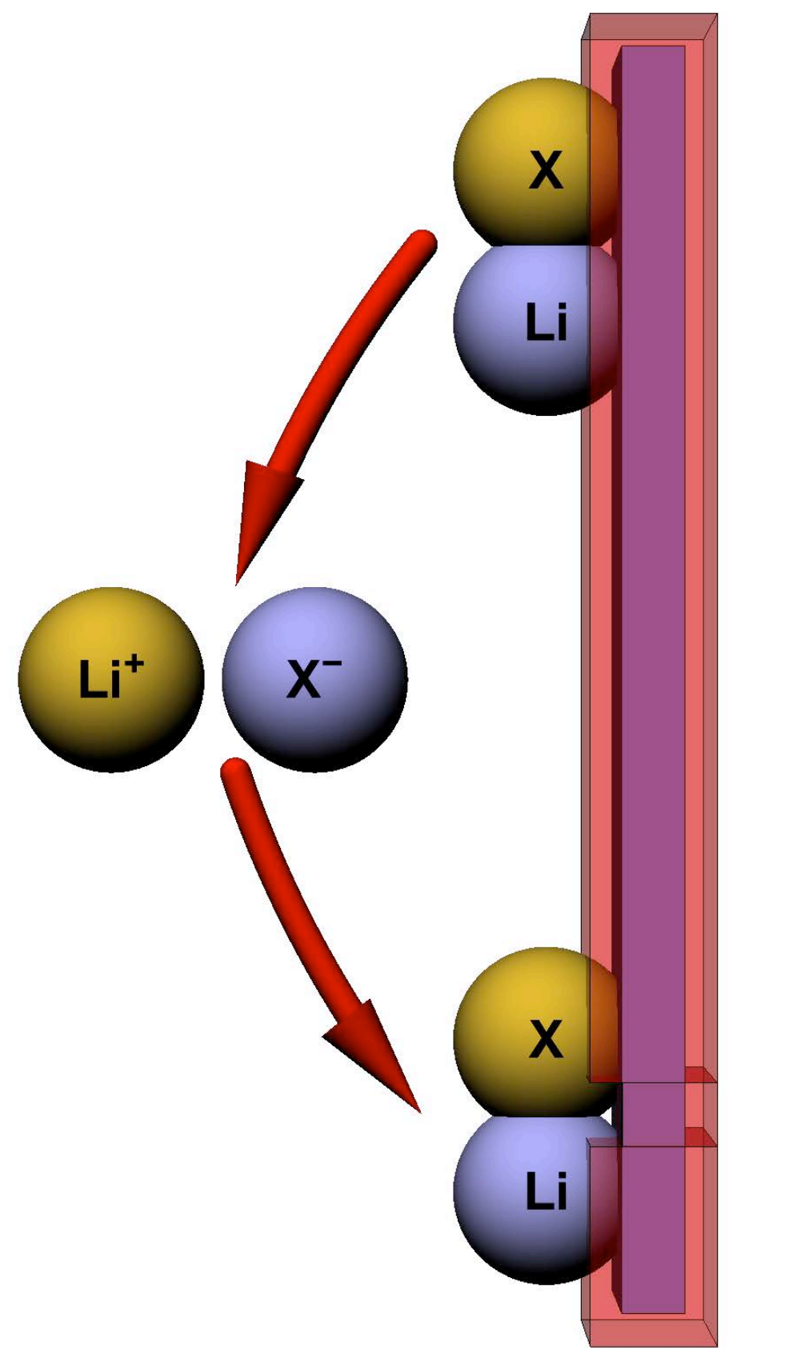
Experimentally, the proposed self-assembling, self-limiting solid electrolytes will initially be formed on lithium metal via metal halide additives to liquid electrolytes. We will use a variety of two-electrode and three-electrode cell constructions to systematically isolate and interrogate formation of solid halide films on lithium metal. Cell designs will include “half-cells” having a lithium working electrode and nonreactive metal counter-electrode, symmetric lithium-lithium cells, and “full cells” including Li-S and Li-intercalation cathode cells. Based on laboratory cell testing, down-selects will be performed and prototype full cells of >10 mAh capacity will be fabricated and delivered to DOE-specified laboratories for testing and evaluation.



Schematic showing the nucleation and growth of the halide layer. The insulating layer shuts off its growth as the layer thickens.

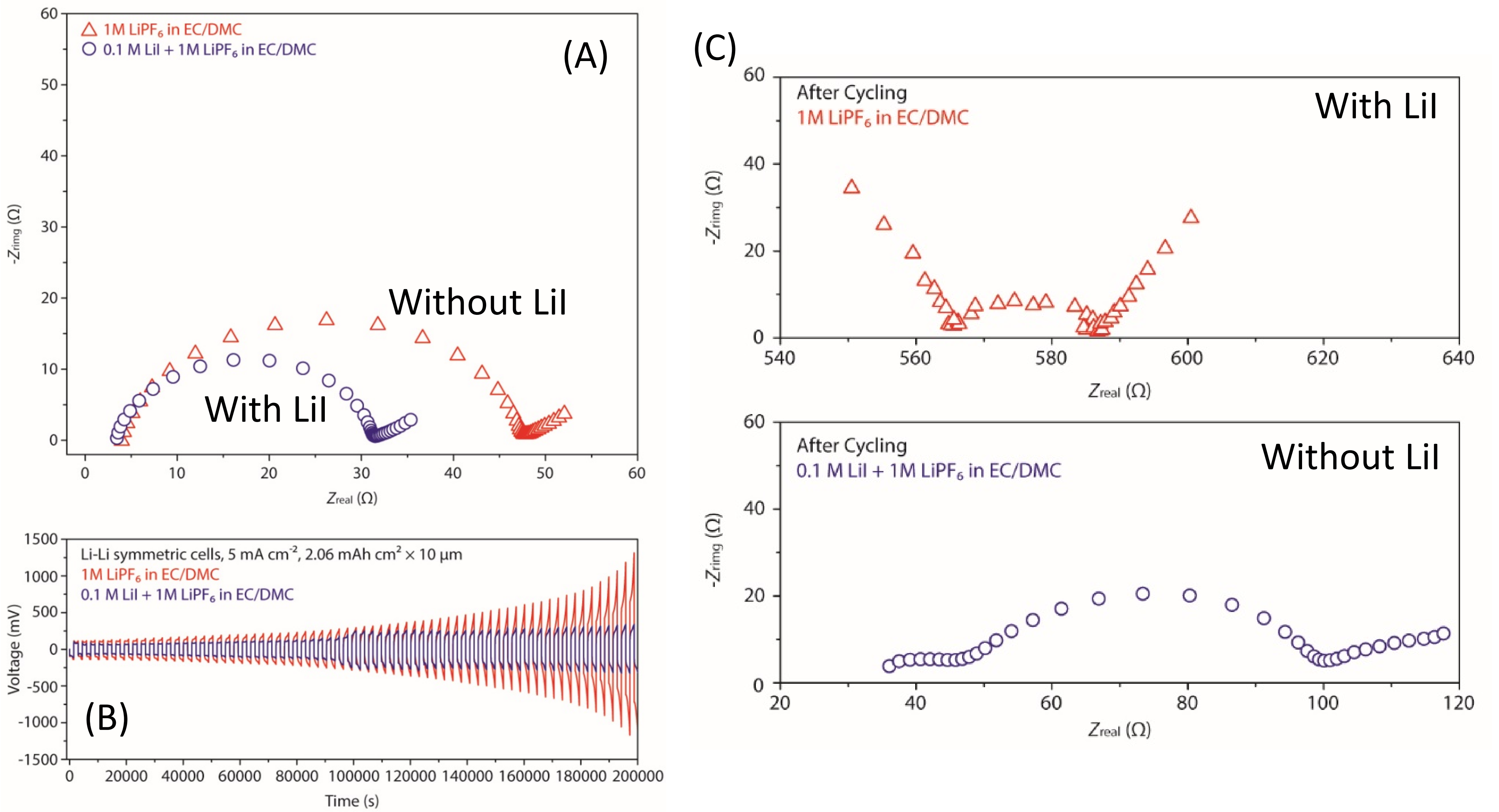


Self-forming mechanism

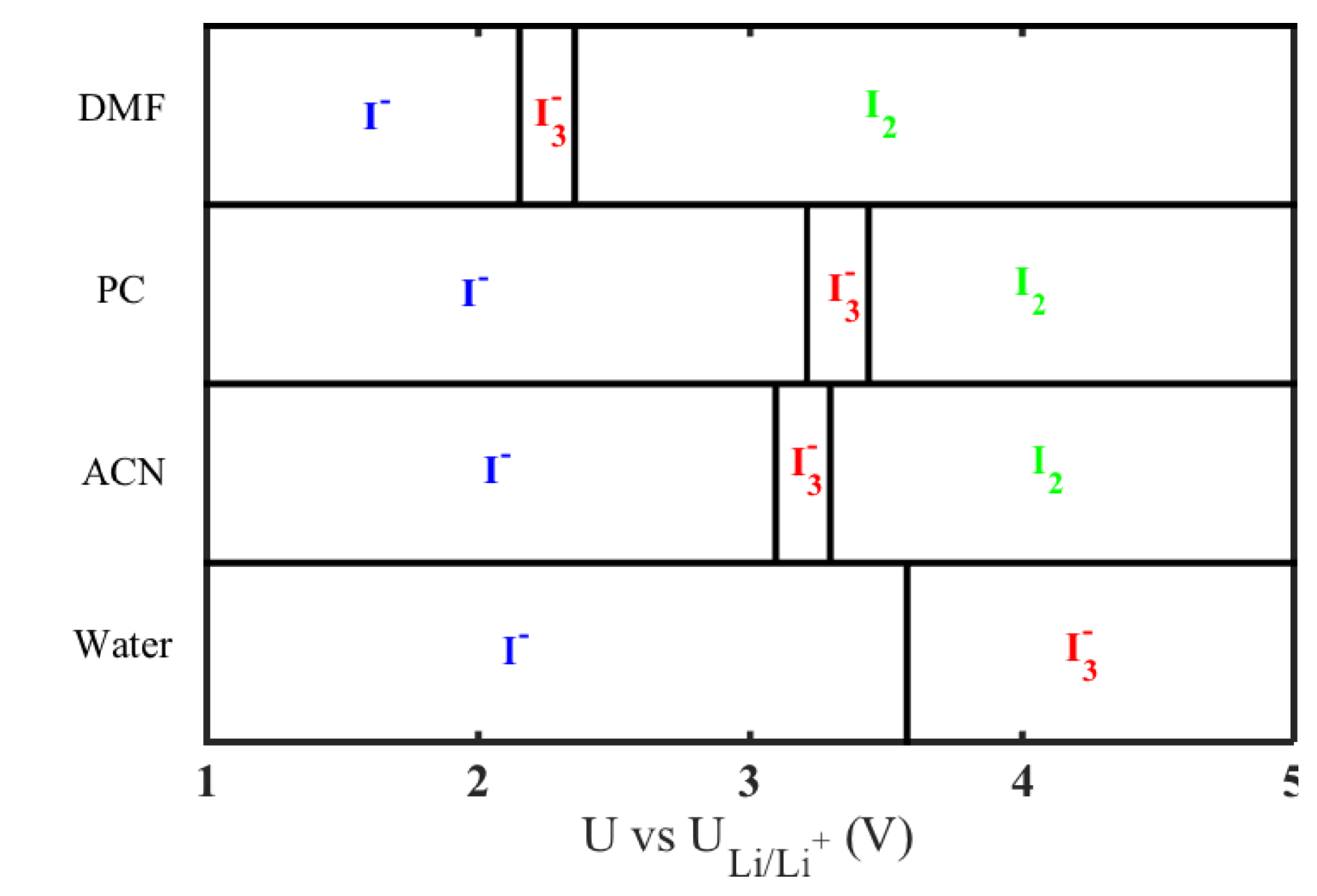


Self-Healing mechanism

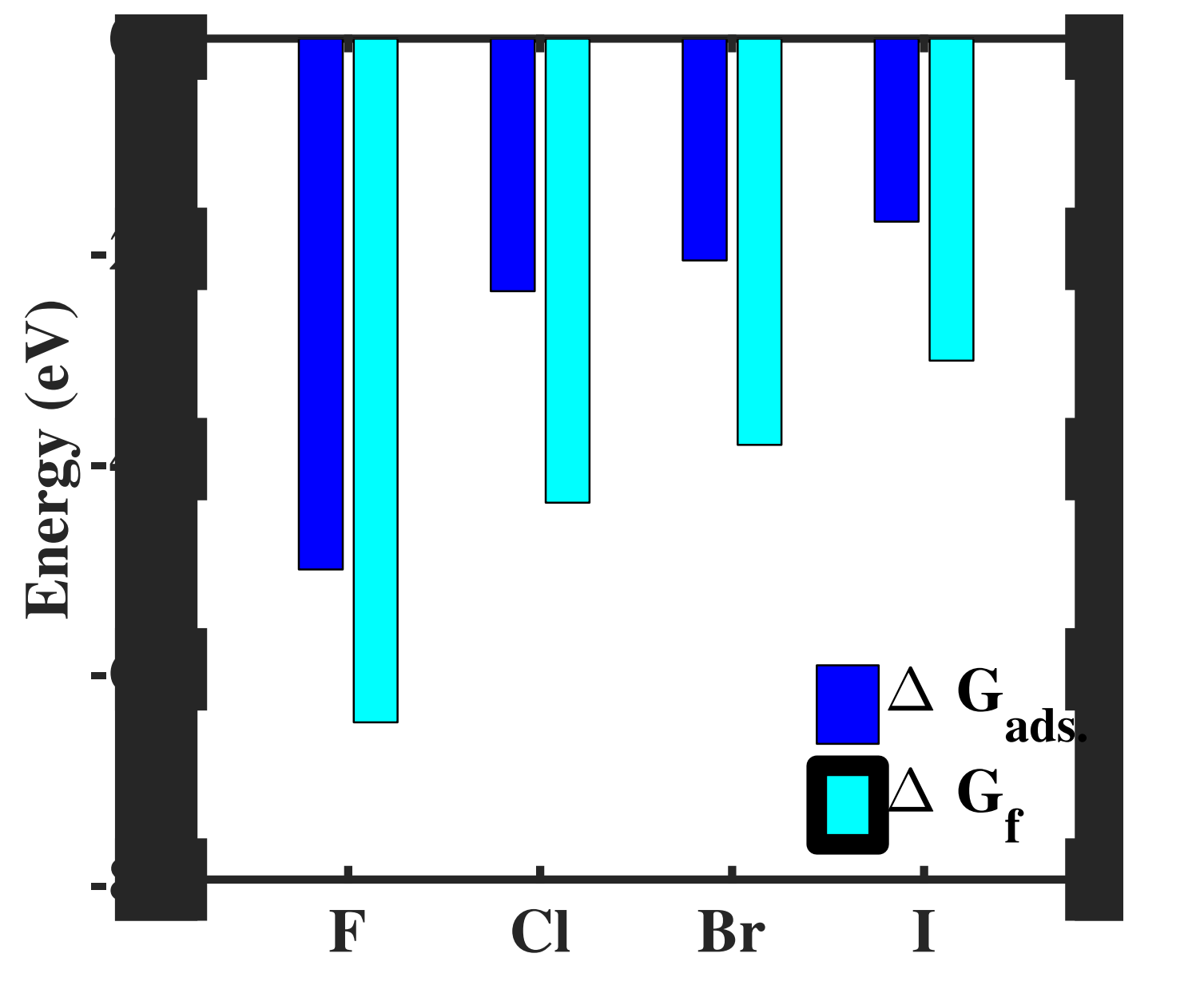
Results and Discussion



(A) Initial impedance for Li-Li symmetric cells using 1M $LiPF_6$ in EC/DMC, with (blue) and without (red) 0.1M LiI. (B) Voltage vs. time during continuous cycling at 5 mAcm^2 to 2.06 mAh/cm^2 capacity (10 µm Li metal thickness). (C) After cycling is complete, the cell with LiI shows a small new arc at the highest frequencies which we attribute to a thin, LiI-stabilized SEI. The cell without LiI exhibits much greater impedance growth, with the appearance of a large impedance arc at high frequencies that suggests uncontrolled growth of SEI.



Phase diagram for $I_2/I^-/I_3^-$ as function of potential in different solvents. So by choosing appropriate solvent and potential, one can control the halide species in solution



Adhesion energy of Lithium halides on lithium using DFT calculations. Adhesion energy indicates overpotential to nucleate/grow on the lithium surface

Summary and Outlook

- Approach for self-forming and self-healing solid electrolyte layer
- Clear evidence that halide additives improve cycling in Li-Li symmetric cells
- Careful choice of electrolyte, electrode (cathode) and halide additive combination and concentration of halide in solution is crucial

References

[1] Z. Ahmad, V. Viswanathan, arXiv, 1702.08406 [cond-mat.mtrl-sci]

Acknowledgements

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy under Contract No. DE-EE0007810.