
DESIGN OF NEXT-GENERATION BATTERY PACKS FOR A SUSTAINABLE FUTURE

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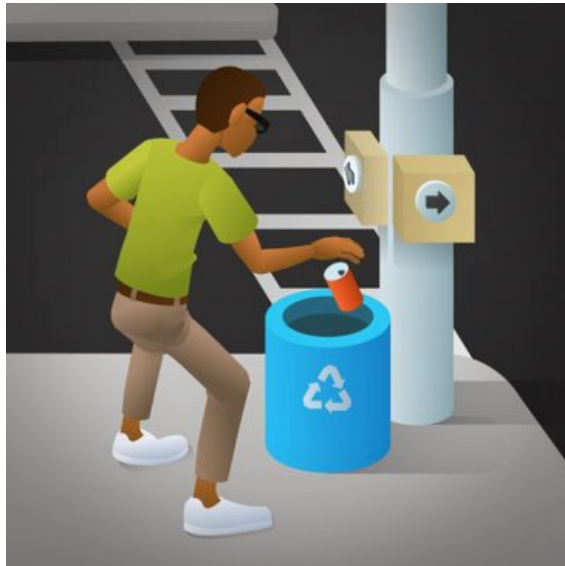
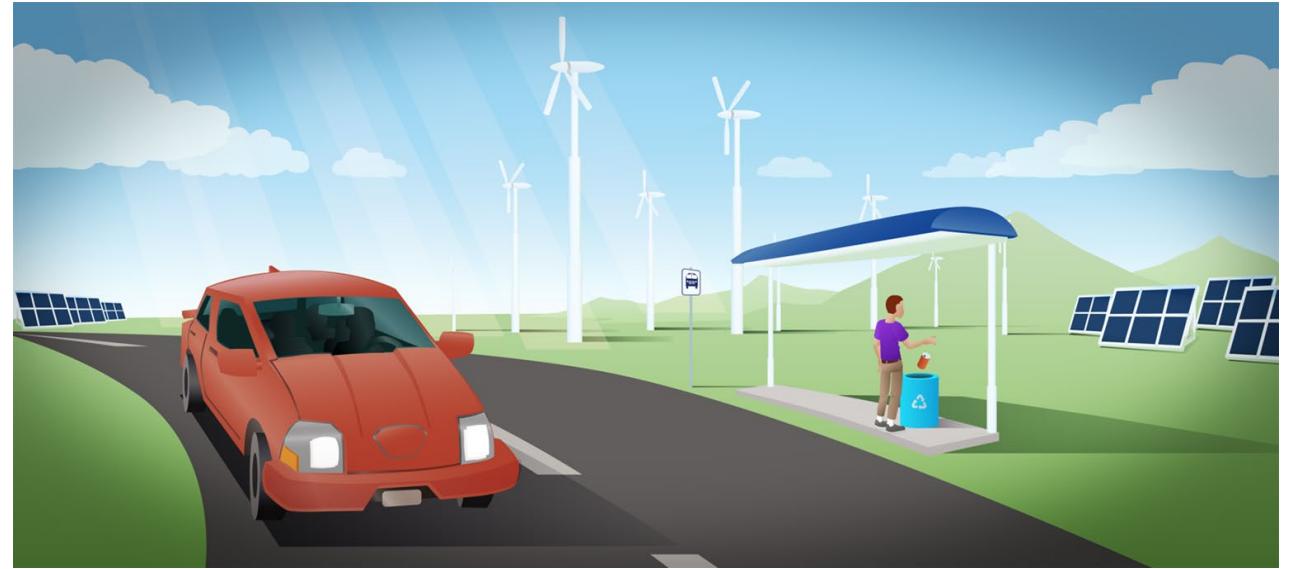
The University of Texas at Austin
Energy Institute



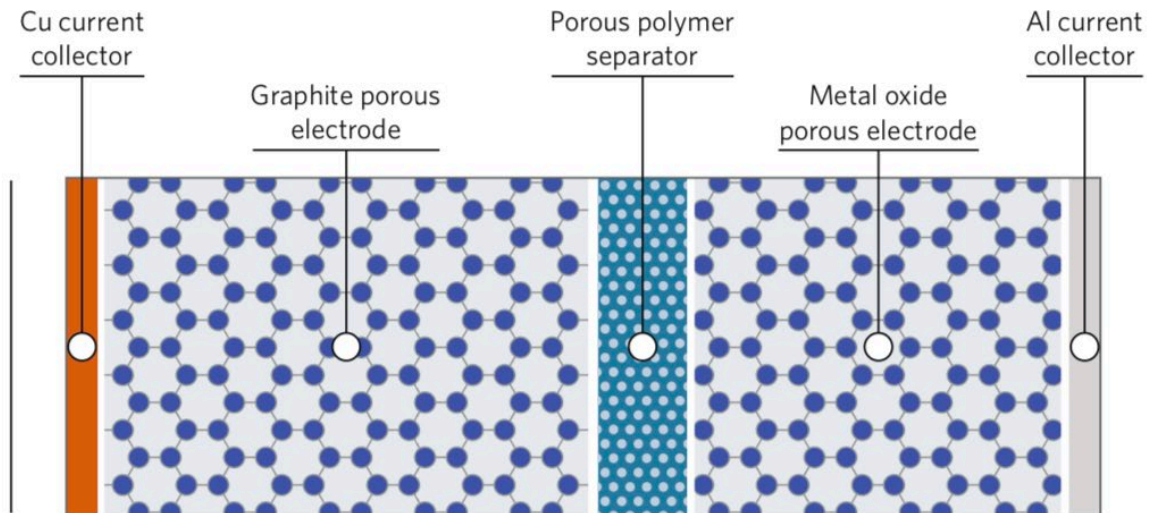
The University of Texas at Austin
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ROLE OF BATTERIES IN A SUSTAINABLE FUTURE

- Electrochemical energy storage is essential for electrified transportation and a clean grid
- The graphite anode constrains battery performance because it is:
 - Too thick due to low capacity
 - Too unsafe due to dendrite formation
 - Too hard to make due expensive processing



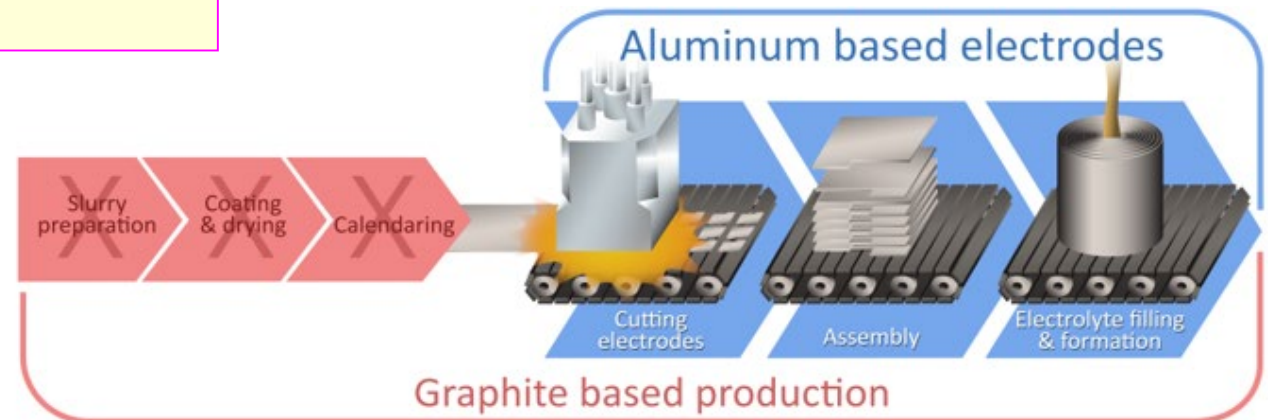
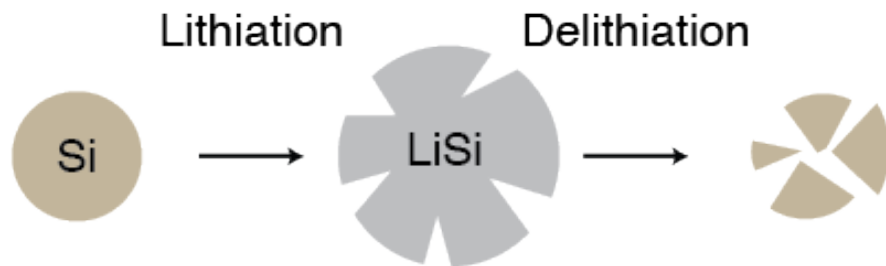
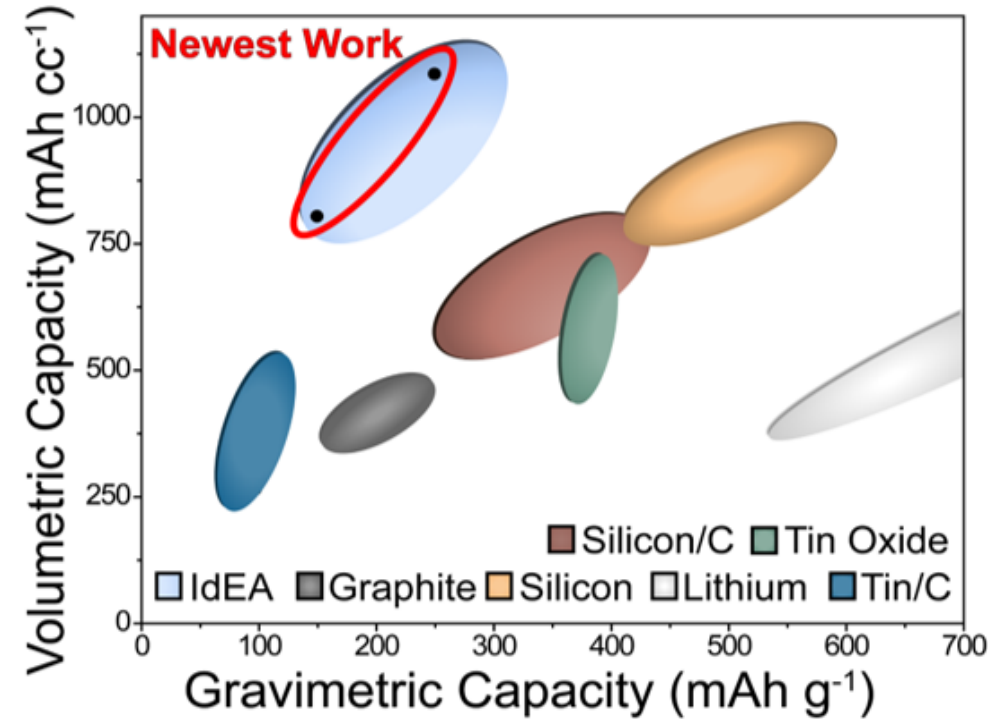
Typical
lithium-ion cell
at the pack level:
~150 Wh kg⁻¹
~250 Wh L⁻¹



P. Albertus, S. Babinec, S. Litzelman, & A. Newman, *Nature Energy* 3(1), 16 (2018).

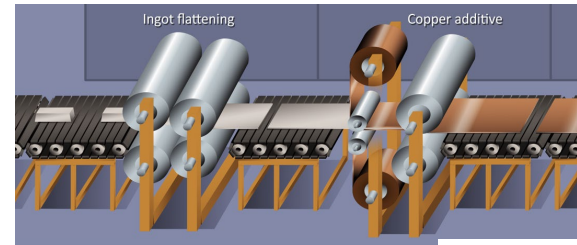
OUR APPROACH: METAL FOIL ALLOY ANODES

- Current alloy anode architectures require dispersion of small particles in a carbon matrix, resulting in low tap density, low volumetric energy density, and high processing cost
- Our approach of using metal foil alloy anodes could:
 - **Improve energy density by > 50%**
 - Reduce cost > 20%
 - Reduce charging time to 10 minutes
 - Be cheaply produced at kiloton scale

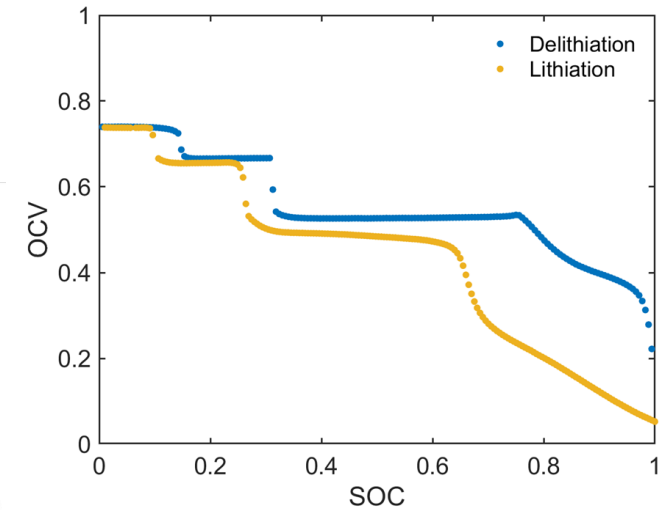
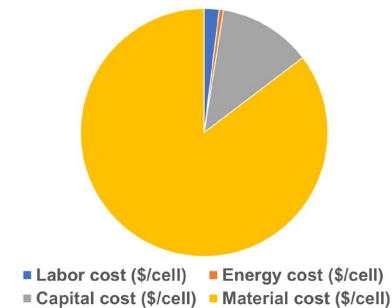


TECHNICAL APPROACH

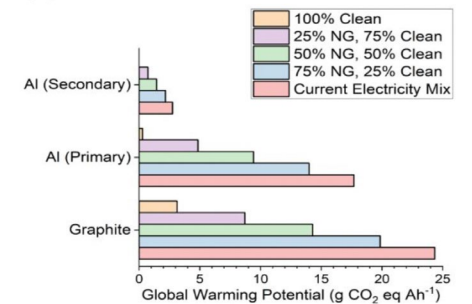
- Diverse academic perspectives were brought together to identify and solve the challenges with alloy foil anodes:
- Experimental Design (Manthiram Group)
- Modeling (Hwang & Subramanian Groups)
- Techno-economic Analysis (Hales & Muthuraman)
- Life Cycle Analysis of Foil Anode Materials (Hales & Manthiram Group)



Anode Cost Distribution

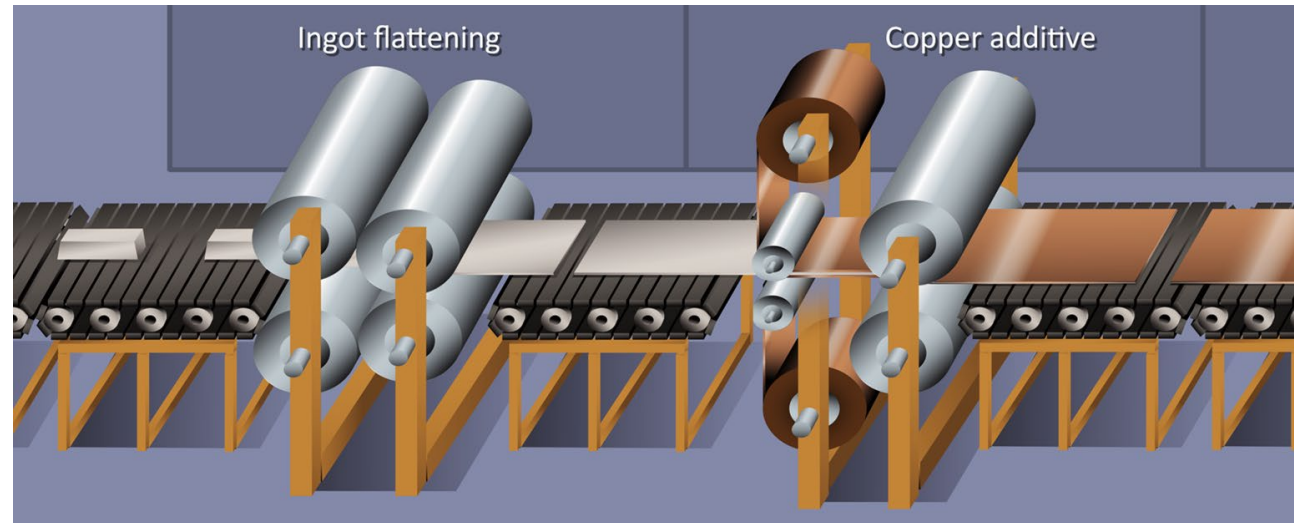
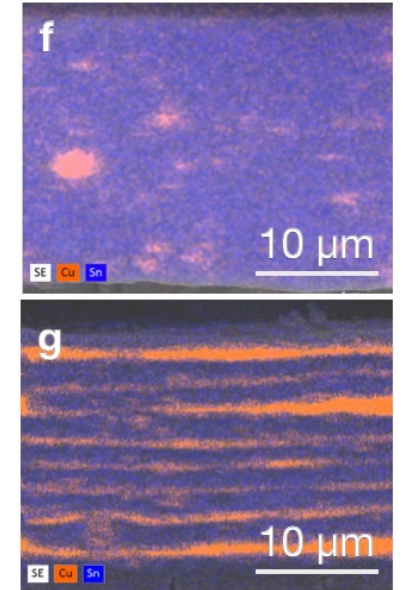
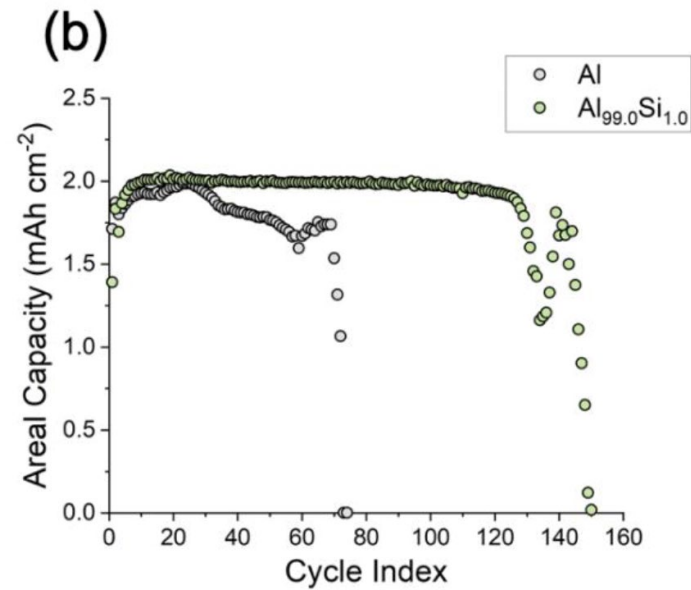


(a)



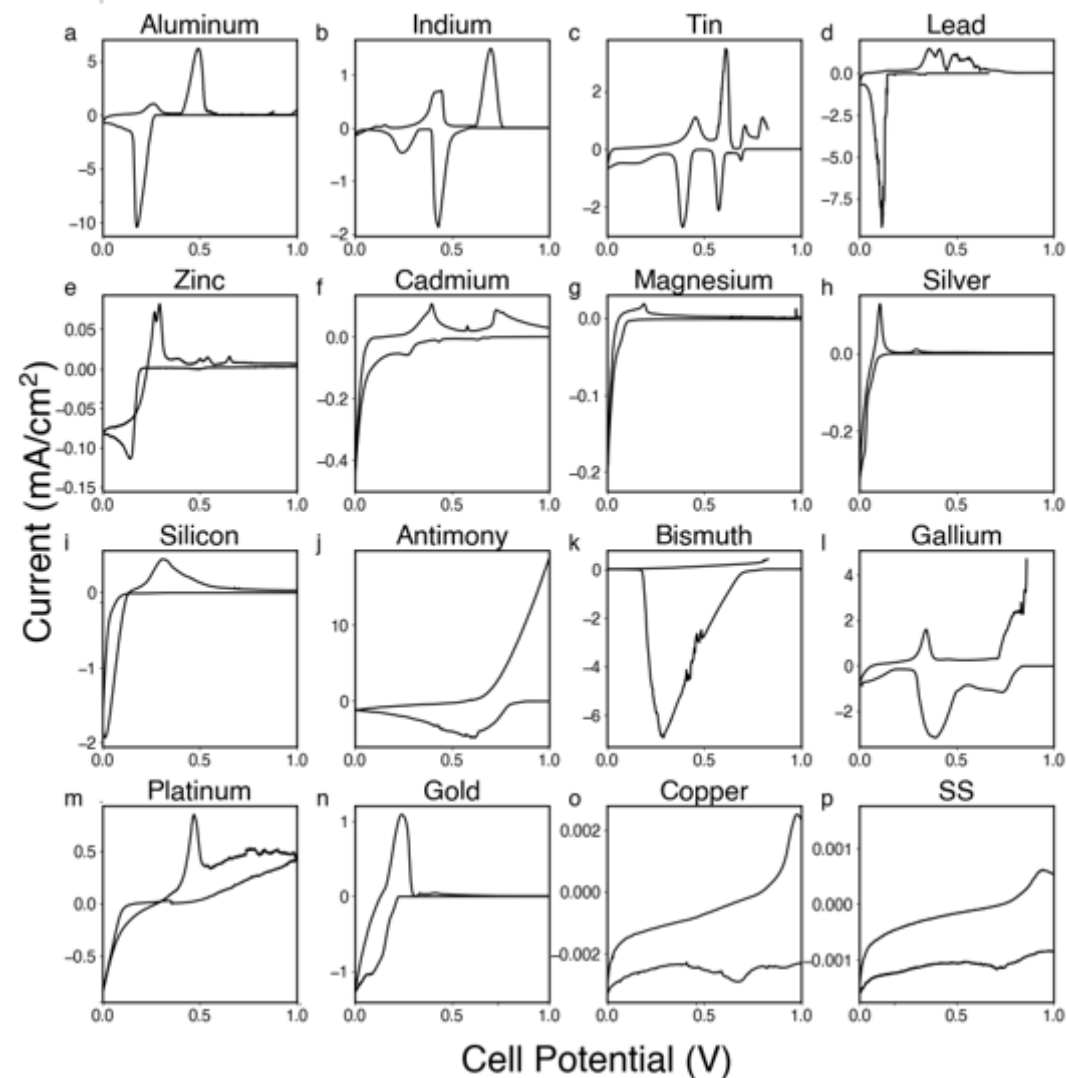
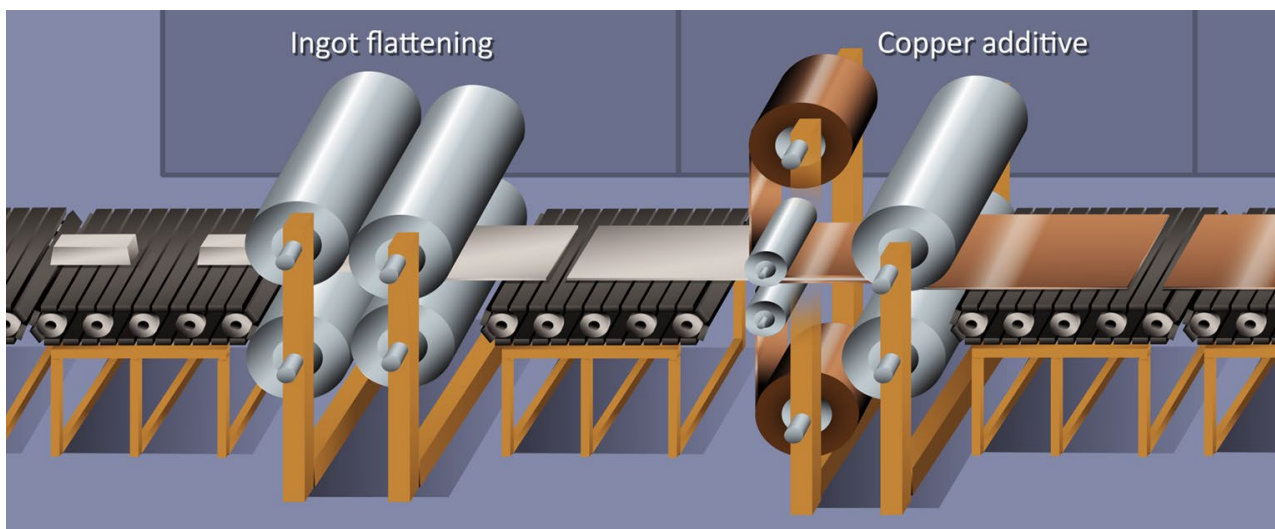
EXPERIMENTAL DESIGN OF FOIL ALLOY ANODES

- The relative ease of manufacturing metal foils translates to the following:
 - Foil composition, structure, and geometry can all be closely controlled
 - Allows for fast screening of numerous materials, and fine tuning for beneficial properties



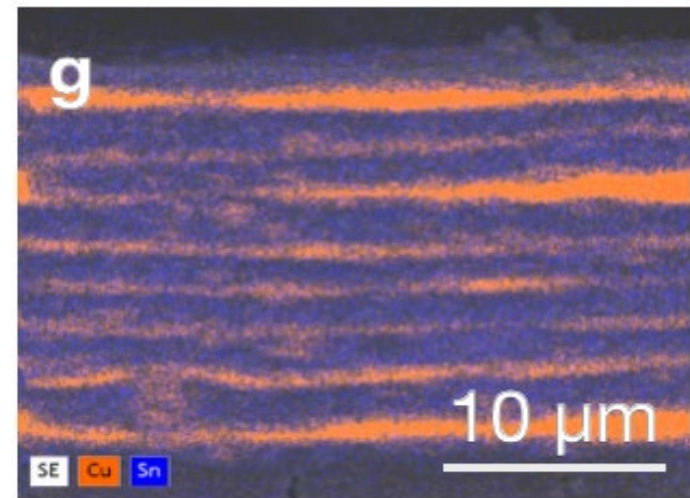
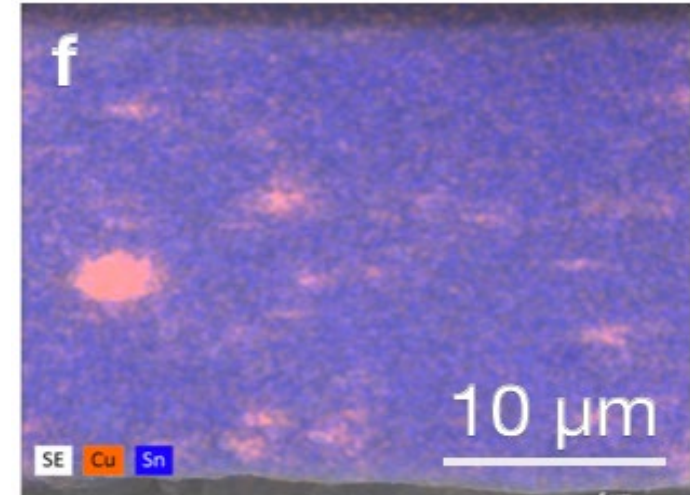
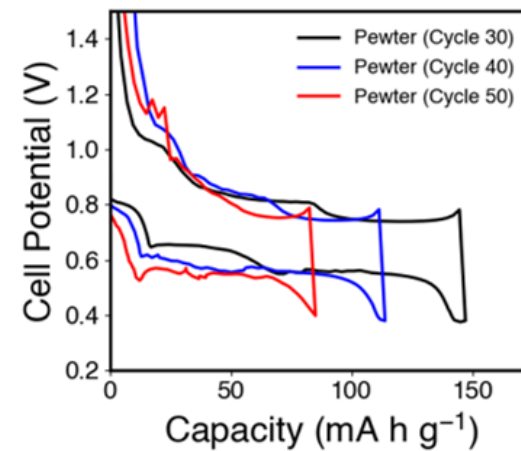
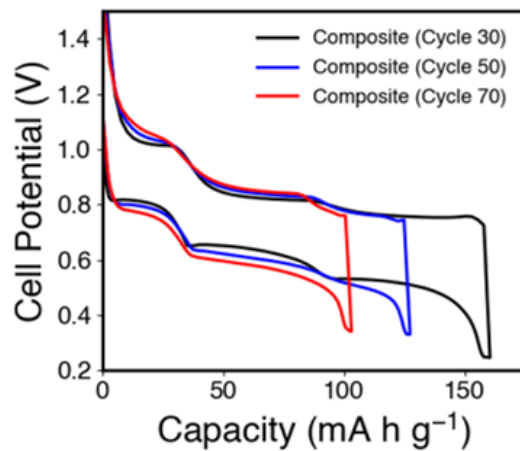
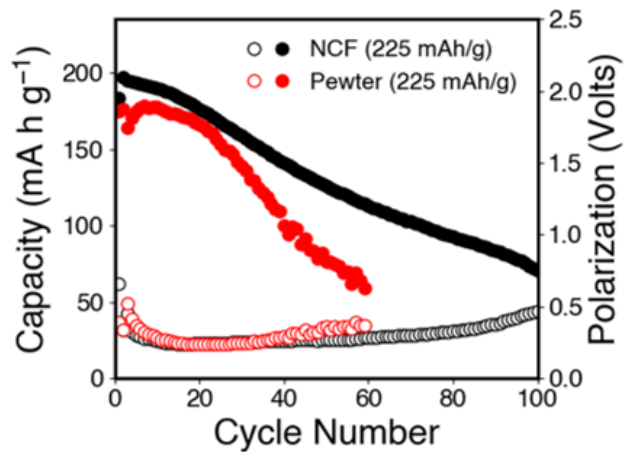
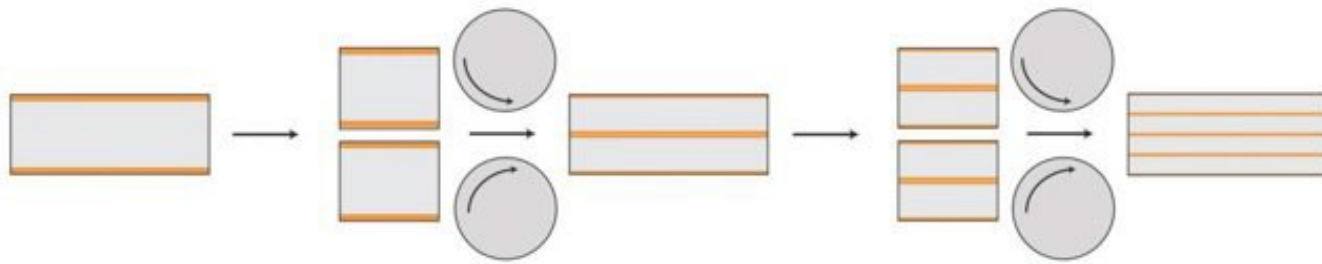
SCREENING OF ELEMENTAL FOILS AS ALLOY ANODES

- Various elemental metal foils were prepared and tested in lithium cells
- 8 elements stored sufficient capacity to be used as bulk active materials
 - 4 were good candidates for foil anodes (Al, In, Sn, Pb)



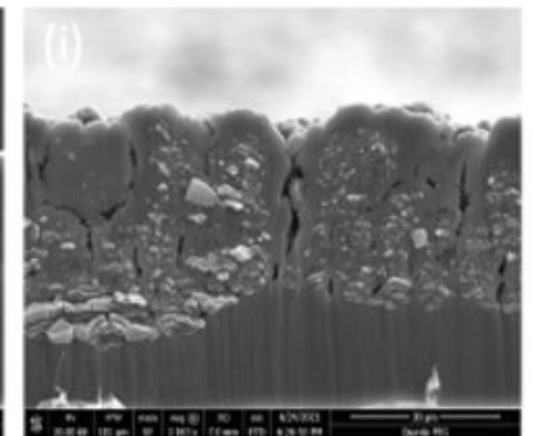
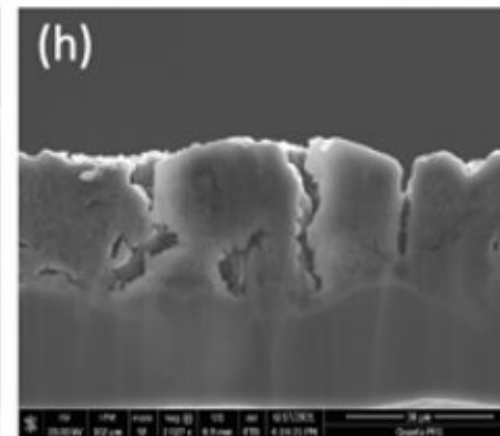
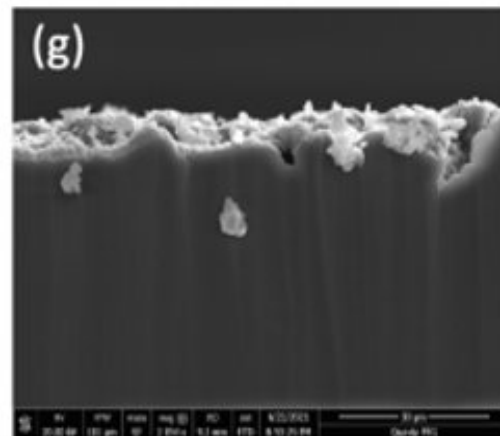
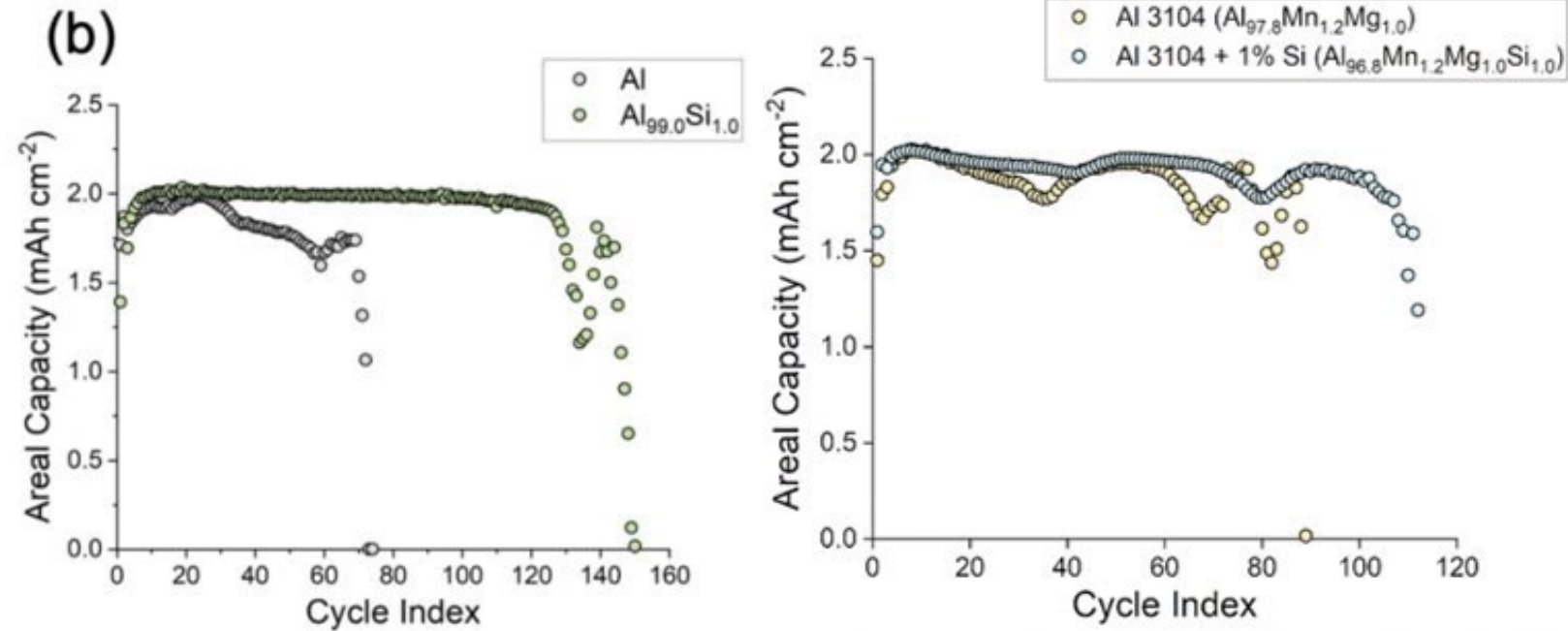
NANOCOMPOSITE FOILS (NCFs)

- Composite foil systems containing an inactive metal matrix prevent pulverization of the active material, which can stabilize cycling
- Tin composite foils were studied extensively



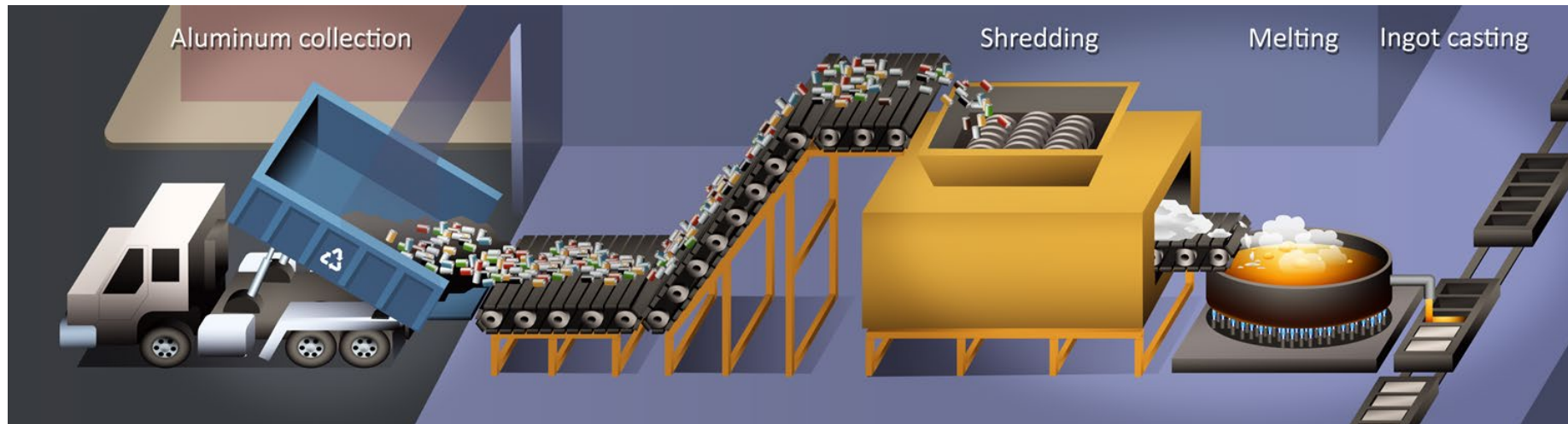
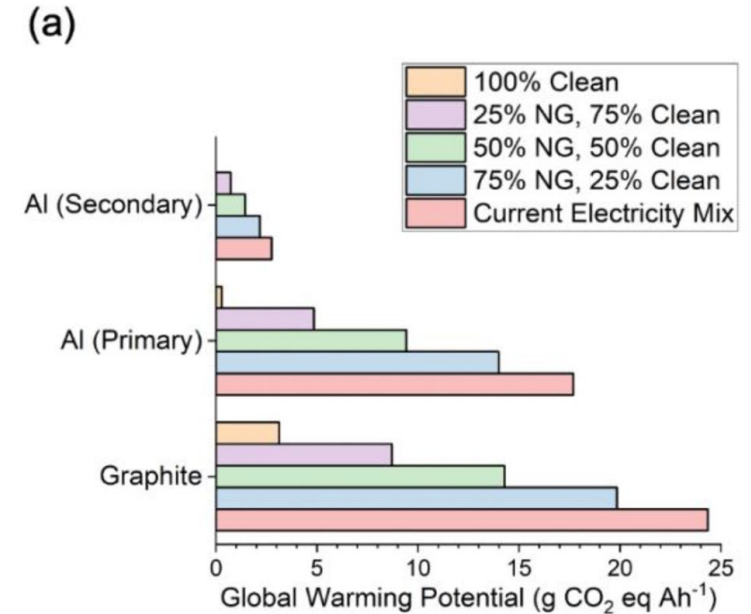
USING DOPANTS TO IMPROVE ALUMINUM FOIL ANODES

- Small amounts of dopants radically alter cell-level performance of foil anodes
- Our new composite foil approach allows us to implement these dopants in engineered electrode systems
- Computational modeling provides insight into mechanisms underlying the alterations in performance



LIFE CYCLE ANALYSIS OF FOIL ANODE MATERIALS

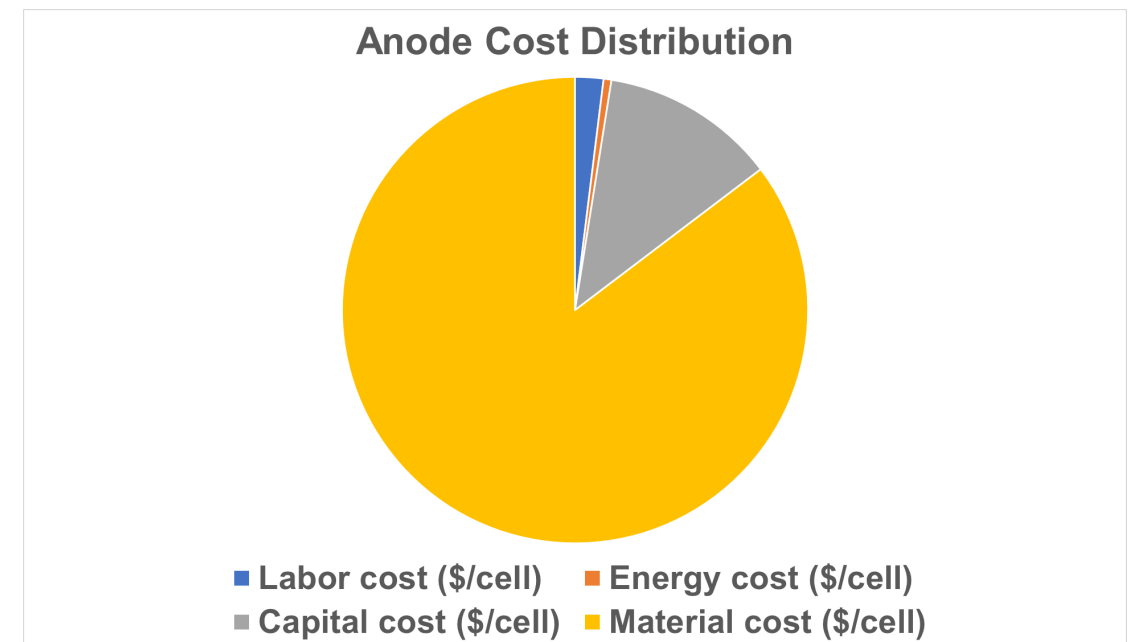
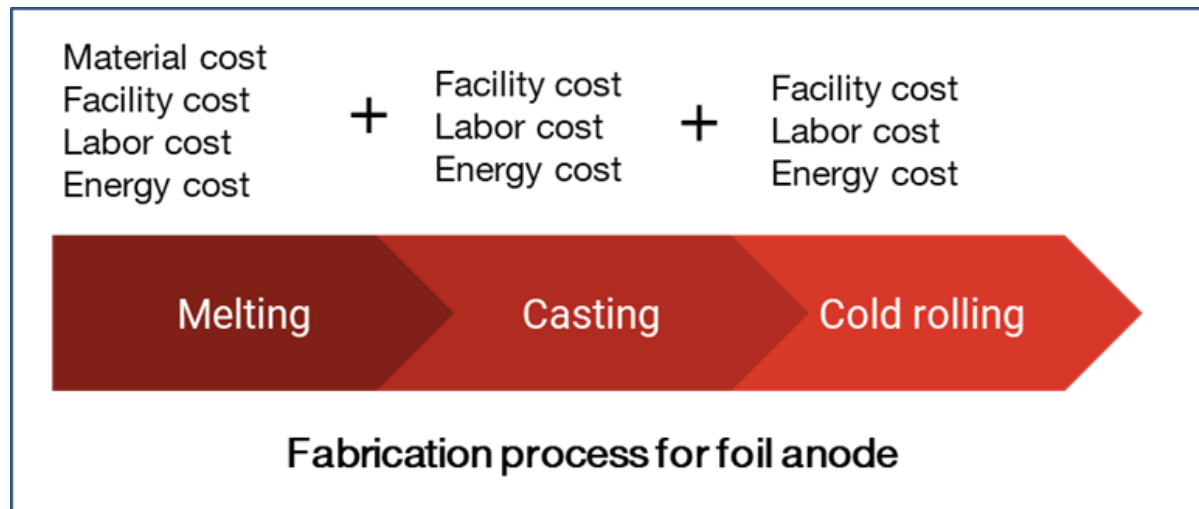
- To maximize the positive impact, environmental and social effects must be taken into account during materials design
- We have created a robust, holistic, and accessible framework for researchers to use for assessing the impacts for any battery material, addressing four issues:
 - (i) total energy use and emissions
 - (ii) toxicity
 - (iii) habitat destruction
 - (iv) social impact



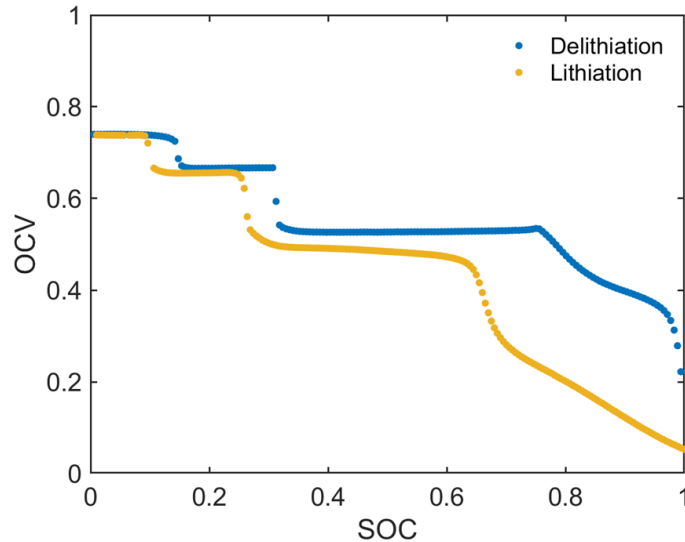
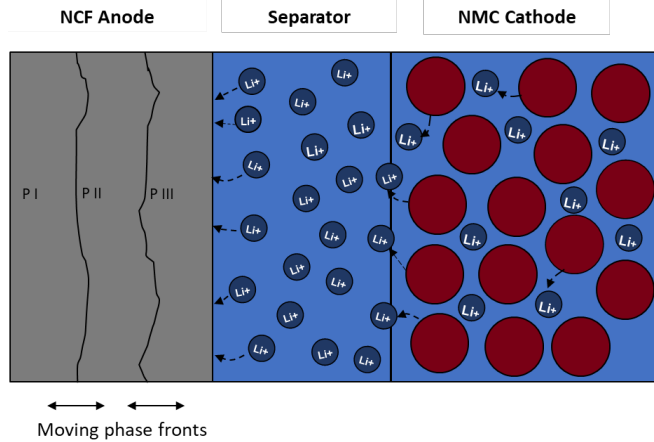
S. Sharma and A. Manthiram,
Energy and Environmental Science (2020)

TECHNO ECONOMIC ANALYSIS

- A tool for calculating the total cost of the $Zn_{0.44}Sn_{0.55}Bi_{0.01}$ (ZTB) anode system is developed in Excel with the help of BatPac



MODELING ZTB ALLOY ANODE



- Detailed moving boundary and phase field modeling to track the microstructural evolution

Diffusion

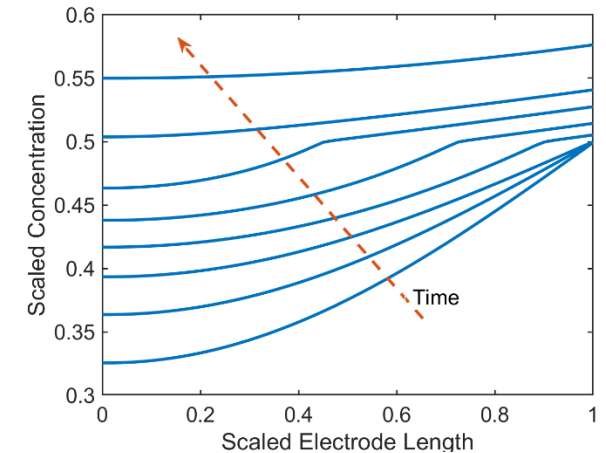
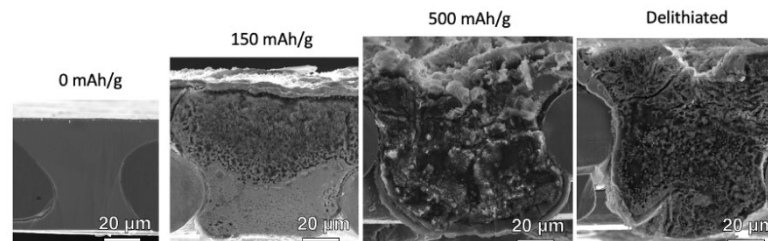
$$\frac{\partial}{\partial x} D_{P,i}(c_s) \frac{\partial c_s}{\partial x} = \frac{\partial c_s}{\partial t}$$

$$-D_{P,i}(c_s) \frac{\partial c_s}{\partial x} = \frac{i_{app}}{F}$$

Kinetics

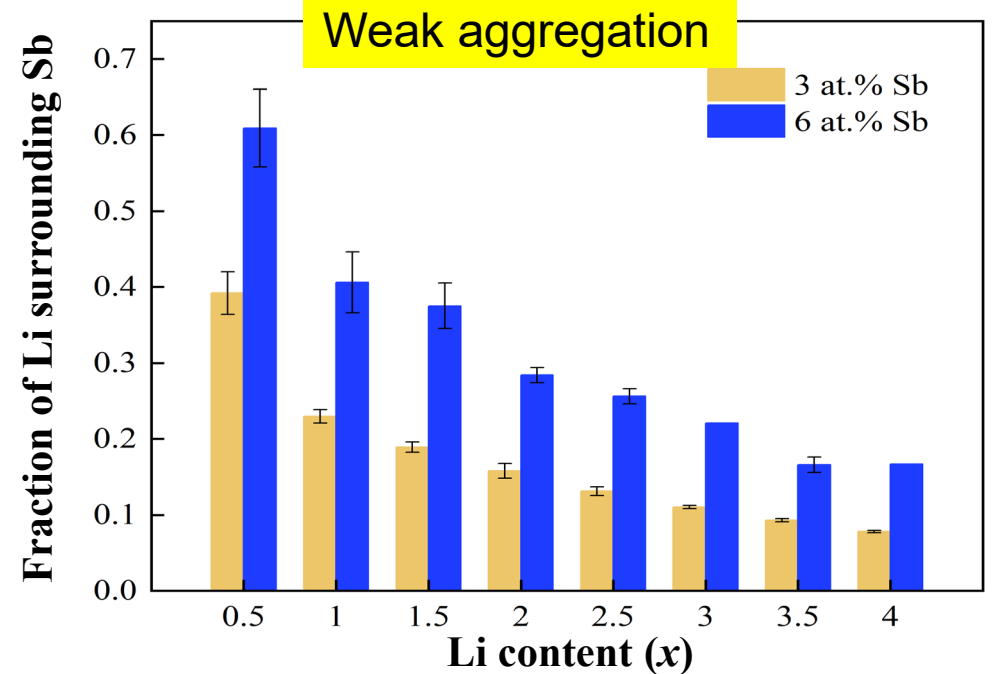
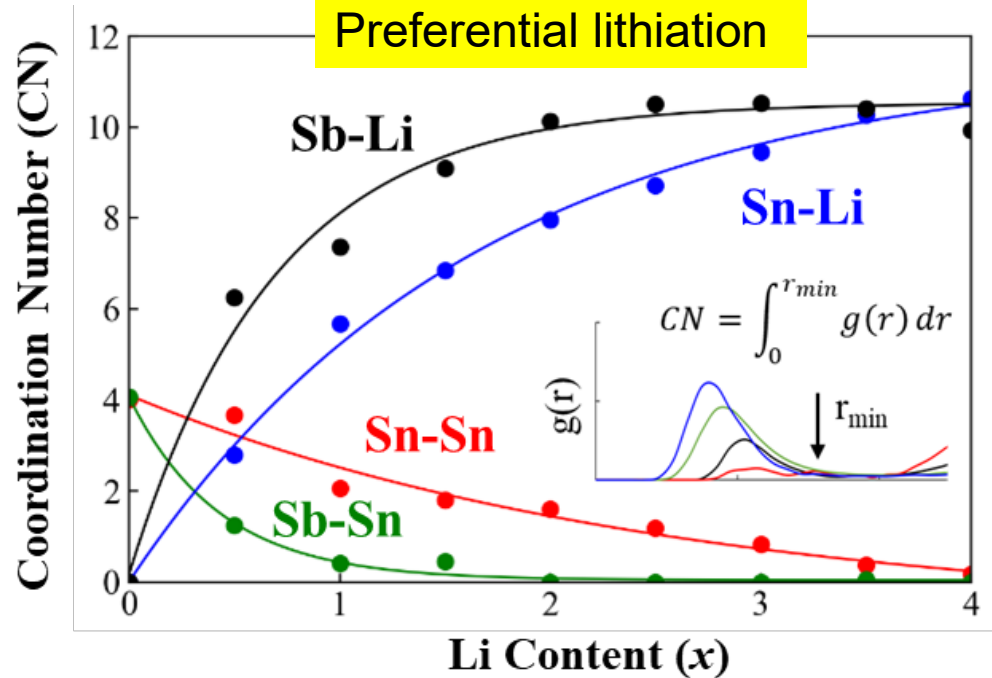
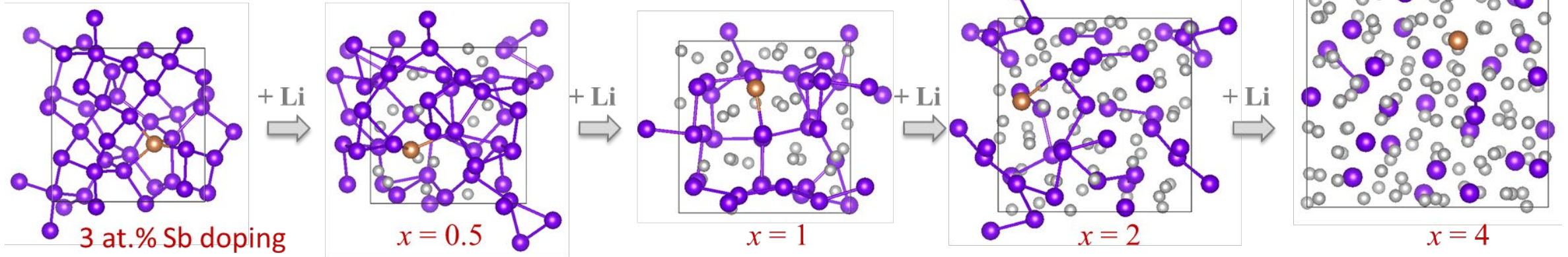
$$i_{app} = 2i_0 \sinh\left(\frac{\eta}{2}\right)$$

Results indicating phase transformation



IMPACT OF Sb DOPING ON Sn ANODE CYCLING STABILITY

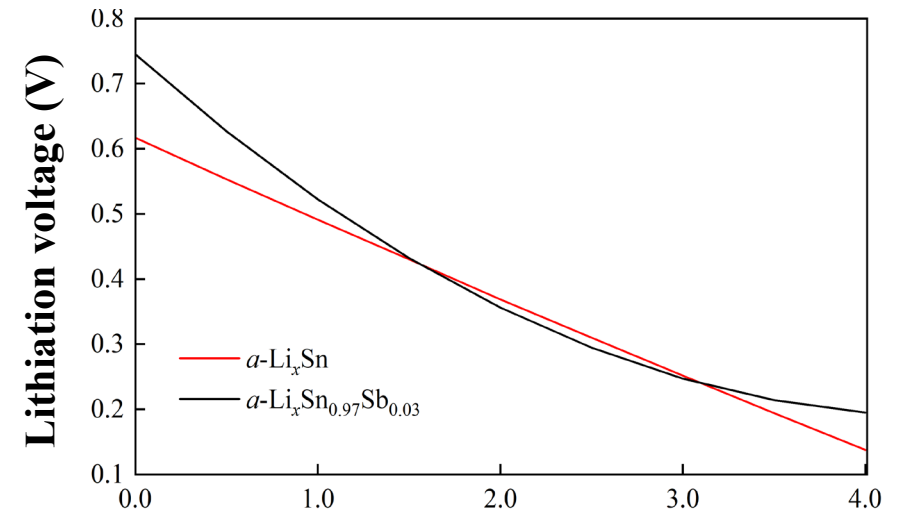
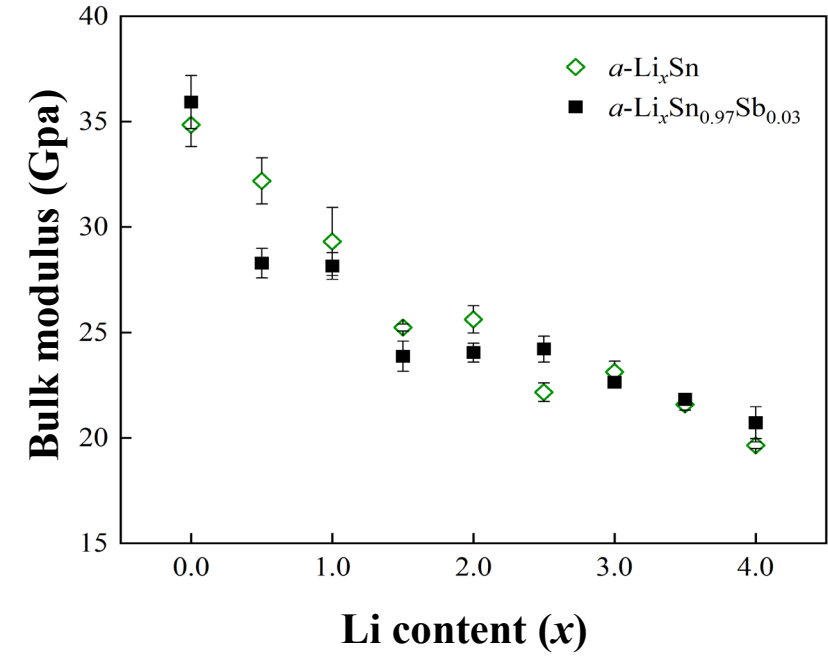
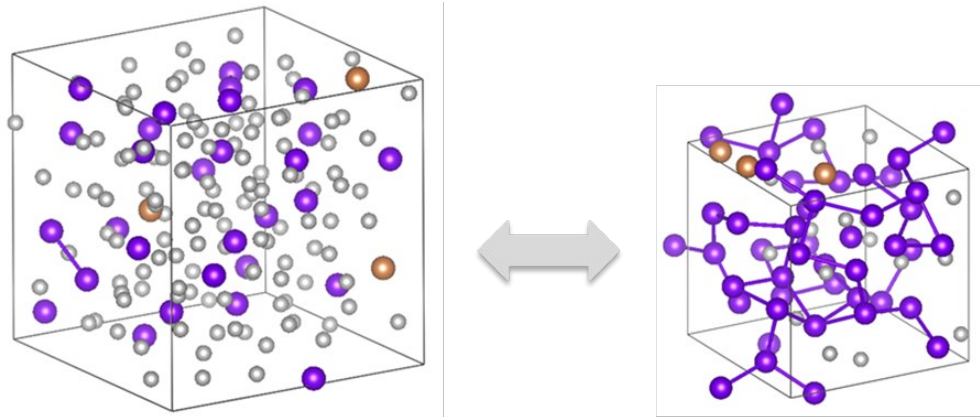
Lithiation behavior of Sb-doped Sn anode ($\alpha\text{-Li}_x\text{Sn}_{0.97}\text{Sb}_{0.03}$)



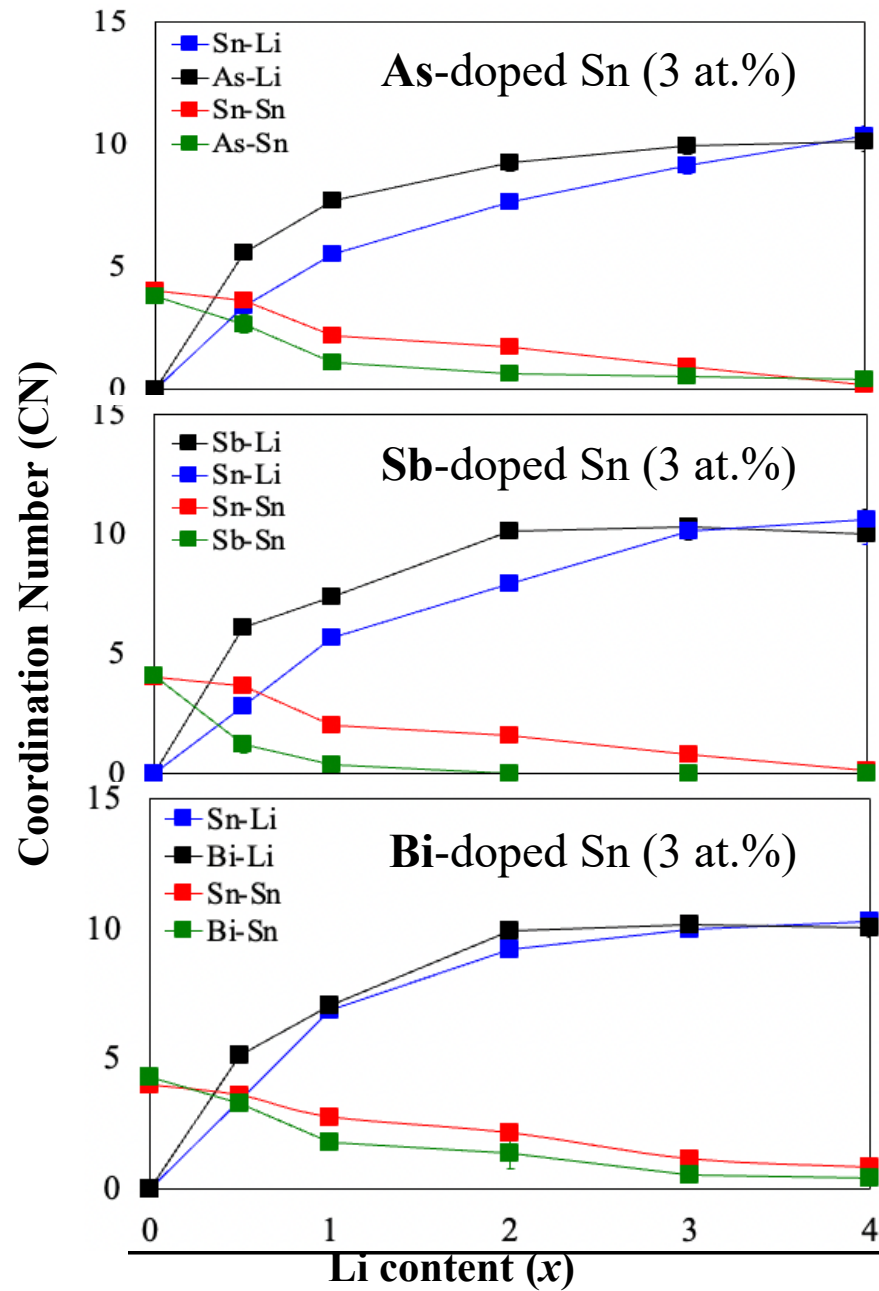
IMPACT OF Sb DOPING ON Sn ANODE CYCLING STABILITY

Predicted Li diffusivity at 300 K ($\times 10^{-7}$ cm²/s)

	x	D_0 (cm ² /s)	E_a (eV)	\underline{D}_{Li} (300K)
Pure Sn	2	6.13×10^{-4}	0.22	1.1×10^{-7}
	3	5.18×10^{-4}	0.22	1.3×10^{-7}
	4	9.43×10^{-4}	0.23	1.3×10^{-7}
Sn _{0.97} Sb _{0.3}	0.5	1.12×10^{-3}	0.32	5×10^{-9}
	1	5.52×10^{-4}	0.28	1.1×10^{-8}
	2	6.69×10^{-4}	0.23	8.6×10^{-8}
	3	6.59×10^{-4}	0.21	1.8×10^{-7}
	4	6.24×10^{-4}	0.19	3.3×10^{-7}



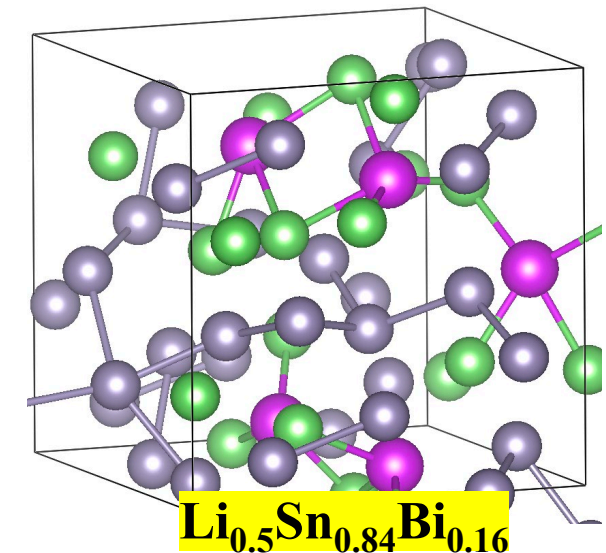
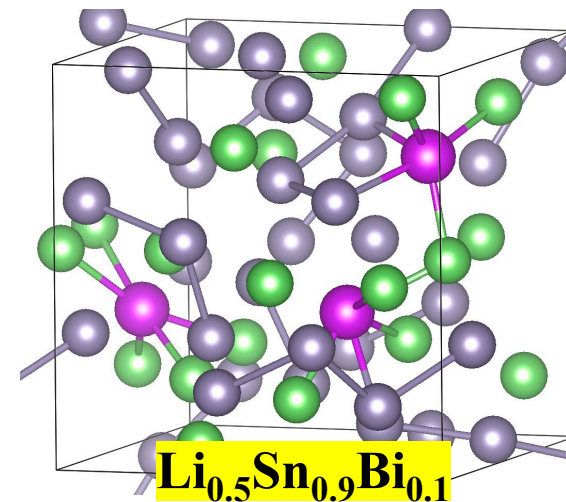
HOW ABOUT OTHER DOPANTS?



Aluminum Post-Transition	Silicon Metalloid	Phosphorus Nonmetal	Sulfur Nonmetal
31 Ga Gallium Post-Transition	32 Ge Germanium Metalloid	33 As Arsenic Metalloid	34 Se Selenium Nonmetal
49 In Indium Post-Transition	50 Sn Tin Post-Transition	51 Sb Antimony Metalloid	52 Te Tellurium Metalloid
81 Tl Thallium Post-Transition	82 Pb Lead Post-Transition	83 Bi Bismuth Post-Transition	84 Po Polonium Metalloid

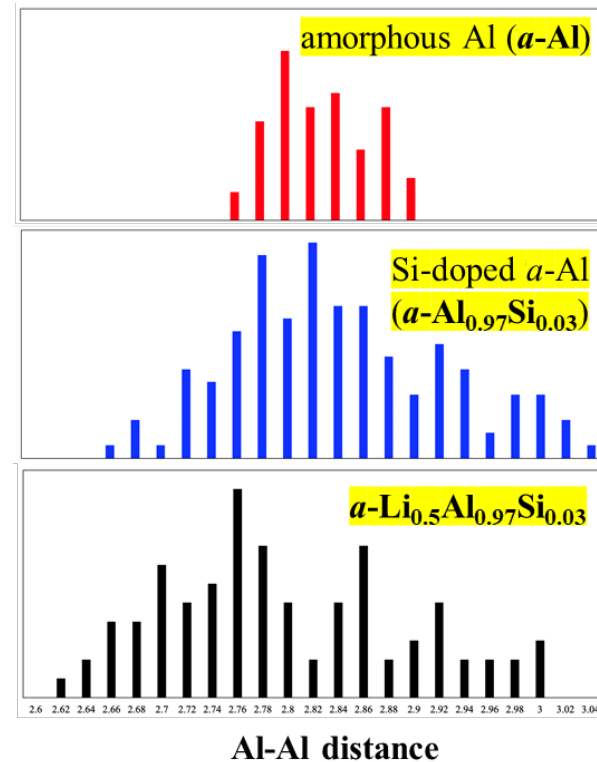
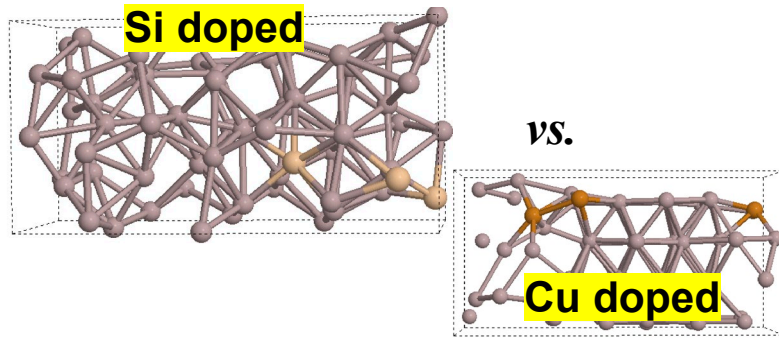
Electronegativity	
Sn	1.96
As	2.18
Sb	2.05
Bi	2.02

Aggregation tendency

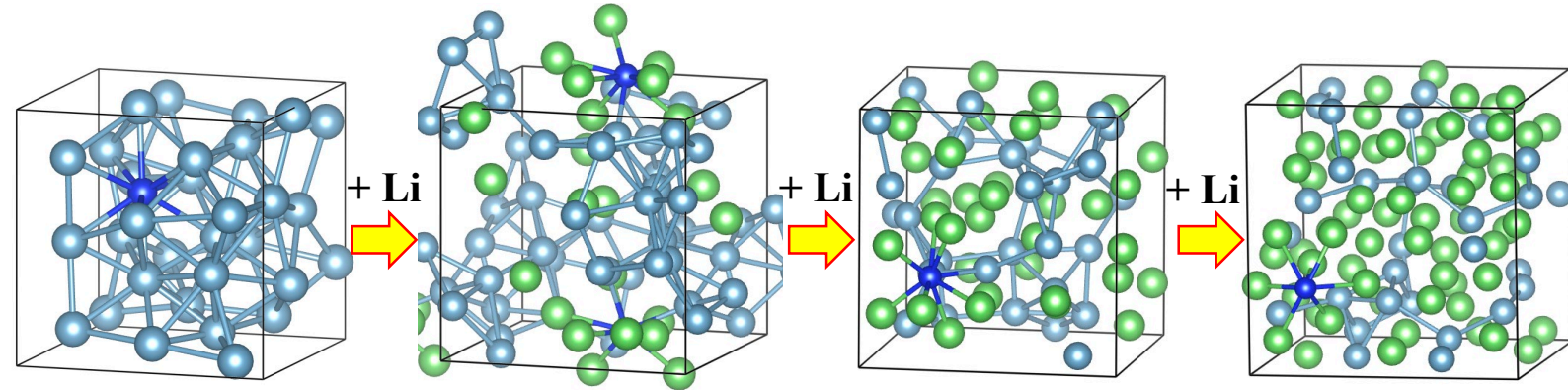


Si DOPING EFFECT ON Al ANODE PERFORMANCE

Si doping induced amorphization

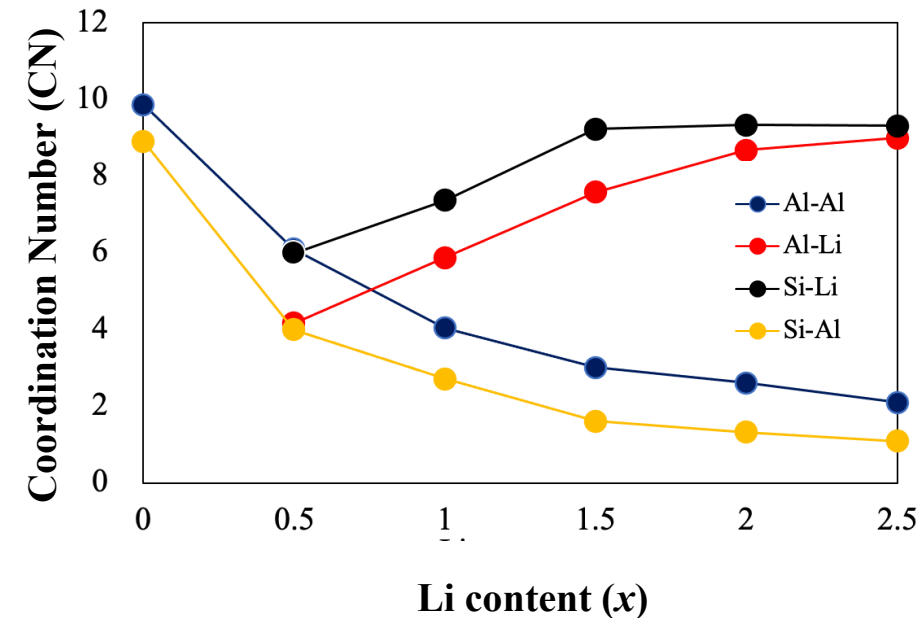


Preferential lithiation of Si

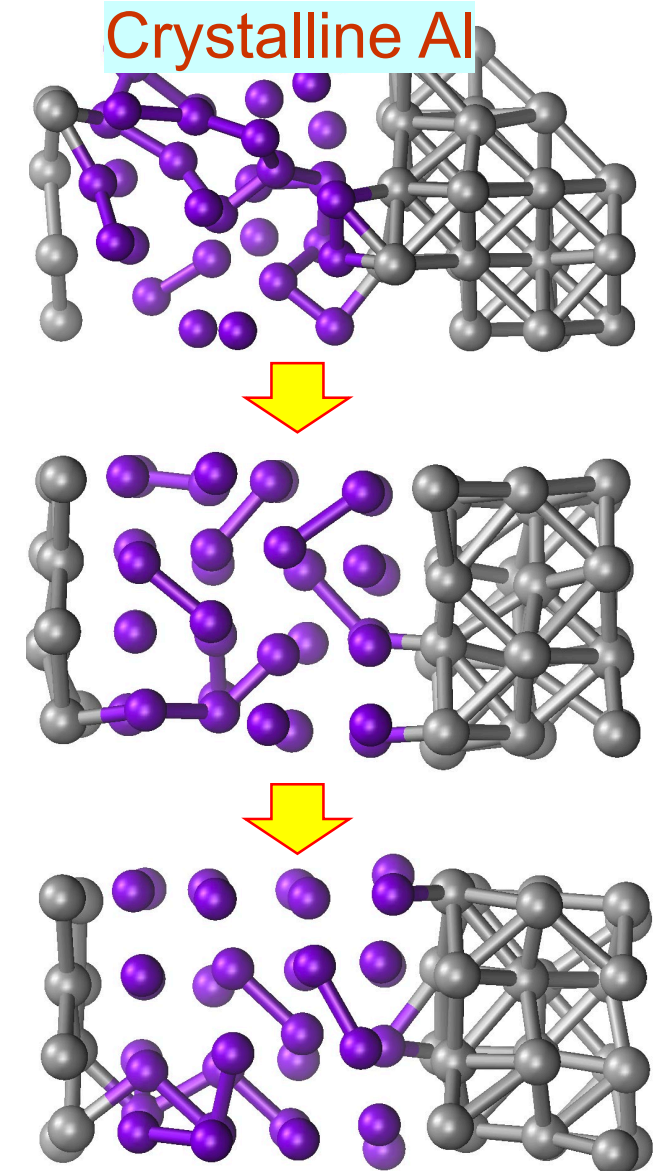
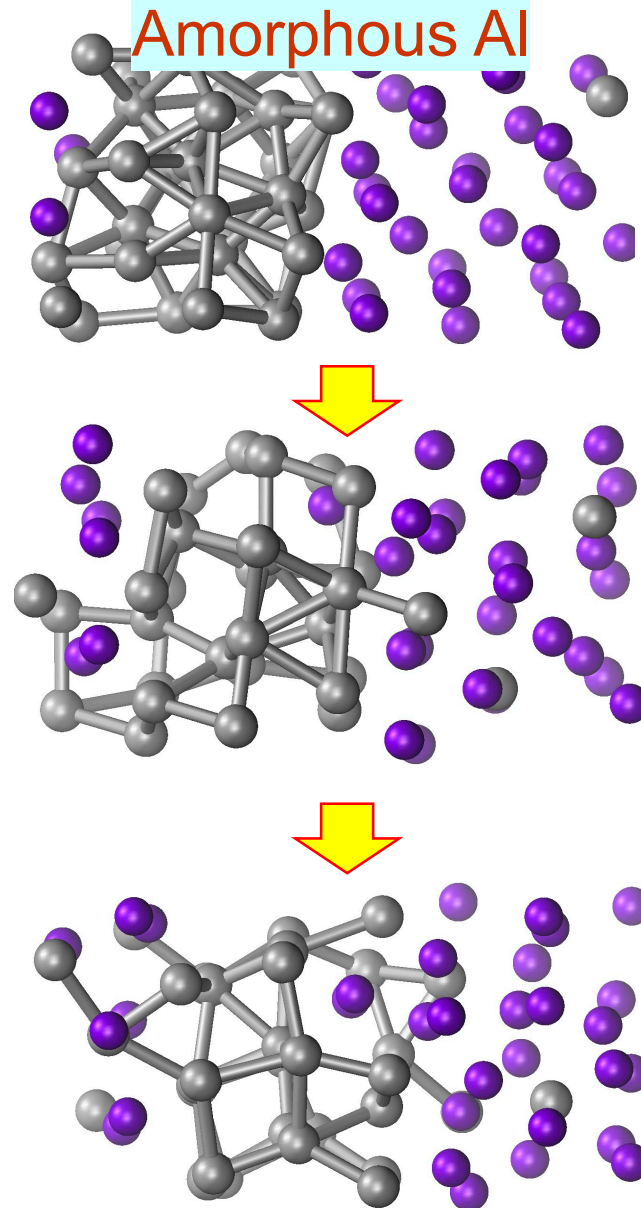
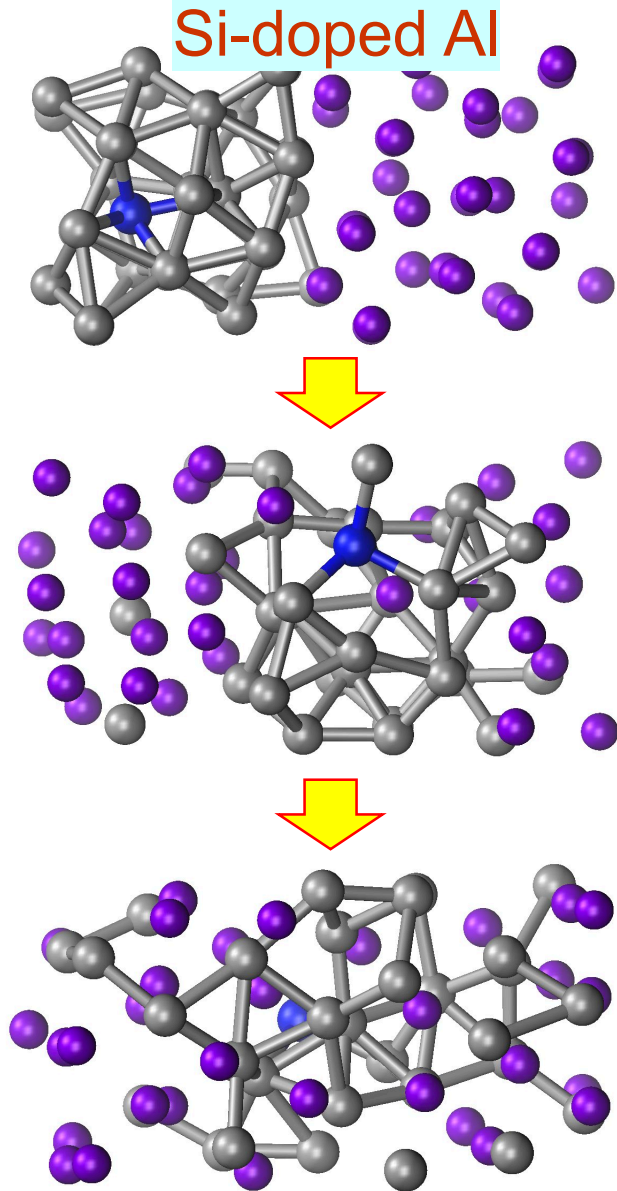


Predicted Li diffusivity at 300 K ($\times 10^{-7} \text{ cm}^2/\text{s}$)

Li content, x	0.5	1	1.5	2
pure <i>a</i> -Al	0.08	0.2	1.3	2.3
<i>a</i> -Al _{0.97} Si _{0.03}	1.1	1.4	2.5	3.6



SYNERGISTIC EFFECT OF DOPANT AND STRUCTURAL DISORDER



SUMMARY

- Replacing the graphite anode in current lithium-ion batteries with low-cost alloy anodes can make the technology sustainable with higher energy density and better safety
- A new approach has been developed with simple processing to obtain nanocomposite foil anodes that overcomes many of the challenges encountered traditionally with alloy anodes
- The integration of experiments and modeling along with techno-economic analyses by the team has provided new insights for materials selection and processing

PROJECT PUBLICATIONS

1. S. Sharma and A. Manthiram, "Towards More Environmentally and Socially Responsible Batteries," *Energy and Environmental Science* **2020**, 13, 4087-4097.
2. K. Shah, A. Subramaniam, L. Mishra, T. Jang, M. Z. Bazant, R. D. Braatz, V. R. Subramanian, "Challenges in Moving to Multiscale Battery Models - Where Electrochemistry Meets and Demands More from Math," *Journal of the Electrochemical Society*, **2020**, 167, 133501.
3. B. Heligman and A. Manthiram, "Elemental Foil Anodes for Lithium-ion Batteries," *ACS Energy Letters*, **2021**, 6, 2666-2672.
4. S. Sharma, P. Crowley, and A. Manthiram, "Aluminum-Silicon Alloy Foils as Low Cost, Environmentally Friendly Anodes for Lithium-ion Batteries," *ACS Sustainable Chemistry and Engineering*, **2021**, 9, 14515-14524.
5. B. Heligman, K. Scanlan, and A. Manthiram, "An in-depth Analysis of Transformation of Tin Foil Anodes during Electrochemical Cycling in Lithium Ion Batteries," *Journal of the Electrochemical Society*, **2021**, 168, 120544.
6. B. Heligman, K. Scanlan, and A. Manthiram, "Nanostructured Composite Foils Produced via Accumulative Roll Bonding as Lithium Ion Battery Anodes," *ACS Applied Materials and Interfaces* (Accepted).
7. J. Yu, T.-H. Yang, W. Hao, M. Lee, and G. S. Hwang, "First-principles prediction on the cyclic stability of antimony-doped tin anodes in lithium-ion batteries" *Journal of Power Sources* (submitted).
8. K. S. Balan, K. A. Shah, J. Lee, B. T. Heligman, A. Manthiram, G. S. Hwang, K. Muthuraman and V. R. Subramanian, "Model based analysis of Nanocomposite foil anodes- A multiscale approach," *Sustainable Energy and Fuels* (planned).
9. J. Yu, T.-H. Yang, B. T. Heligman, A. Manthiram, and G. S. Hwang, "First-principles evaluation of doping effects on the lithiation behavior of tin anodes for lithium-ion batteries," *Journal of Physical Chemistry C* (planned).
10. K. Balan, K. Shah, B.T. Heligman, J. Lee, G. S. Hwang, A. Manthiram and V. R. Subramanian, "DFT guided electrochemical-transport model for next-generation foil anodes," *Journal of the Electrochemical Society* (planned).
11. J. Yu, S. Sharma, A. Manthiram, and G. S. Hwang, "Anomalous effects of silicon doping on the lithiation behavior and structural changes of aluminum anodes for lithium-ion batteries," *ACS Sustainable Chemistry and Engineering* (planned).