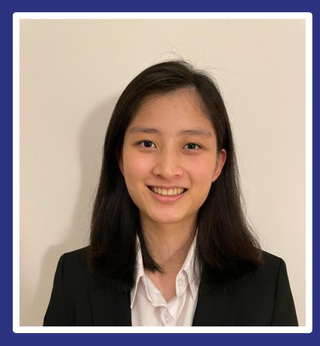
A NO COMPROMISE APPROACH TO BATTERIES

Quantifying lithium losses in anodeless solid-state batteries



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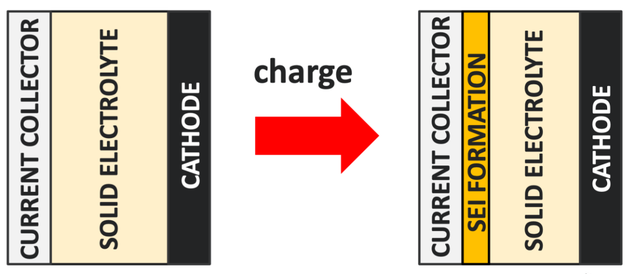
ABSTRACT

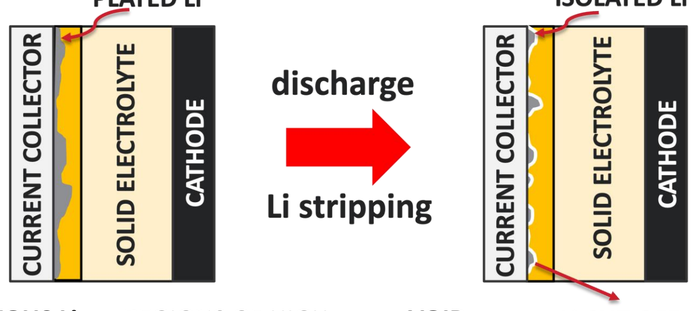
Lithium losses are a key challenge in anodeless solid-state batteries (SSBs) leading to capacity fade due to the absence of excess lithium. The major sources of these losses are *solid electrolyte interface (SEI) formation* and *isolated lithium*.

These losses are quantified with mass spectrometry techniques. Results obtained inform how modifications can be made to the cell to reduce Li losses and improve anodeless SSB performance.

1. Solid Electrolyte Interface (SEI) formation[1]

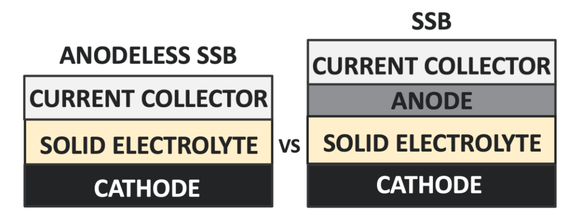


2. Isolated Lithium[2]



MOTIVATION

Anodeless SSBs has advantages over conventional SSBs by forming the Li anode *in situ* during first charge:[3]

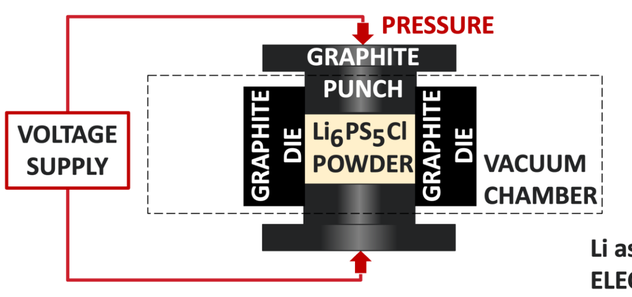


- IMPROVED ENERGY DENSITY
- SIMPLER MANUFACTURING PROCESS
- LOWER CELL COST

It offers a *no compromise battery solution*, holding the potential for high energy, high performance, and low cost.

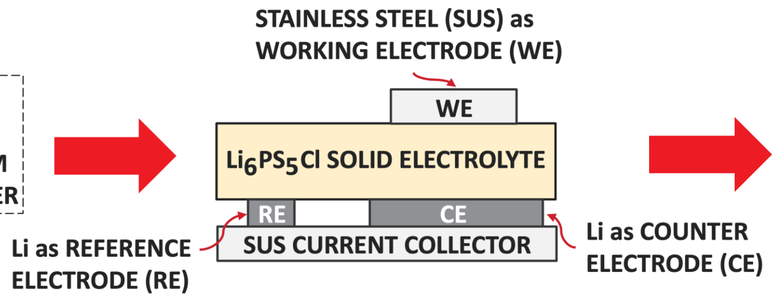
METHOD

1. Preparation of solid electrolyte



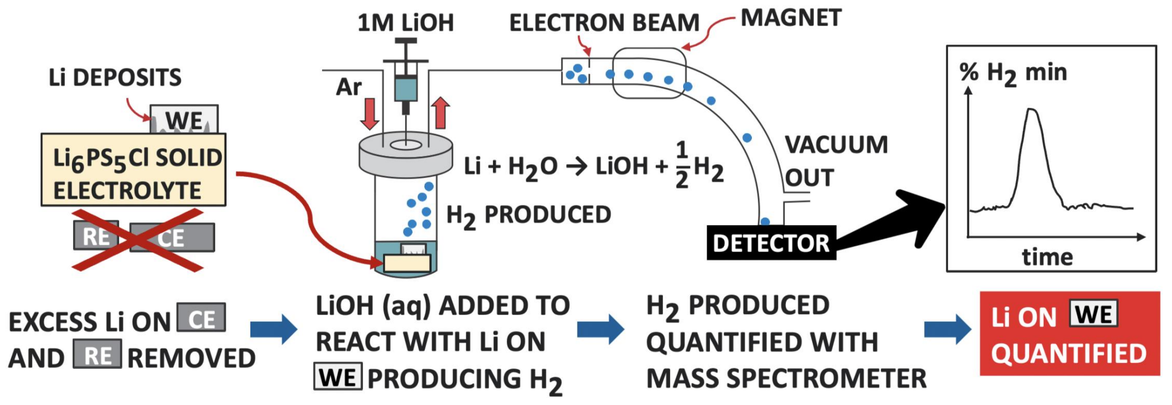
SPARK PLASMA SINTERING CONDITIONS:
- 15.7 kN
- 23 mins
- 400 °C

2. Assembly and cycling of cell



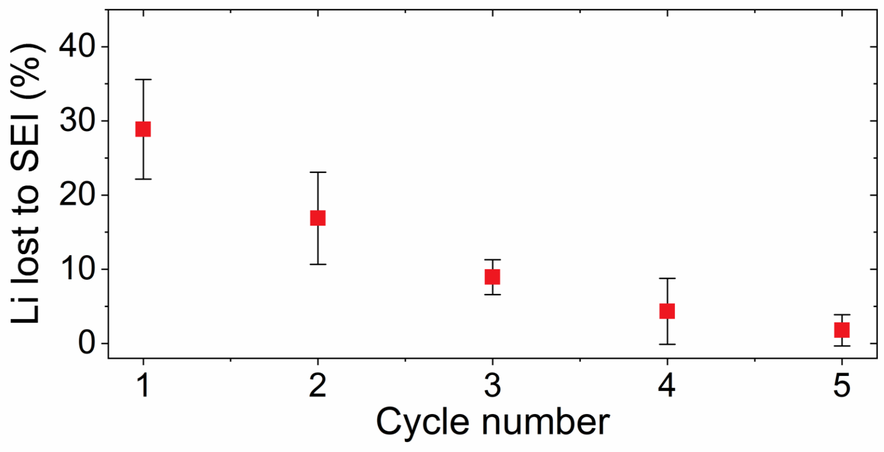
CYCLING CONDITIONS:
- 1.5 MPa
- 30 °C
- 1 mA cm^{-2}
- 5 mAh cm^{-2}

3. Quantification of Li deposited on working electrode WE



Li lost to isolated Li is determined by the quantity of Li deposited on the WE *after discharge (Li stripping)*. Loss to SEI is found from the difference between Li deposited *after charge (Li plating)* and its theoretical value calculated from the theoretical capacity of Li.

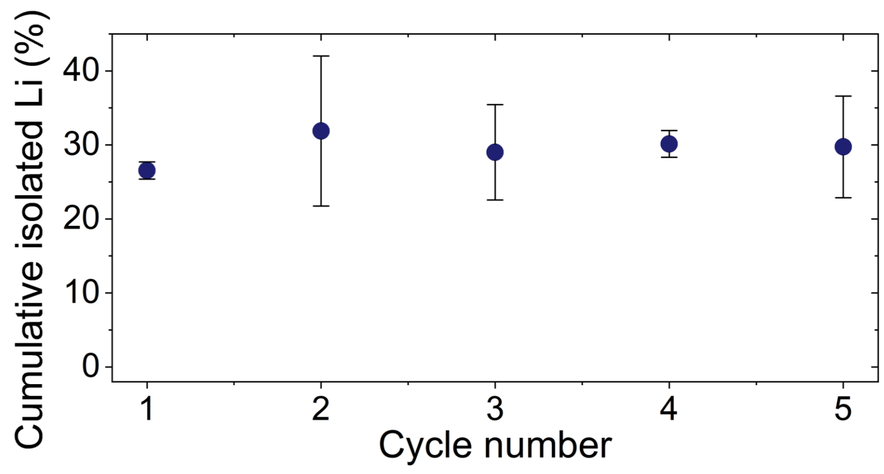
QUANTIFICATION OF Li LOST TO SEI AND ISOLATED Li



■ **Li lost to SEI**

***Key Trend*:**
Li lost decrease with cycle number.

Why?
Initial charging (plating of Li) forms a self-passivating SEI layer on the Li_6PS_5Cl surface, which insulates further SEI formation in subsequent cycles.



● **Li lost to isolated Li**

***Key Trend*:**
Li lost remain constant with cycle number.

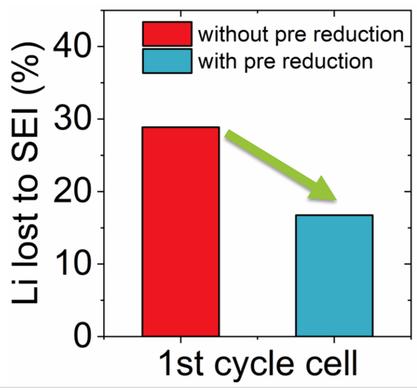
Why?
Formation of isolated Li is inherent to the incomplete stripping of Li in anodeless SSB, which is independent of cycle number.

OUR PROPOSAL TO REDUCE Li LOSS TO SEI

The majority of Li is lost to SEI during first charge. Such losses can be mitigated by pre-reducing the surface of the solid electrolyte so that a self-passivating SEI layer is formed pre-charge.

REDUCING Li LOSSES THROUGH PRE-SEI FORMATION

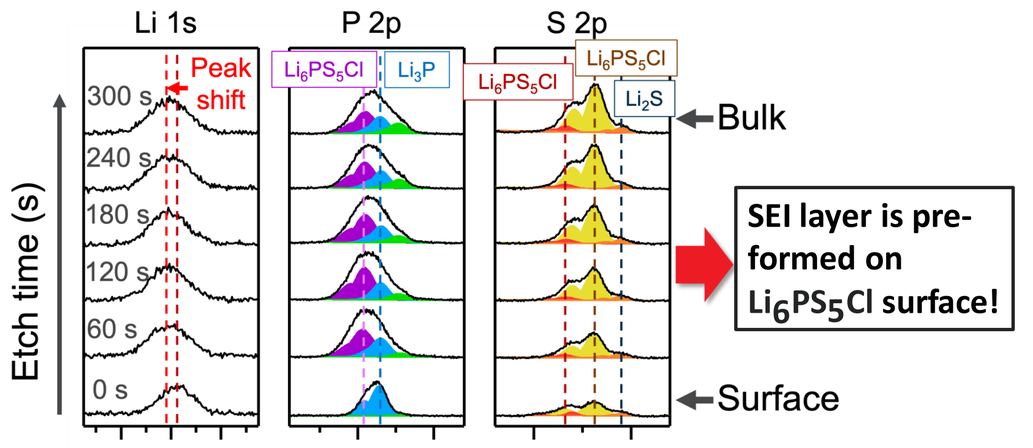
Li_6PS_5Cl is heated to 500°C in a reducing atmosphere (argon) for 10 mins so that an SEI layer of Li_3P, Li_2S and LiCl is formed pre-charge.



***Key Findings*:**
Presence of a pre-formed SEI layer decreases Li lost to SEI substantially.

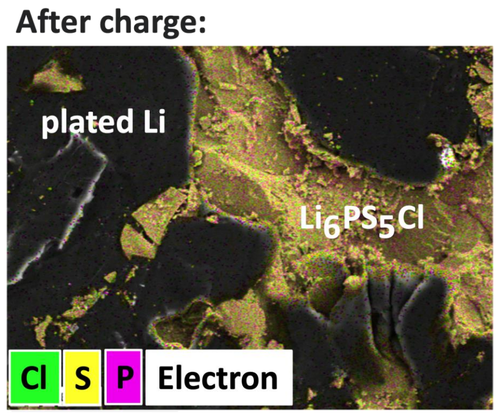
Why?
Pre-formed SEI layer electronically and ionically insulates further SEI formation, as predicted.

XPS SPECTRUM OF PRE-REDUCED SOLID ELECTROLYTE

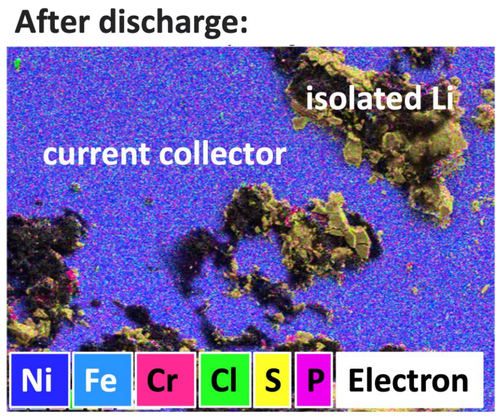


SEM IMAGING OF Li PLATING/STRIPPING SURFACE

After charge:



After discharge:



✗ **Inhomogeneous plating of Li** ✗ **Incomplete stripping of Li**

SEM imaging shows the inhomogeneous plating of Li during charge, causing incomplete stripping of Li at the current collector.

IMPACT/NEXT STEPS

- To achieve commercially viable anodeless SSBs with high Coulombic efficiencies, ***Li losses need to be significantly reduced***.
- ***Li lost to SEI is highest during first charge***. This is **reduced by *pre-forming a passivating SEI layer***. As a next step, the effect of a pre-formed layer on the performance of a full cell should be investigated to better reflect commercial anodeless SSBs.
- ***Loss to isolated Li is cycle independent***, driven by factors affecting the ***incomplete stripping of Li*** such as poor interfacial contact, surface inhomogeneities, and pressure variations. A proposed solution involves adding a layer of conducting nanoparticles to act as ***preferential nucleation sites for a more uniform deposition/stripping of Li***.

REFERENCES

1. Gialampouki, M.; Hashemi, J.; Peterson, A.; *The Journal of Physical Chemistry C* 2019 123 (33), 20084-20092
2. Lewis, J.; Sandoval, S.; Liu, Y; Nelson, D.; Yoon, S.; Wang, R.; Zhao, Y.; *Adv. Energy Mater.* 2023, 13, 2204186.
3. Huang, W.-Z.; Zhao, C.-Z.; Wu, P.; Yuan, H.; Feng, W.-E.; Liu, Z.-Y.; Lu, Y.; Sun, S.; Fu, Z.-H.; Hu, J.-K.; Yang, S.-J.; Huang, J.-Q.; Zhang, Q.; *Adv. Energy Mater.* 2022, 12, 2201044.

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