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

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]

Methods
Stainless Steel (SS) Substrate Deposition for CCD Measurements:

- Sputtered LiPON
- Laser deposition
- Cell Assembly

LiPON Deposition Target: The sputtering ion gun is a mixed species, including LiPON and MgO. The target material is LiPON.

Impact / Next Steps

- 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.

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

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. L_iO increases in atomic content quickly before LiPON has not reached zero but at a lower rate afterward as there is only unreacted Li oxidized in not perfectly vacuum environment.
- Li,N concentration peaks at 27 minutes.
- Li,P concentration peaks at 15 minutes and reaches zero after 70-minute lithium sputtering.

Possible SEI Configuration
- Reason for peaks of Li,N and Li,P:
  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, nitrates and phosphate trends 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.

References

Qualitative Analysis of XPS Results

- Lithium Component Evolution

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,O, Li,N, and Li,P, 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 LCD at a thickness with sufficient lithium.

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

- The conductivity is 4 × 10−7 S/cm. This configuration gives a reference of LiPON conductivity.

Trial 2: Lower Li layer thickness = 6 μm

- 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 two Li electrodes.

Trial 4: Lower Li layer thickness = 0.05 μm

- 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. 

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.