Battery Chemistries for Relieving Supply Chain Issues of Today, Tomorrow, and Day-after-tomorrow

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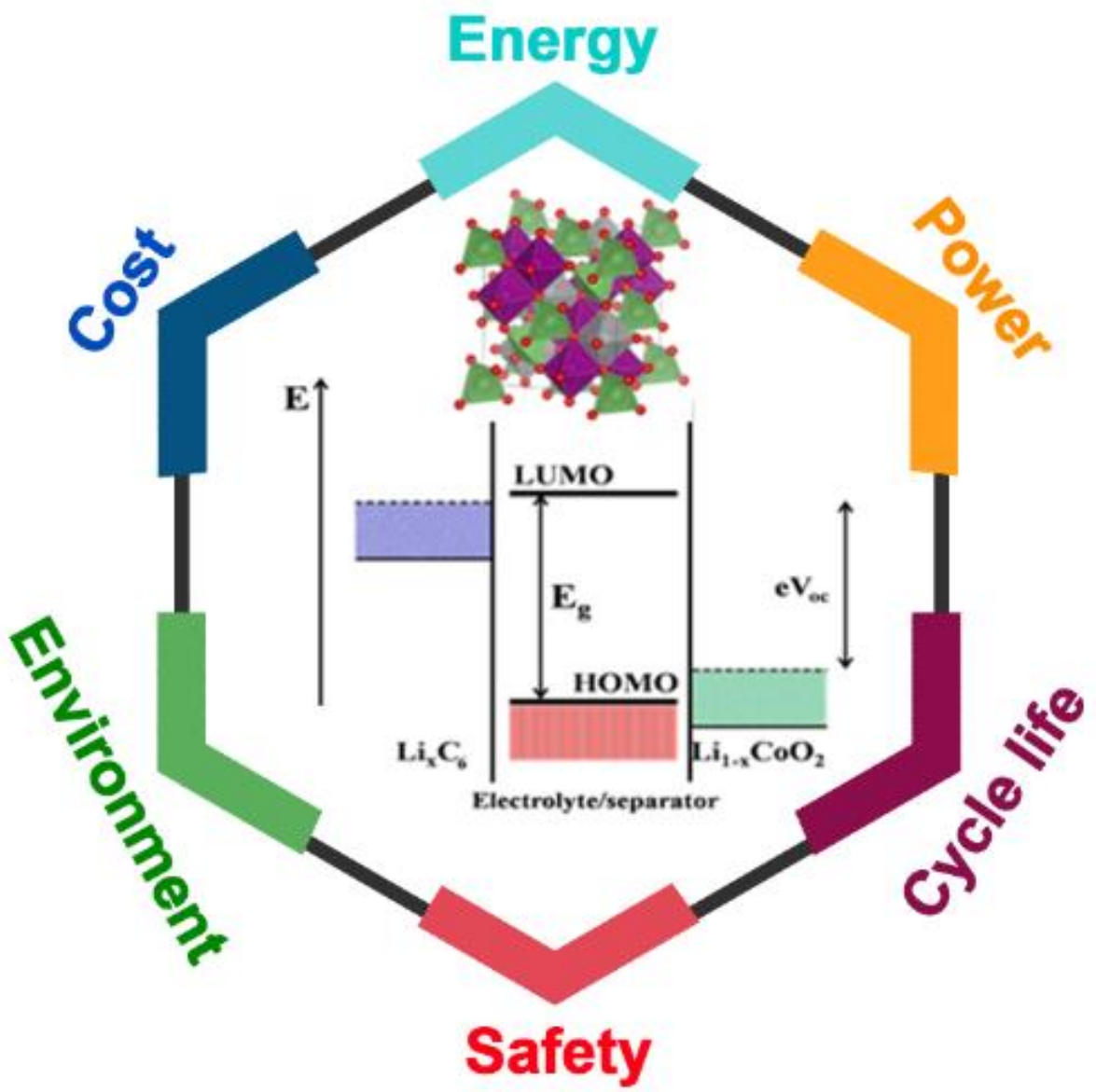
Battery Performance Parameters



- Cost, sustainability, and supply chain issues will be the single dominant issue as we move forward

Challenges with supply chain and sustainability

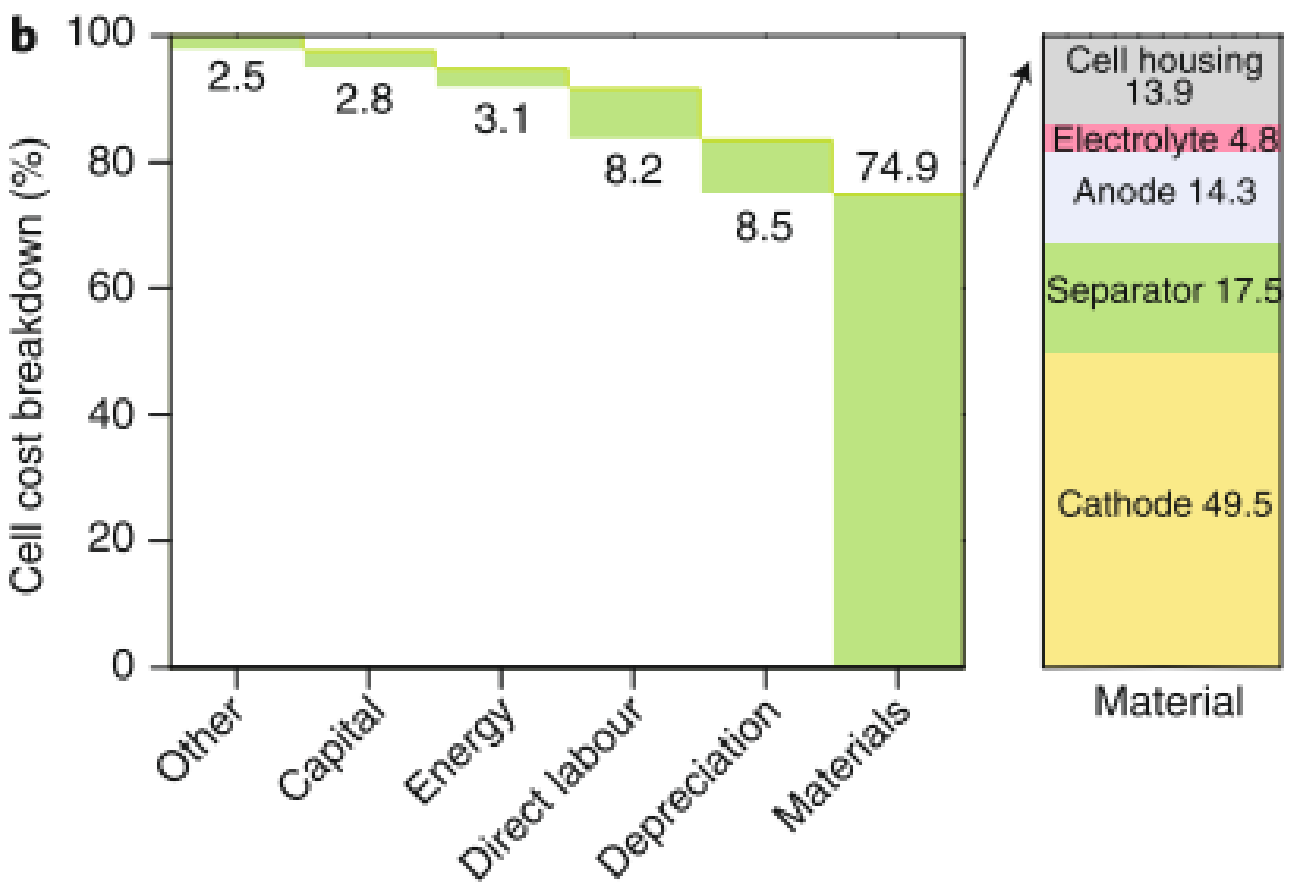
- Commercialization of lithium-ion batteries began in 1991 with $LiCoO_2$ and graphite
  - Cobalt is expensive; both cobalt and graphite have supply chain problems
  - Cobalt is mined in DRC in Central Africa, political tensions, child labor, air pollution

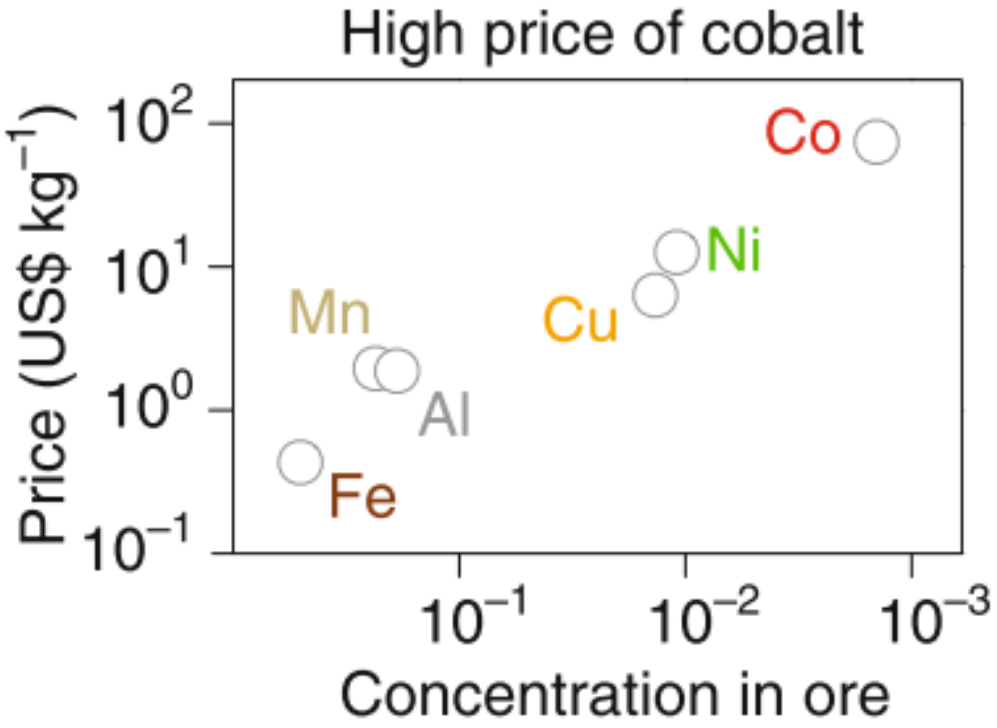
- The trend since then is to reduce cobalt by increasing nickel: $LiNi_{1-x-y}Mn_xCo_yO_2$ (NMC)
  - NMC622 (60% Ni and 20% Co) is commercial
  - High-nickel leads to cycle, thermal, and air instabilities
  - Nickel cost is lower than cobalt, but not a whole lot

- **Cobalt is a problem today**
- **Nickel is a problem tomorrow**
- **Lithium could become a problem day-after-tomorrow**

- What do we do?
  - Focus on sustainable battery technologies progressively
  - Can batteries be free from mined metals?

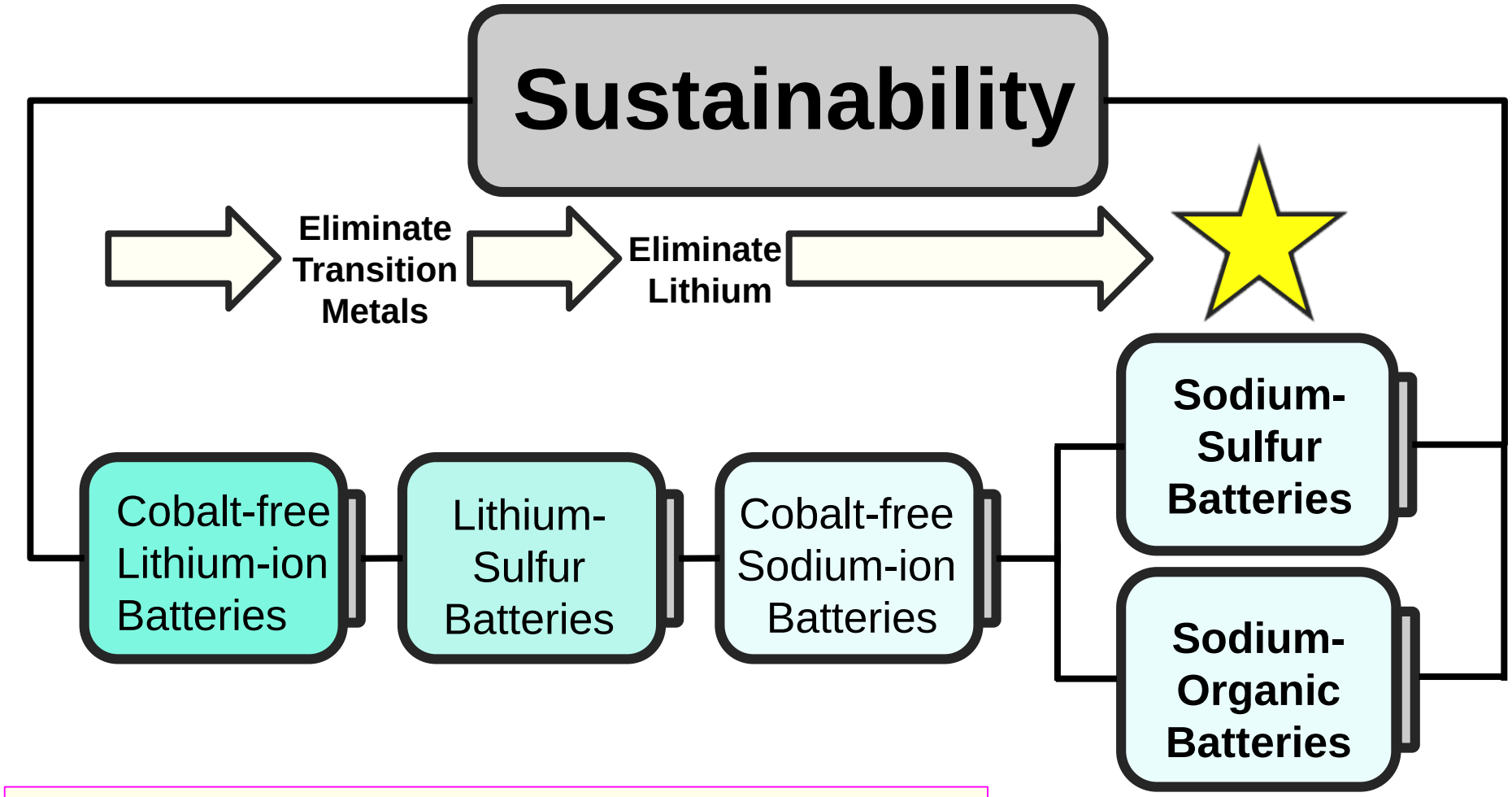
Cost Considerations





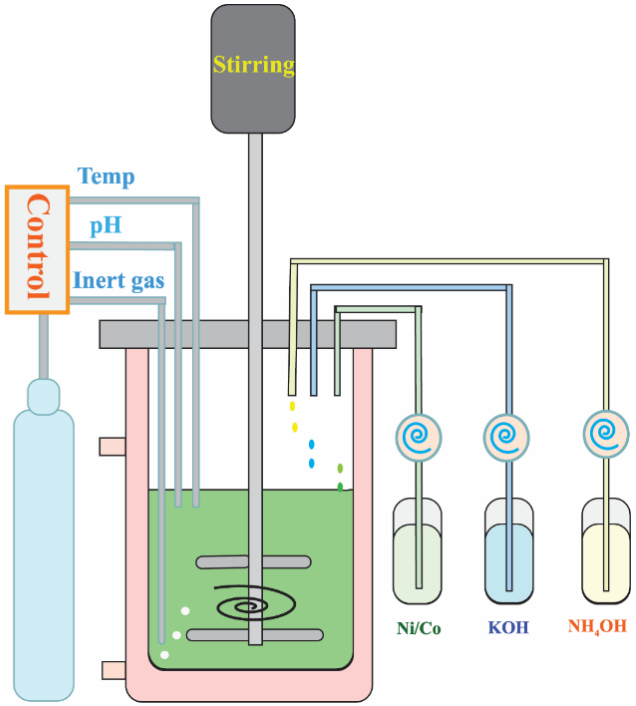
W. Li, E. M. Erickson, and A. Manthiram, *Nature Energy* **5**, 26 (2020)

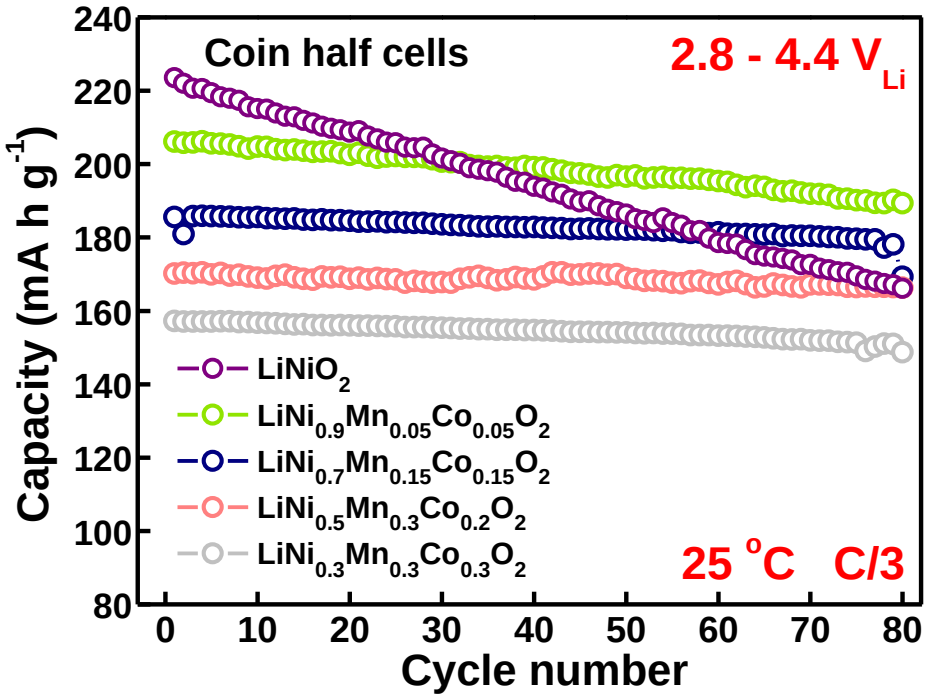
Vision: A Path to Sustainable Battery Technologies

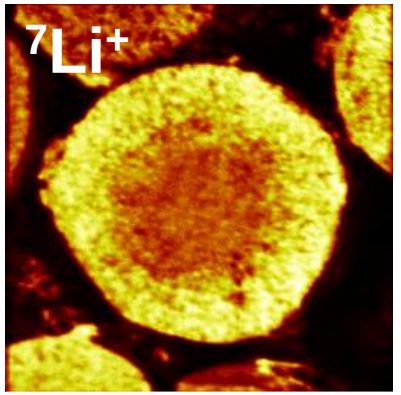


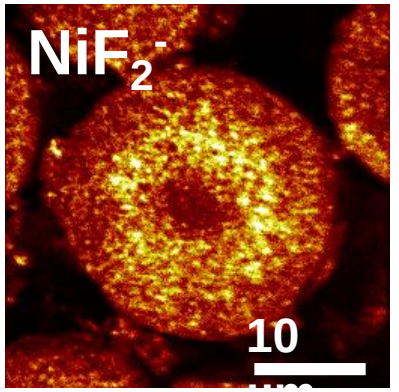
- Cobalt-free cells: high-nickel cells
- Cobalt- and nickel-free cells: lithium-sulfur cells
- Mined-metal-free cells: sodium-sulfur

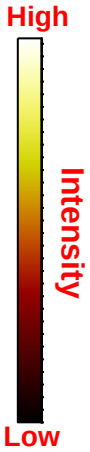
Low-cobalt or Cobalt-free, High-nickel Cathodes

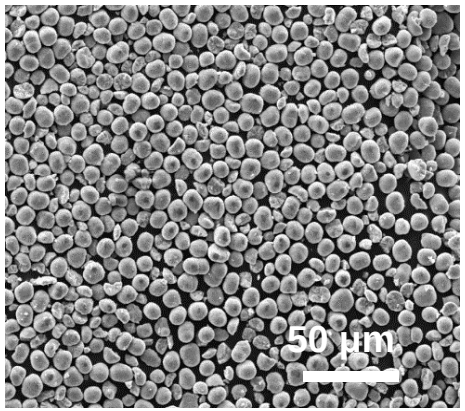


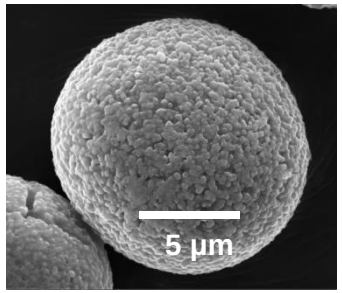






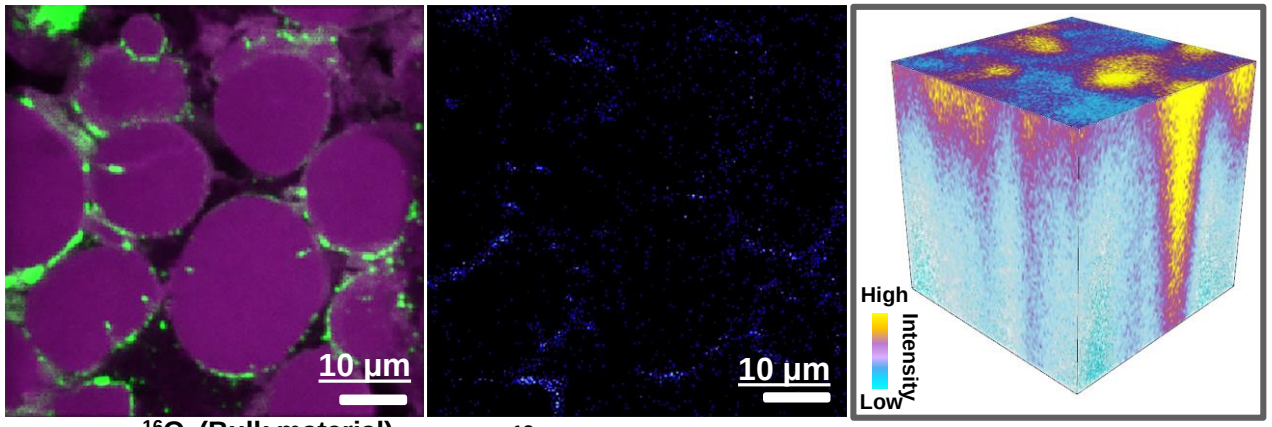


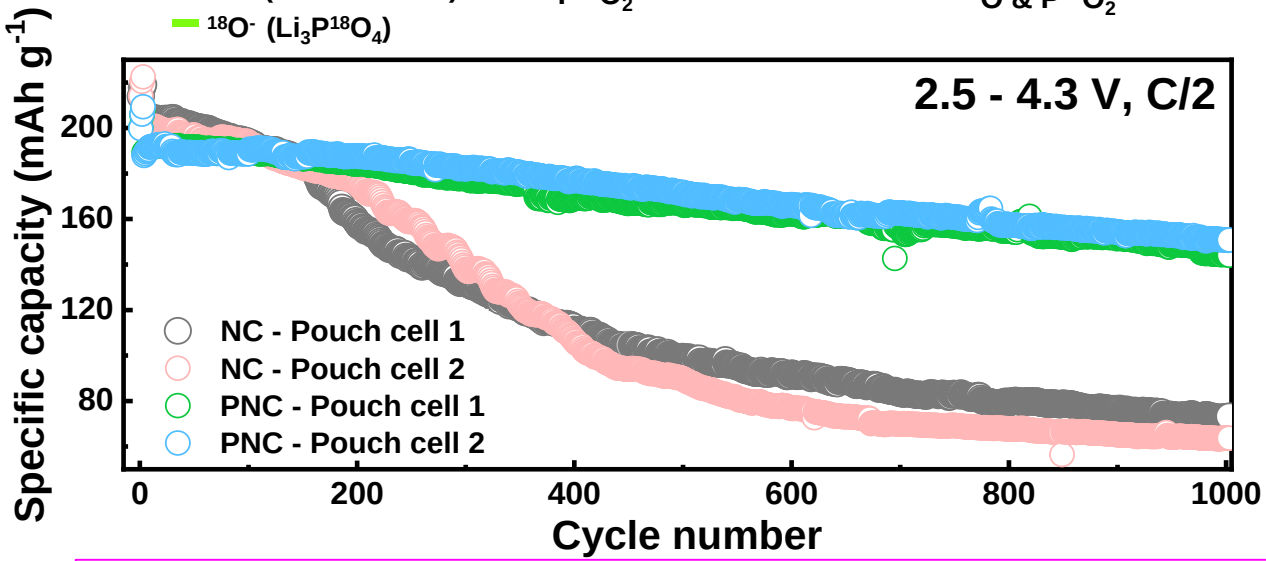


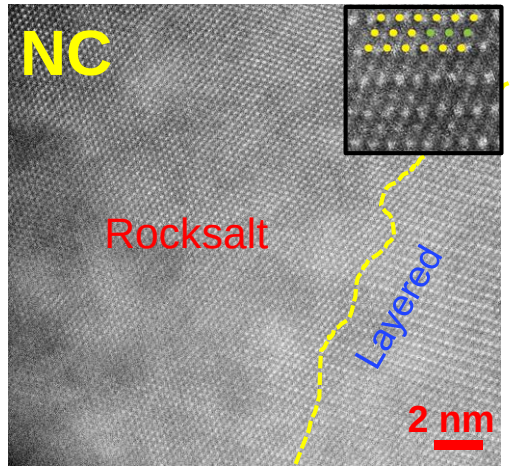


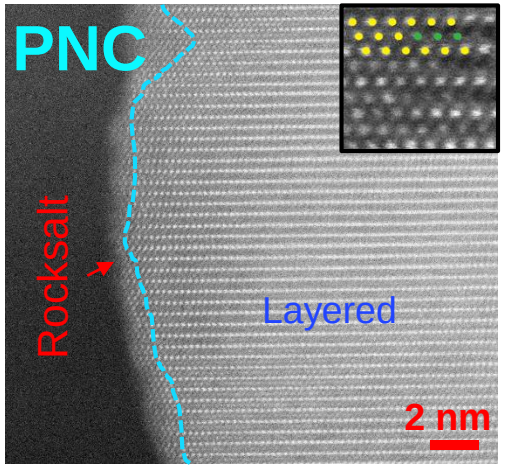
- 10 kg per batch of hydroxide precursor with any Ni content (0 – 100%)
- Incorporation of hard-to-dope ions like Al, Mg, *etc.* during coprecipitation
- XPS, TOF-SIMS, SEM, TEM, NMR, ….. synchrotron

A Low-cobalt Cathode $LiNi_{0.94}Co_{0.06}O_2$: Surface Stabilization with H_3PO_4





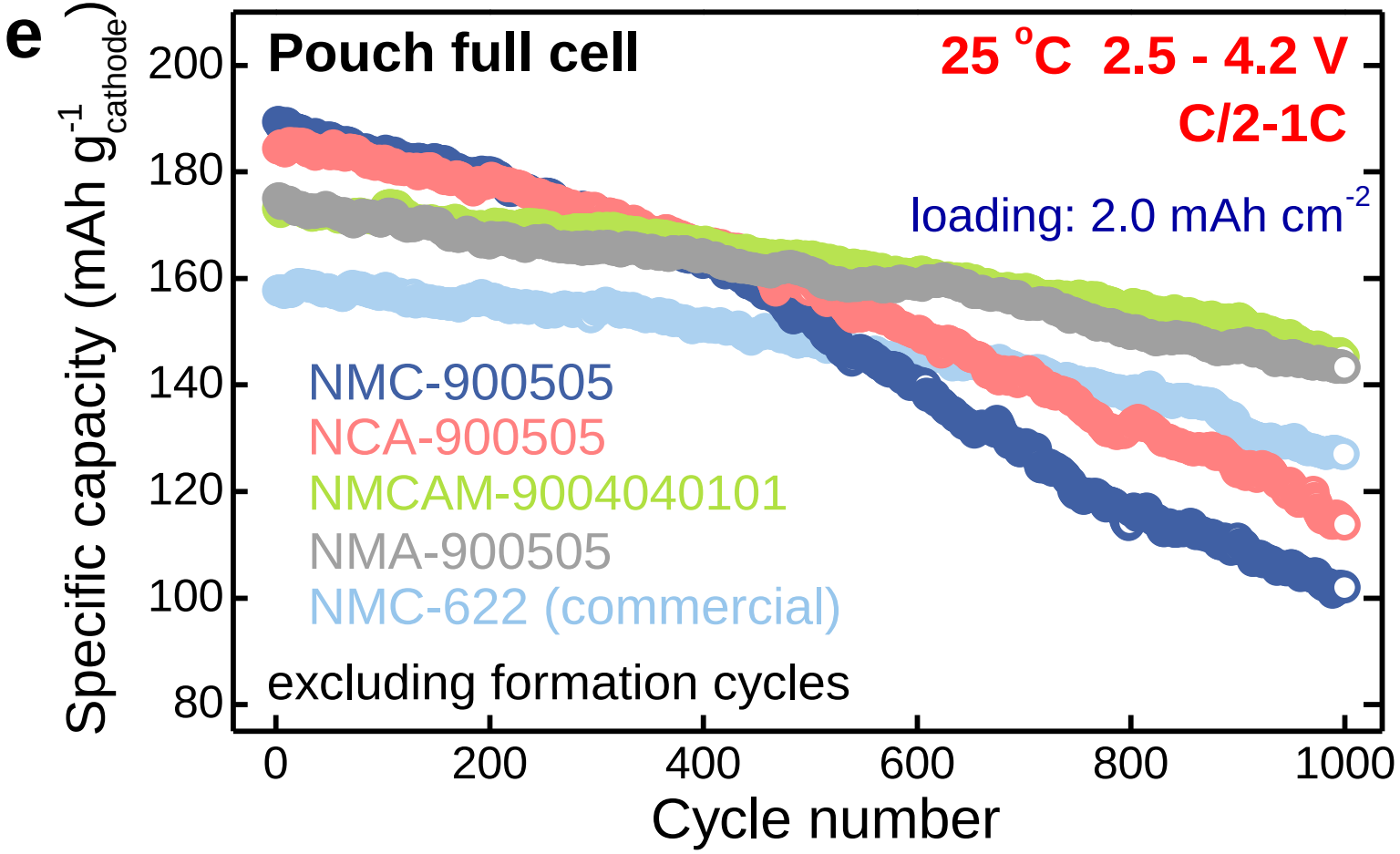


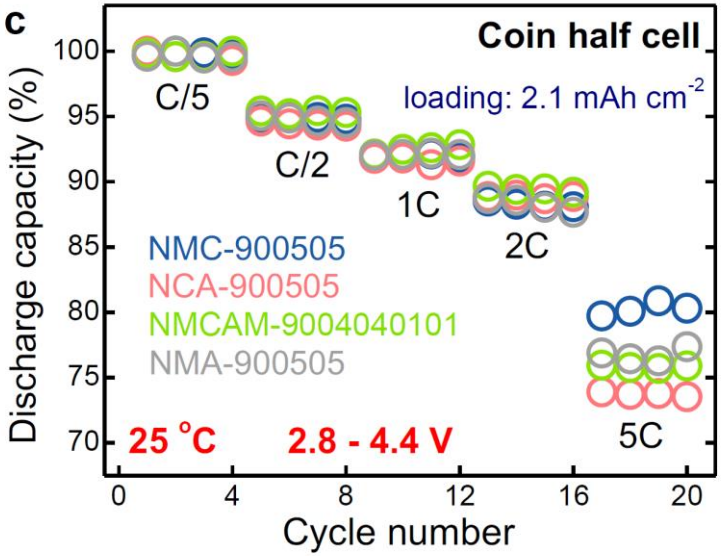


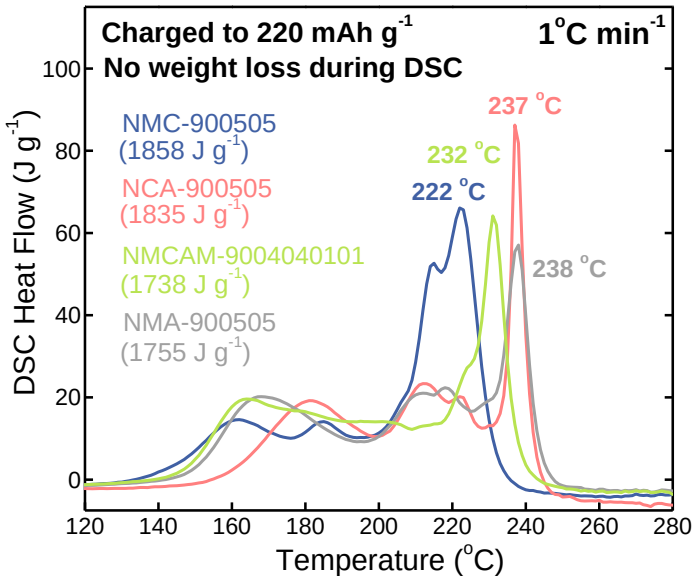
- Phosphoric acid treatment leads to ~ 10 nm Li_3PO_4 layer on P-$LiNi_{0.94}Co_{0.06}O_2$ (PNC)
- Much thicker rock salt layer (~ 15 nm) on NC than on PNC (~ 3 nm) after 1,000 cycles

Q. Xie and A. Manthiram, *Chemistry of Materials* **37,** 7413 (2020)

A Cobalt-free Cathode: $LiNi_{0.9}Mn_{0.05}Al_{0.05}O_2$ (NMA-900505)







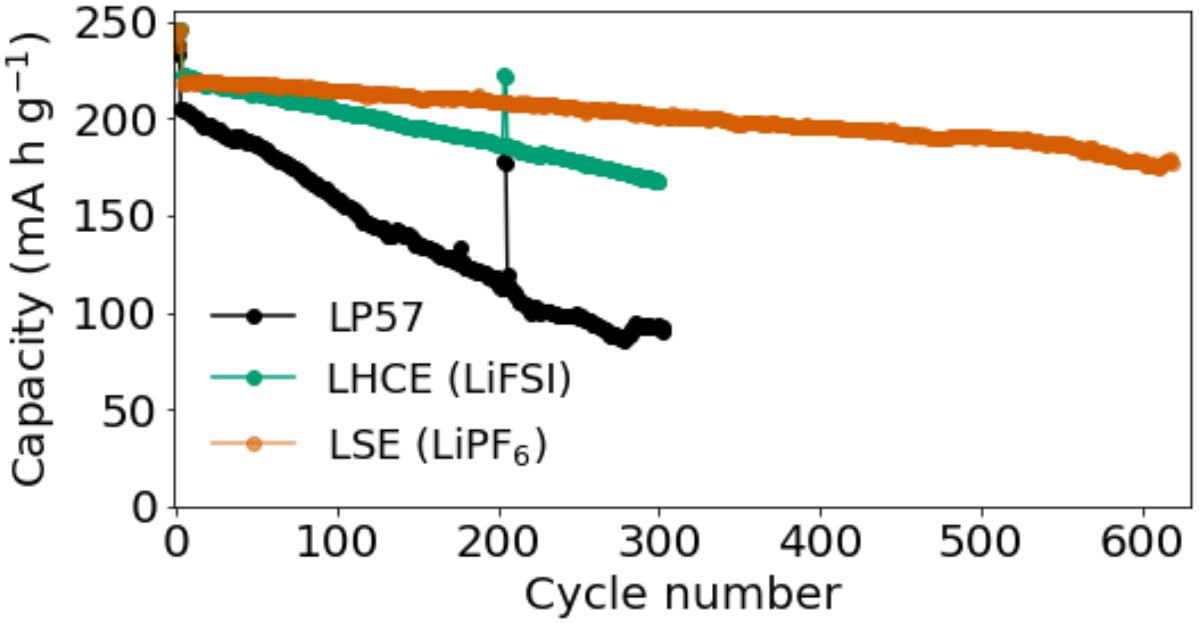
W. Li, S. Lee, and A. Manthiram, *Advanced Materials* **2002718** (2020)

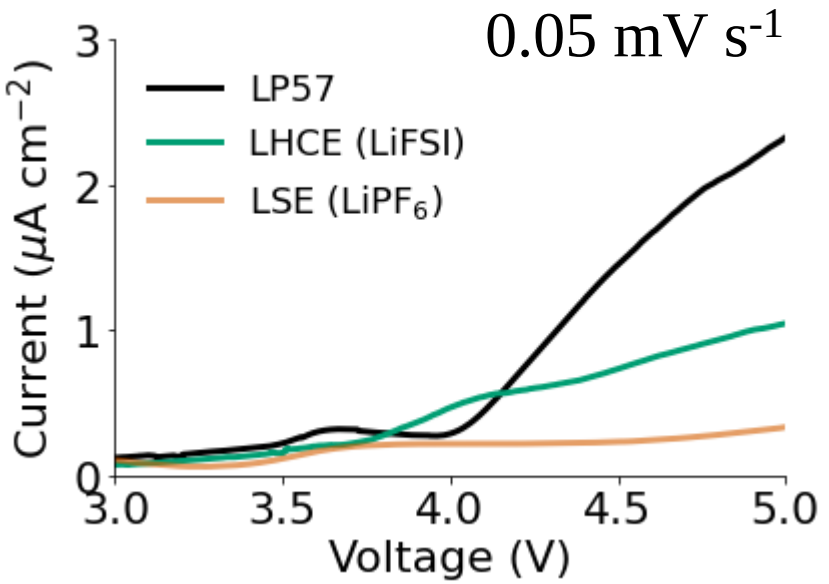
Domestic Production of Cobalt-free Cathodes

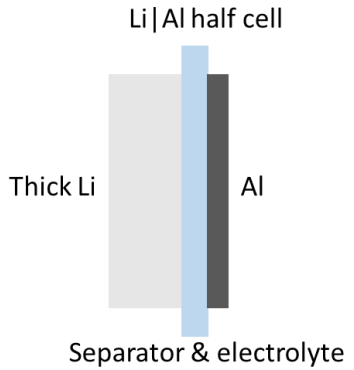
- TexPower EV Technologies is a startup out of UT Austin, located in Houston
  - Has licensed an issued cobalt-free cathode patent from UT Austin
  - U.S. Patent Number: 11,233,239
  - Is in the process of setting up a pilot plant
  - Planning to produce 150 tons of cobalt-free cathodes per year for domestic supply

Cobalt- and graphite-free Cells: $LiNiO_2$ with Lithium-metal Anode

Role of electrolyte





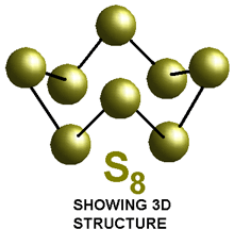


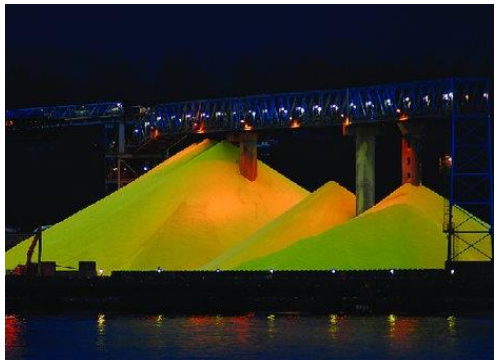
- LP57: 1 M $LiPF_6$ in EC/EMC (3/7, g/g)
- LHCE (LiFSI) or M47: LiFSI : DME : TTE = 1 : 1.2 : 3 by mol
- LSE ($LiPF_6$): $LiPF_6$: EC : EMC : TTE = 1 : 1.2 : 2.4 : 4.4 by mol

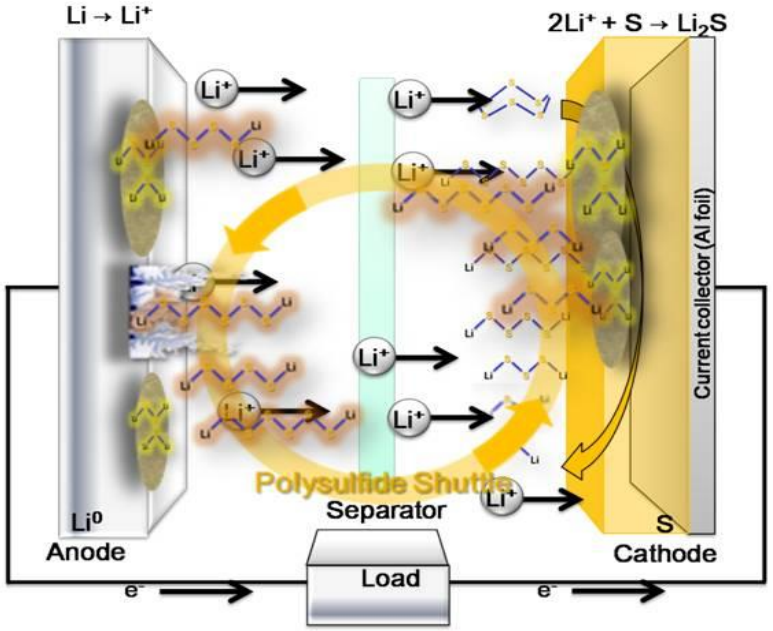
- $LiPF_6$-based LSE offers better cycle life and high-voltage stability than LP57 and LHCE

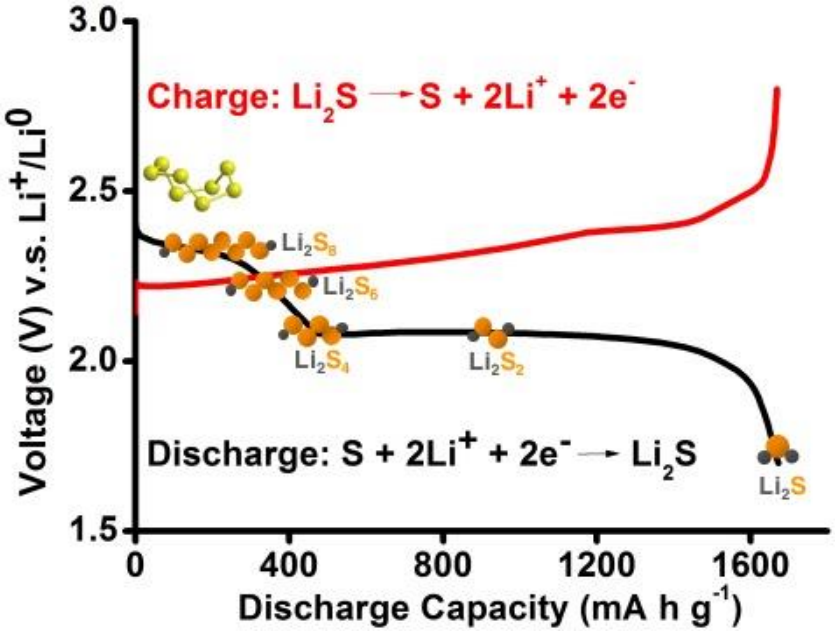
L. Su, E. Jo, and A. Manthiram, *ACS Energy Letters* ***7***, 2165 (2022)

Lithium-sulfur Batteries: Prospects and Challenges



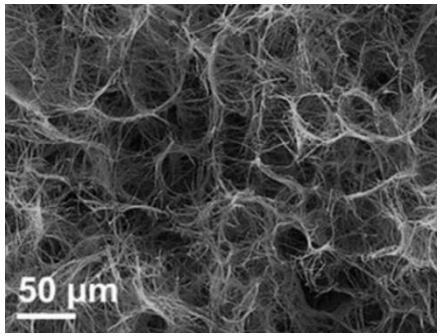






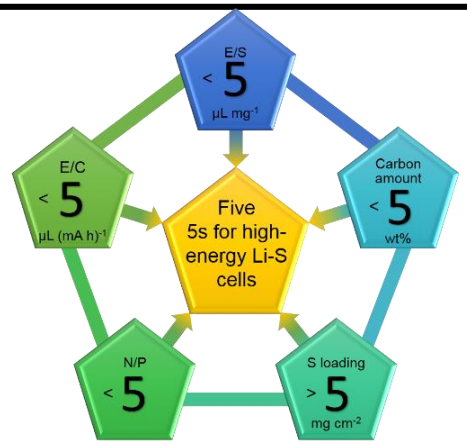
2−electron transfer; 1,672 Ah/kg; 2,500 Wh/kg; abundant, environ. benign

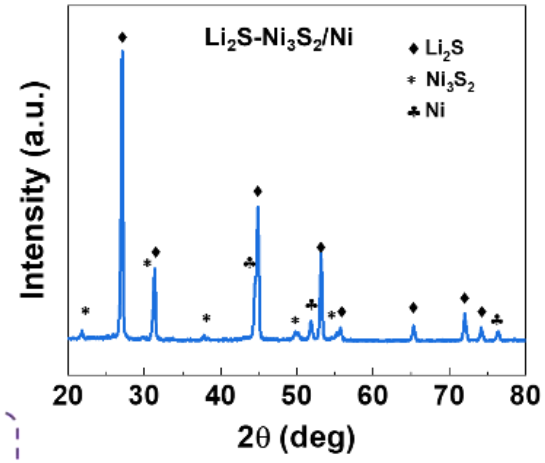
Poor electronic/ionic conductivity	Low utilization, low capacity
Polysulfide shuttle	Poor cyclability, self discharge
Lithium-metal anode degradation	Poor cycle life, safety concerns

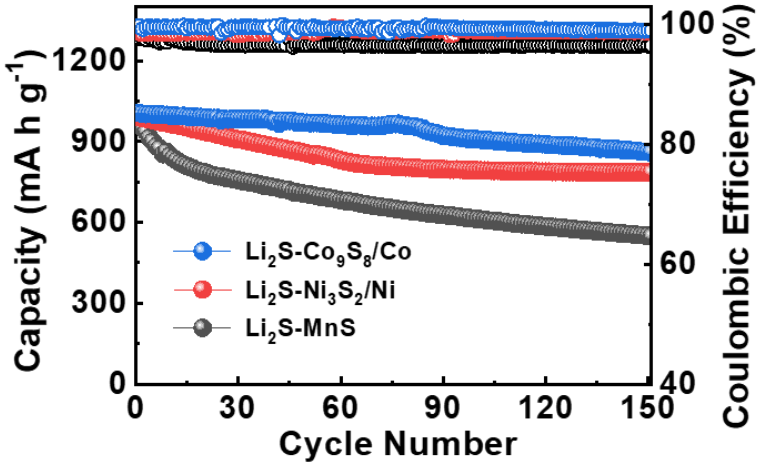


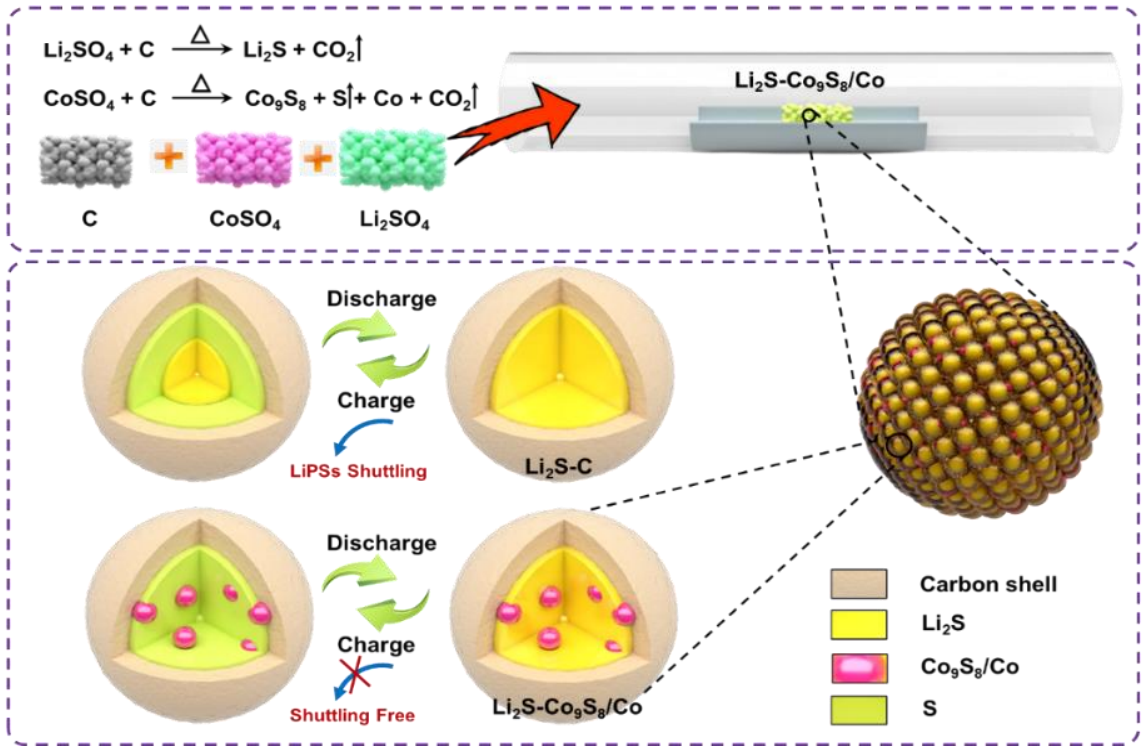
S.-H. Chung and A. Manthiram, *Advanced Materials* **31**, 1901125 (2019)
A. Manthiram, S.-H. Chung, & C. Zu, *Advanced Materials* **27,** 1980-2006 (2015)
A. Manthiram, Y.-Z. Fu, S.-H. Chung, C. Zu, & Y.-S. Su, *Chemical Reviews* **114,** 11751 (2014)
A. Manthiram, Y.-Z. Fu, & Y.-S. Su, *Accounts of Chemical Research* **46,** 1125 (2013)

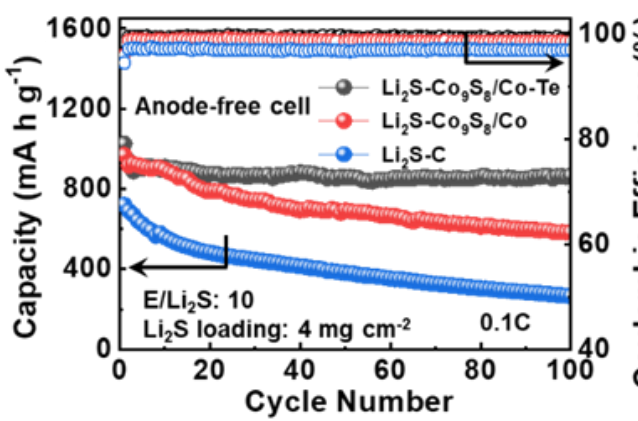
Dense Lithium-sulfur Cells with Electrocatalyst and Controlled Cell Parameters

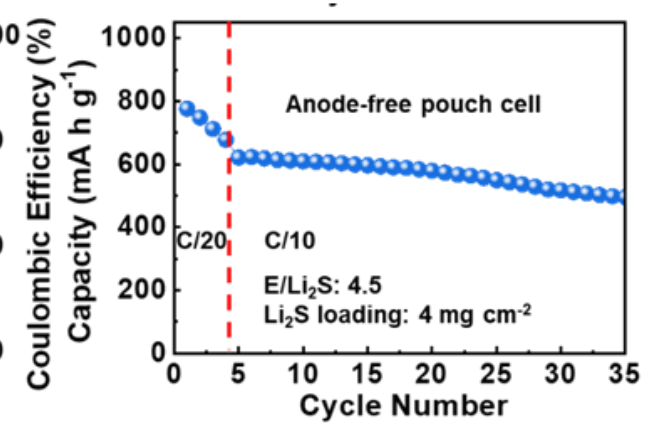






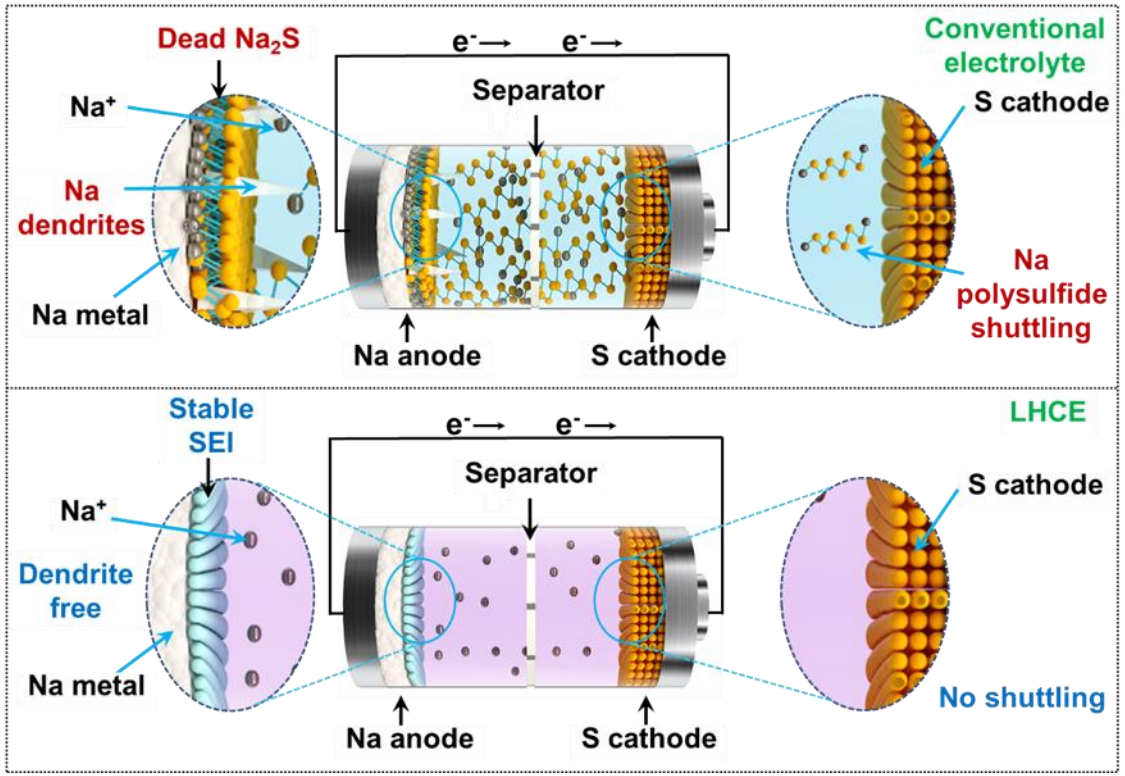


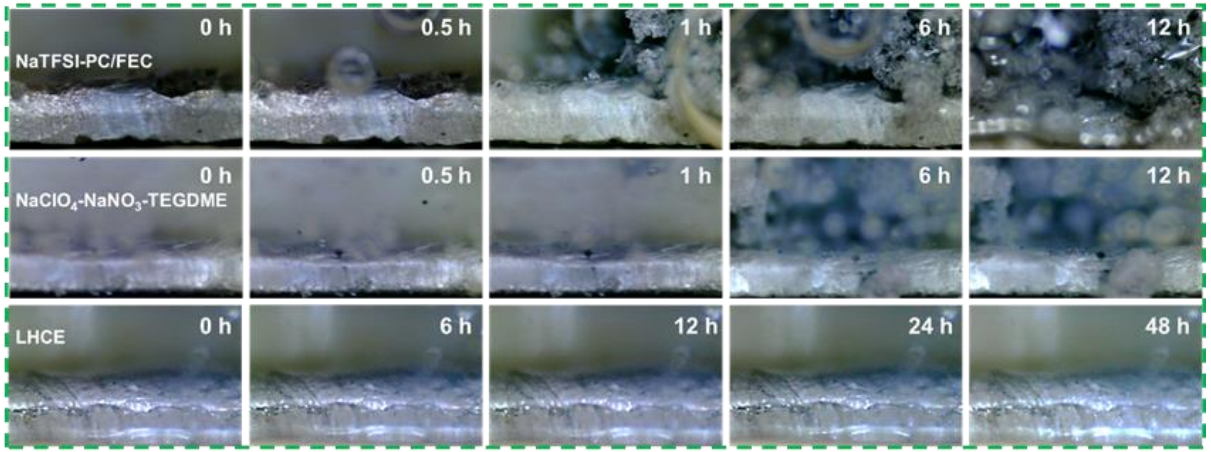


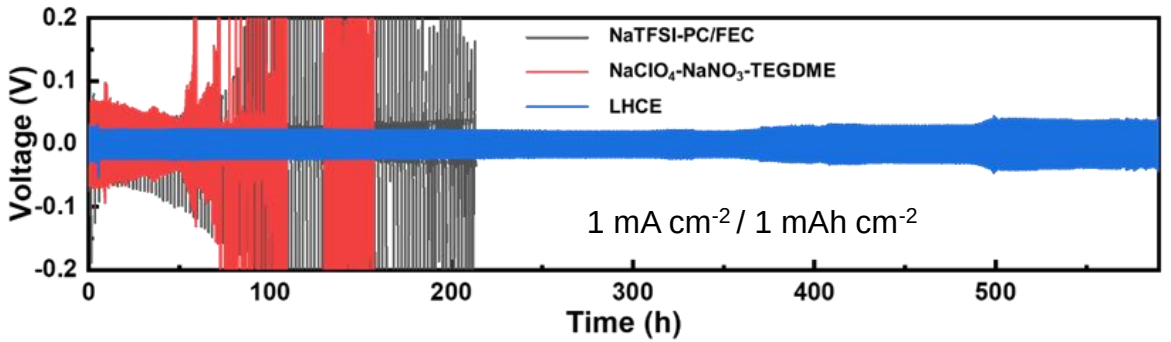


J. He, A. Bhargav, and A. Manthiram, *ACS Energy Letters* ***7***, 583 (2022)

Sodium-sulfur Batteries: a Dream Technology



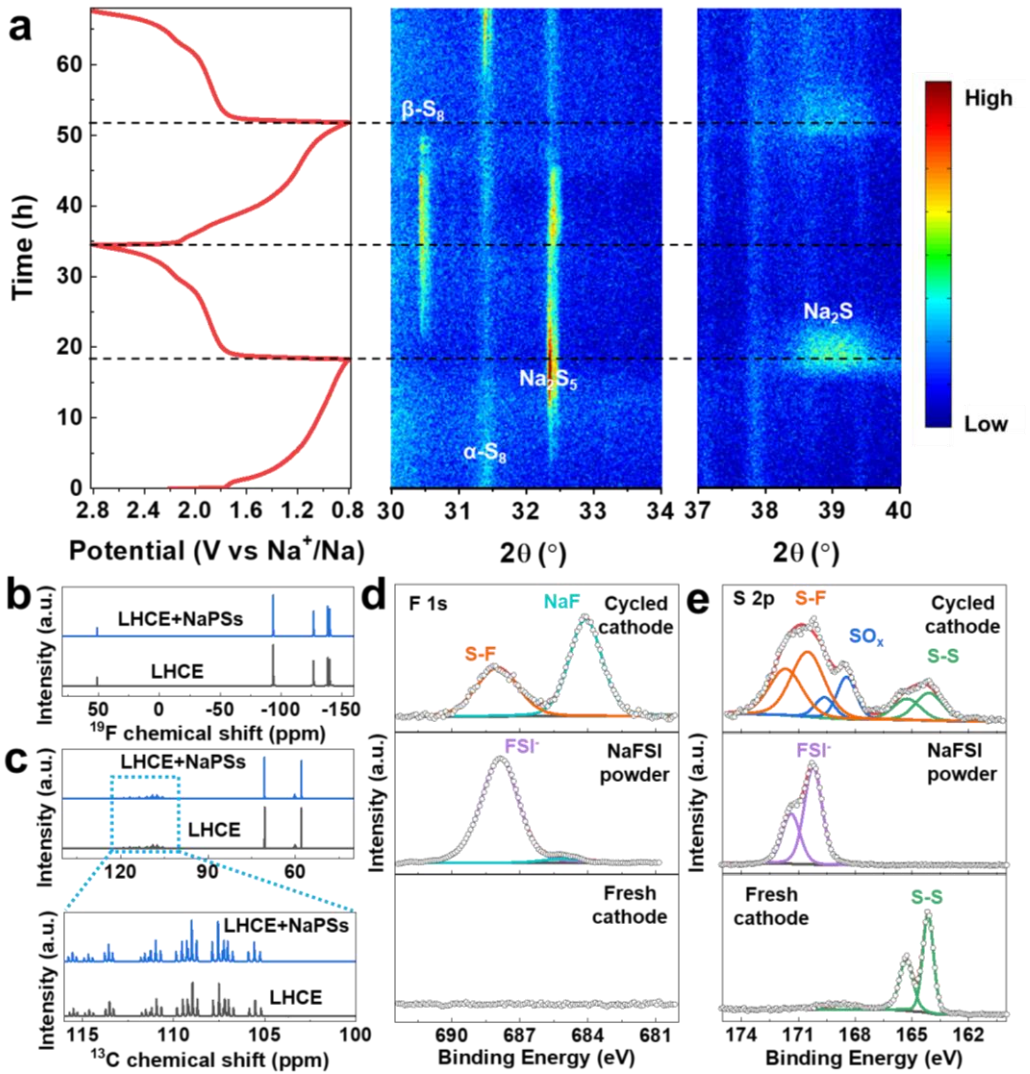


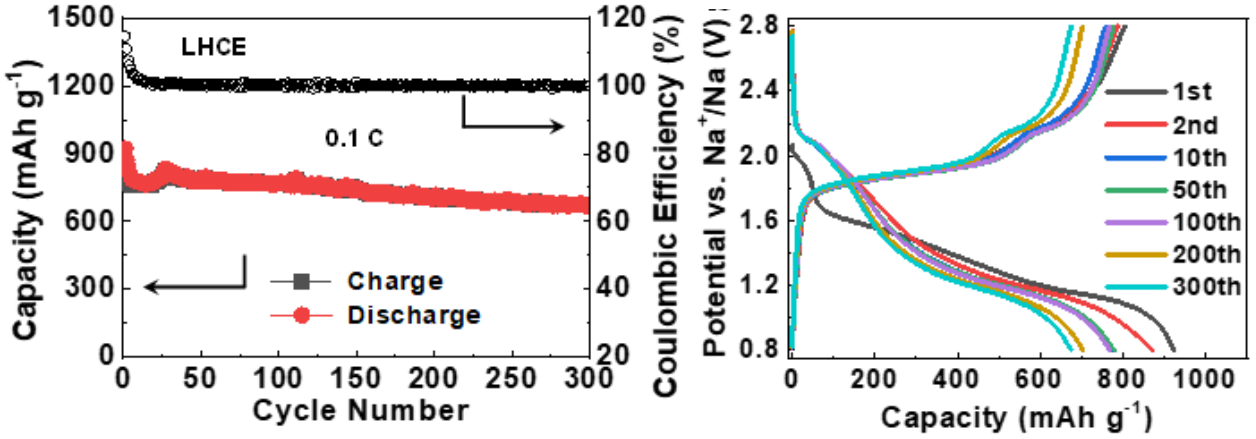


- Currently used electrolytes suffer from sodium polysulfide shuttling and severe Na-metal anode instability
- *In-situ* observation of Na||Na symmetric cells show rapid dendrite formation and severe gassing
- Localized high-concentration electrolyte (LHCE) shows uniform Na-metal stripping/plating and prevents dendrites. LHCE contains NaFSI, DME and TTE (1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether)

J. He, A. Bhargav, W. Shin, and A. Manthiram, *Journal of the American Chemical Society* **143**, 20241 (2021)

Altering the Reaction Pathway in Sodium-sulfur Cells





- NaFSI salt employed in the LHCE interacts with the NaPS generated during first cycle to form a cathode SEI containing S-F species and NaF
- *In-situ* XRD shows that this reaction changes Na-S chemistry from dissolution-precipitation reaction into a quasi-solid-state reaction
- LHCE enables stable cycling of Na-S batteries over 300 cycles without any advanced cathode design

J. He, A. Bhargav, W. Shin, and A. Manthiram, *Journal of the American Chemical Society* **143**, 20241 (2021)

Conclusion: A Path Forward to Sustainable Battery Technologies

Near-term

- Elimination of cobalt altogether

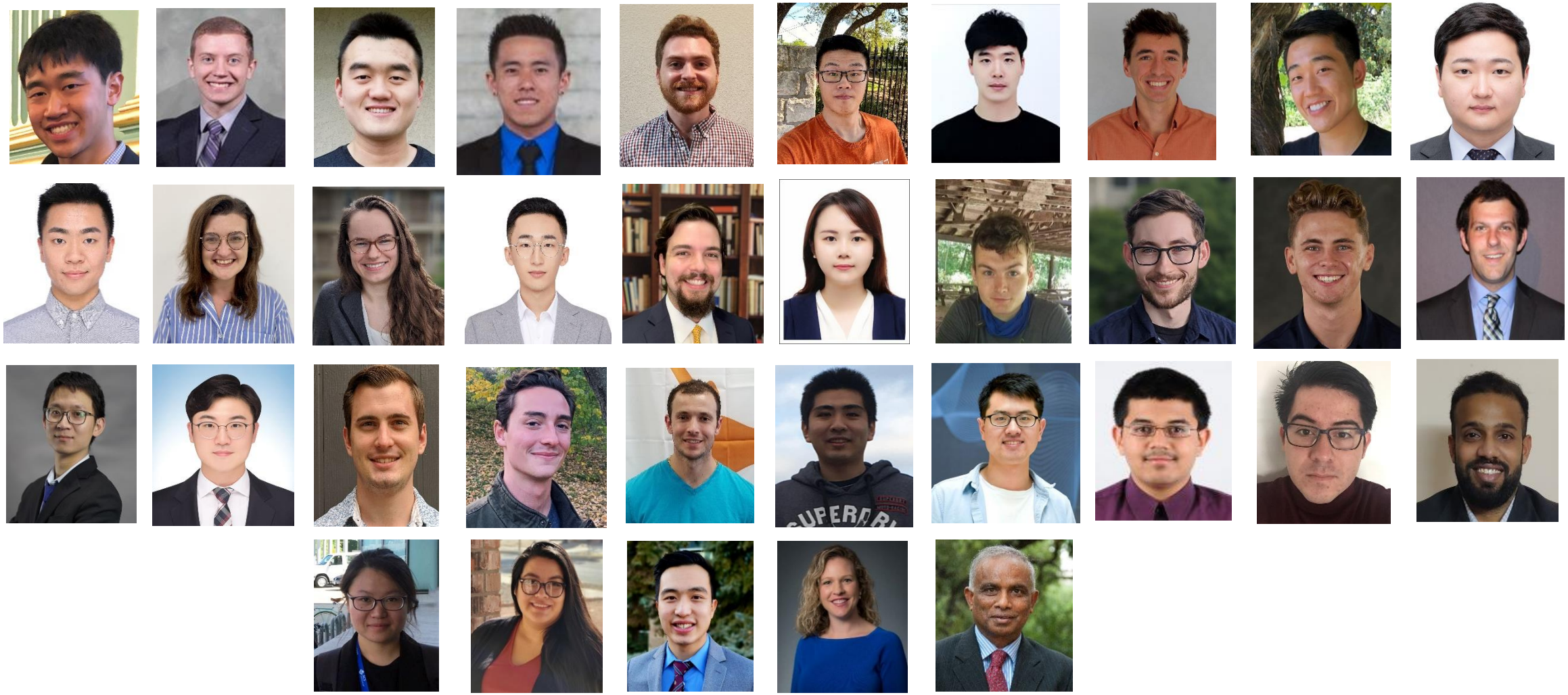
Mid-term

- Elimination of nickel

Long term

- Elimination of lithium
- Elimination of mined metals

Acknowledgements



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