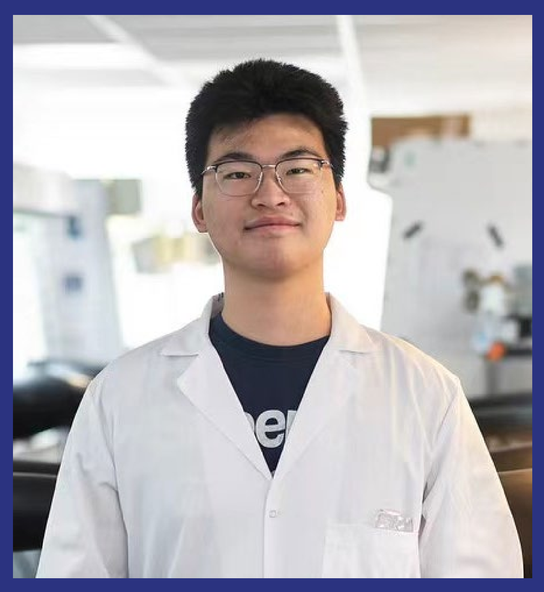
Study of the Interfacial Stability of Thin-film LiPON Electrolytes

Attempts to measure the critical current density accurately and reveal the SEI evolution of LiPON|Li



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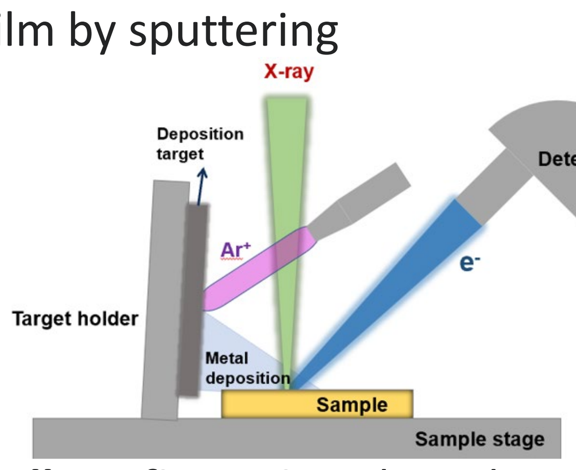
Abstract

Our work aims to provide key information for understanding the remarkable performance of dendrite suppression:

i. **XPS analysis** of in-situ Li deposition on LiPON film by sputtering



Schematic XPS Experimental Set-up
[By courtesy of Yi Liang]

ii. **Cell configurations** have been iterated in attempts to confirm a precise value of **critical current density**, indicative of interfacial stability
   - The main challenge is to sputter an intact LiPON thin film homogeneously upon the bottom electrode

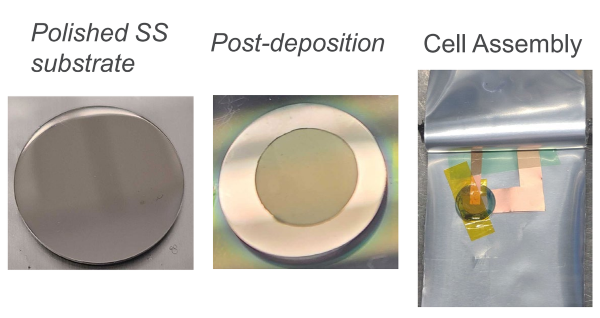
Motivation

- Li metal anodes, expected to boost energy density by 30% more than graphite-based ones, are practically difficult to incorporate due to the Li dendrite penetration which leads to cell shorting over repeated cycling. **RF magnetron sputtered LiPON can completely suppress Li dendrites.** One impressive example is to visualize dendrite propagation as completely constrained in a 2D plane between two transparent LiPON layers. [1]

Source: http://pubs.acs.org/journal/aelccp

Methods

Stainless Steel (SS) Substrate Deposition for CCD Measurements:



Substrates stuck to the rotating disc upside down with Kapton tape

Li_3PO_4 Sputtering Target The sputtering rate is detected with a probe above.

❖ The red glow is seen during the magnetron sputtering discharge for LiPON.

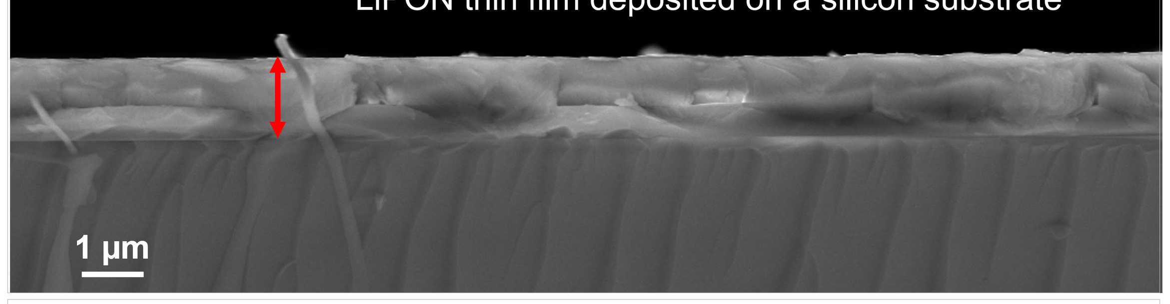
The **nickel layer** is also sputtered with a nickel target.

Evaporation set-up requires **lithium** granules held in a lithium melting boat. The evaporation rate is monitored by quartz oscillation frequency.

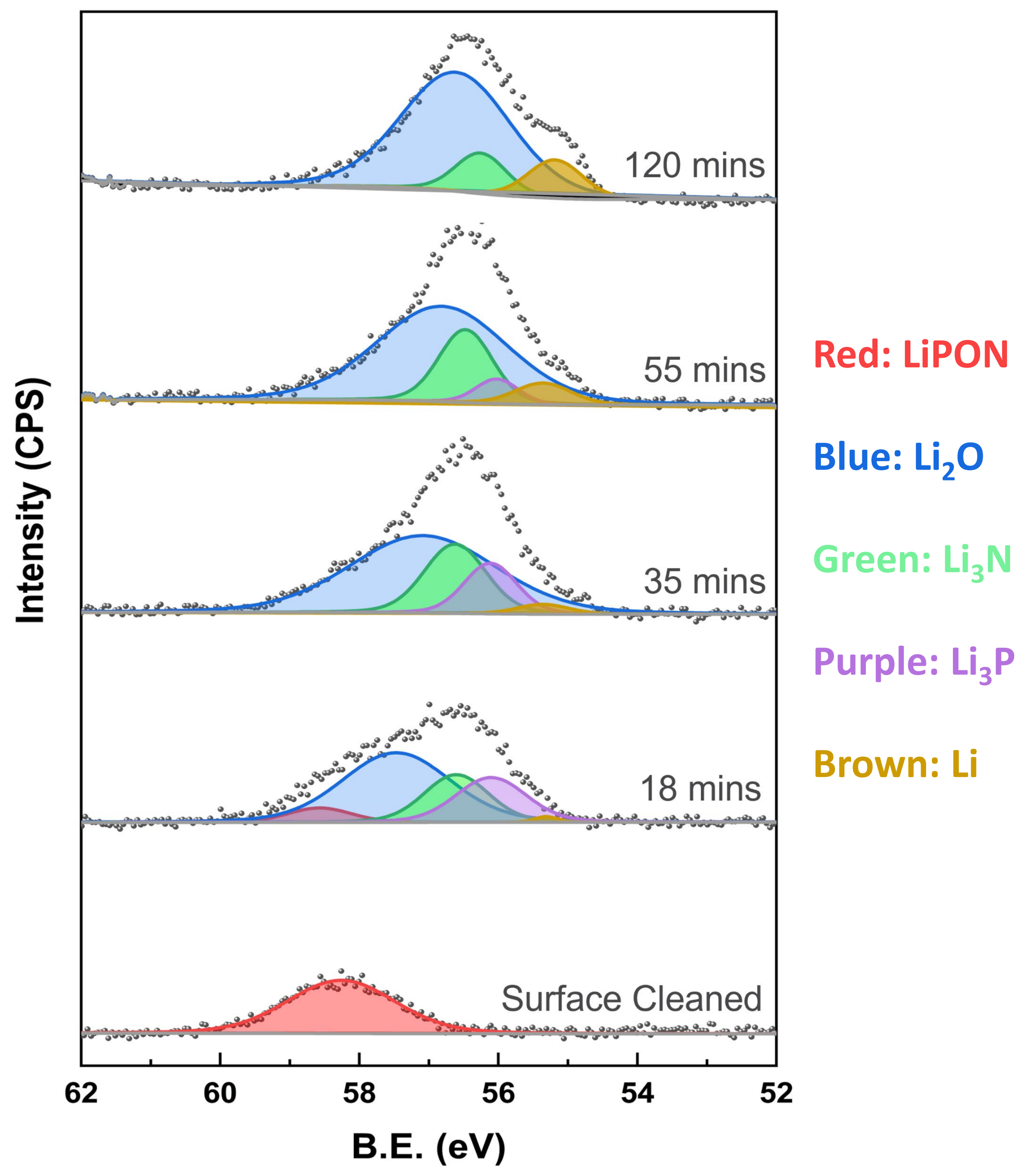
The evaporation rate is ~2 Å/s.

Cross-sectional SEM Image of LiPON film

1.3 µm **homogeneous** and **pore-free** LiPON thin film deposited on a silicon substrate



XPS Peak Fitting

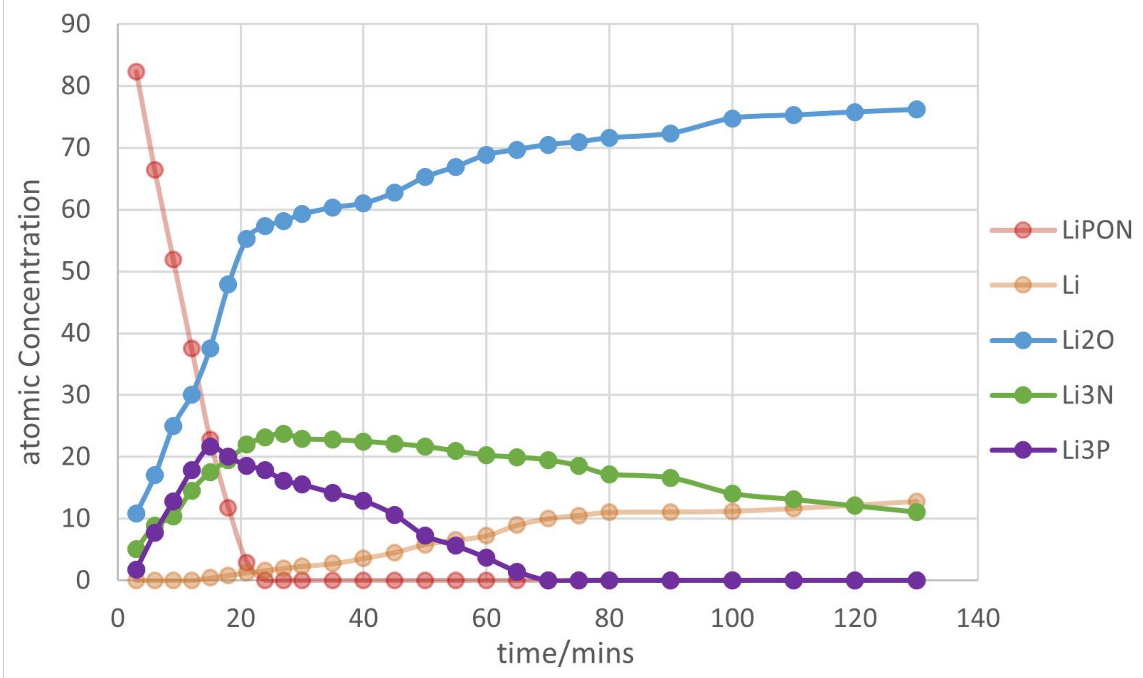


Red: LiPON
Blue: Li_2O
Green: Li_3N
Purple: Li_3P
Brown: Li

- ➢ The XPS signal shows 100% LiPON after the surface is cleaned and without Li sputtered
- ➢ Five component peaks evolve as lithium is sputtered in situ for a longer time

Qualitative Analysis of XPS Results

- Lithium Component Evolution



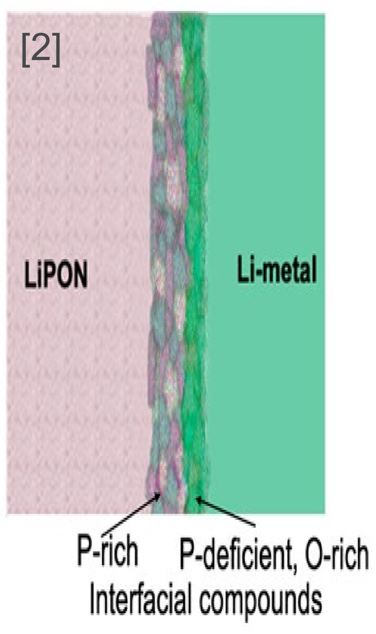
Main Features:

- ➢ Atomic concentration of **LiPON** in lithium decreases monotonically and quickly drops to zero after 21-minute lithium sputtering.
- ➢ **Li** starts to be detected after 15 minutes, indicating roughly the time at which the SEI is established stably.
- ➢ **Li_2O** increases in atomic content quickly before LiPON has not reached zero but at a lower rate afterward as there is only unreacted Li oxidised in not perfectly vacuum environment.
- ➢ **Li_3N** concentration peaks at 27 minutes
- ➢ **Li_3P** concentration peaks at 15 minutes and reaches zero after 70-minute lithium sputtering

- Possible SEI Configuration

Reason for peaking of Li_3N and Li_3P:

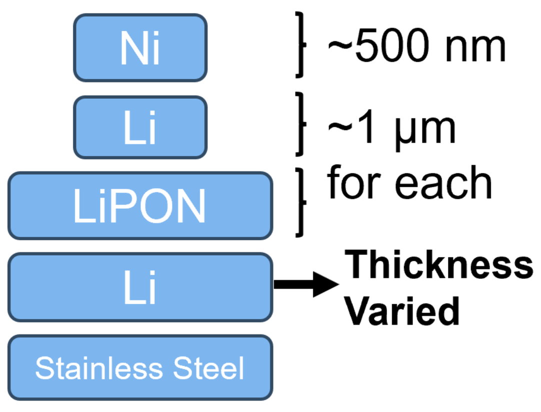
1. There is an atomic concentration gradient due to the *diffusion* and thus as thicker Li sputtered and the *X-ray detection range* is lifted; therefore, nitrate and phosphate trendlines increase firstly;
2. Time, at which peaks are reached, indicates the interfaces between two adjacent layers;
3. Atomic concentrations decrease as more side products get outside the detection range than those produced in reactions with Li.



Source: pubs.acs.org/NanoLett

These XPS trends match well with **stacking-layer SEI configuration**

Cell Configuration Development for CCD Measurements

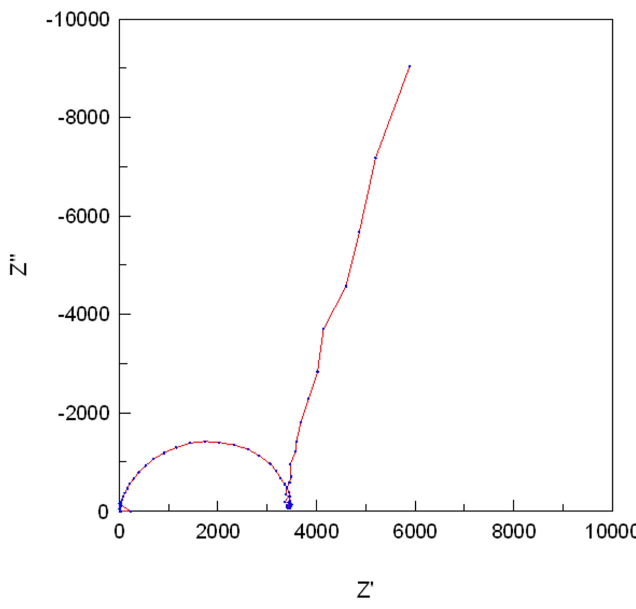


The schematic diagram shows the **Li|LiPON|Li** cell configuration iterated to make critical current density measurements possible

Trial 1: Lower Li layer thickness = 0 µm

EIS:
The conductivity is $4 \times 10^{-6} S/cm$

- This configuration gives a reference of LiPON conductivity



Trial 2&3: Lower Li layer thickness = 6 µm & 1 µm

EIS:
Measurement failures due to **short-circuit**:

- Sputtered LiPON molecules bombard the soft lithium bed and deform the thick lithium layer plastically to form protrusions.
- Therefore, **the unevenness of the thin LiPON film** on soft lithium results in contact between the two Li electrodes.

Trial 4: Lower Li layer thickness = 0.05 µm

EIS:
The impedance due to **inductance** is detected:

- The protrusions are smaller relative to the LiPON film thickness
- Reduction in Lithium layer thickness to **nanometre region** is promising for allowing critical current density measurements.

Impact / Next Steps

✓ In this work, SEI evolution is suggested, and its stacking layer structure is confirmed by in situ XPS analysis of lithium sputtering on LiPON
   - Considering close binding energies of Li_2O, Li_3N, and Li_3P, peak fitting can be more accurate if the binding energy of each is determined in our equipment beforehand.
   - To confirm trends obtained by the in situ XPS technique, instead of sputtering lithium on LiPON, lithium is produced by Li/Li^+ charging.

✓ For Li|LiPON|Li cells, it is hopeful that successful CCD measurements can be made when the Li layer below the LiPON is less than 50 nm
   - Replace the bottom Li layer with harder and stiffer LCO at a thickness with sufficient lithium.

References

1. Westover, A.S., Dudney, N.J., Sacci, R.L. and Kalnaus, S., 2019. Deposition and confinement of Li metal along an artificial LiPON–LiPON interface. *ACS Energy Letters*, *4*(3).
2. Hood, Zachary D., et al. "Elucidating interfacial stability between lithium metal anode and Li phosphorus oxynitride via in situ electron microscopy." Nano Letters 21.1 (2020).

Intern bio

Tiancheng is a second-year undergraduate studying Materials Science at the University of Oxford, aspiring to pursue a Ph.D. degree in Materials Science. He completed his first official summer research internship in Professor Mauro Pasta's group at the University of Oxford.

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