Intrinsic Properties of Individual Constituents of Silicon-Electrolyte Interphase

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Topical Abstract

Motivation: provides a better understanding of complicated reactions and interactions within an silicon-electrolyte interphase (SiEI), and clearly delineates which components are critical for stabilizing the SiEI, thus enabling rational design of new electrolyte additives and functional binders for the development of next generation Li-ion batteries (LIBs).[1)]

Background: The stabilization of a solid electrolyte interphase (SEI) is one of the great challenges to utilize superior theoretical capacity of a Si as an anode in a next-generation advanced LIB. The SEI remains a poorly understood and hardly studied topic relative to the research devoted to battery components due to its intrinsic properties of complexity, reactivity and continuous evolution.[2)] However, the SEI plays a key role in prevention of further electrolyte reduction and desolvation of Li^+ ions, which is directly related to electrochemical performance, lifetime and safety of batteries. In this study, thus, 'individual' constituents of SiEI was prepared as a thin film, and the physical, electrochemical, mechanical and structural properties of prepared films were characterized using a variety of analytical equipment.

Main Questions

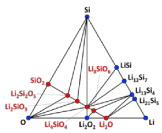
1. What kind of factors (e.g., chemical composition, morphology and roughness) can influence on intrinsic properties of SiEI components?

2. Which SiEI components are critical for stabilizing the SiEI?

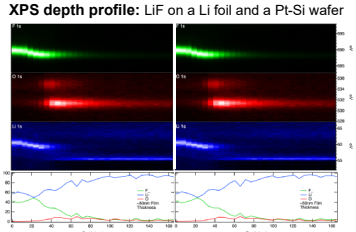
I. Chemical Composition and Homogeneity

- **System:** thin films of individual SiEI components on Li foils / Pt-Si wafers
- **Analytical techniques:** x-ray photoelectron spectroscopy (XPS) & electron energy loss spectroscopy (EELS)
- **Experimental purpose**: chemical composition verification

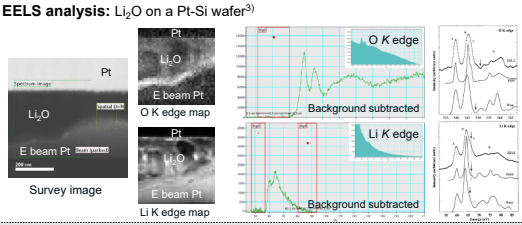
Phase diagram of ternary Li-Si-O system



XPS depth profile: LiF on a Li foil and a Pt-Si wafer



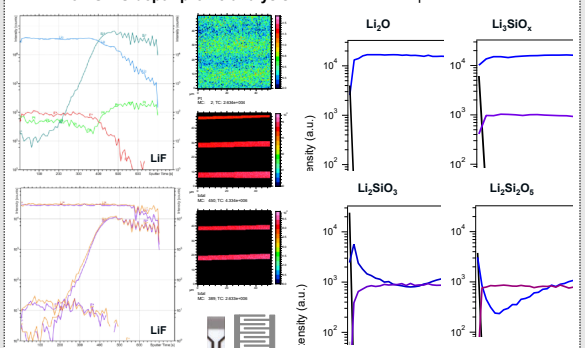
EELS analysis: Li_2O on a Pt-Si wafer[3)]



Key Points:
XPS depth profiling and EELS analysis confirm the chemical composition of individual SiEI component samples.

- **System:** thin films of individual SiEI components on interdigitated Pt-electrodes (IPEs)
- **Analytical technique:** time of flight secondary ion mass spectroscopy (ToF-SIMS)
- **Experimental purpose**: homogeneity (impurity) verification

ToF-SIMS depth profile analysis: individual SiEI components on IPEs



- Almost none or negligible amount of impurities for the thin films
- Similar chemical composition for the deposited thin film in between and on top of Pt digits

Analysis Parameters:
PI: Bi_3^+
Energy: 30 keV
Current: 0.8pA
Area: 50x50 μm²
PIDD: 3.3E11 Ions/cm²

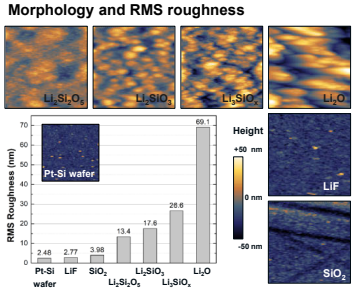
Sputter Parameters:
SpI: O_2^+
Energy: 3 keV
Current: 5nA
Area: 150x150 μm²
SpIDD: 1.4E17 Ions/cm²

Key Points:
ToF-SIMS has in general ppm or better sensitivity, and negligible impurities were detected in the deposited films.

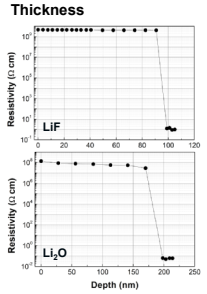
II. Morphology, Roughness and Thickness

- **System:** thin films of individual SiEI components on Pt-Si wafers
- **Analytical techniques:** atomic force microscope (AFM) and scanning spreading resistance microscopy (SSRM)
- **Experimental purpose**: morphology, roughness and thickness characterization

Morphology and RMS roughness

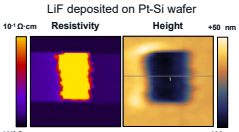


Thickness



- $Li_xSi_yO_z$ surfaces display different nanoscale features (1x1 μm)
  - $Li_2Si_2O_5$: small scale features
  - Li_2SiO_3: large scale features
  - Li_2SiO_x: intermediate scale features
  - Li_2O: largest scale features
- For $Li_xSi_yO_z$ surfaces, increased Li:Si ratio has the trend of increased roughness. Li_2O has the greatest roughness of all samples (5x5 μm).

LiF deposited on Pt-Si wafer

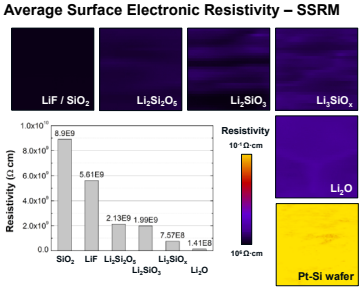


Key Points:
a. Each SiEI component film shows different morphology and roughness.
b. SSRM profiles show good agreement with deposition estimate of thickness.

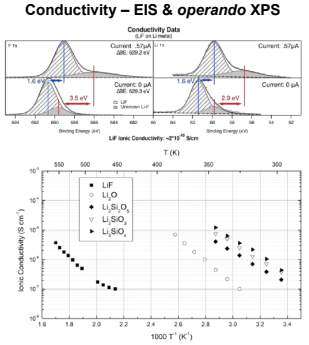
III. Physical, Electrochemical and Mechanical Properties

- **System:** thin films of individual SiEI components on IPEs / Pt-Si wafers
- **Analytical techniques:** electrochemical impedance spectroscopy (EIS), *operando* XPS, SSRM and AFM-scanning probe microscopy (SPM)
- **Experimental purpose**: physical, electrochemical and mechanical properties characterization

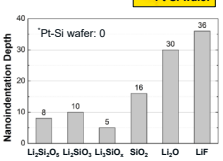
Average Surface Electronic Resistivity – SSRM



Conductivity – EIS & *operando* XPS



Nano-Indentation – AFM-SPM



- Protocol: 30 μN probe force, exerted for 10 s
- Hardness: $Li_xSi_yO_z$ > SiO_2 > Li_2O > LiF

- Assess conductivities (Li^+, e^-) paired with phase compositions[4)]
  - *virtual electrode* approach: e-gun to create negative surface charge
  - provides order-of-magnitude conductivities

Key Point:
a. Li:Si ratio influences on electrochemical and mechanical properties.
b. Li_3SiO_x (conductivity) *vs.* LiF (hardness) can be a beneficial component(s).

Conclusion and Future Work

- The chemical composition, homogeneity, morphology and roughness of amorphous thin films of 'individual' SiEI components were analyzed using a variety of analytical tools.
- The physical, electrochemical and mechanical properties of individual SiEI components were characterized.
- The chemical/electrochemical reactivity and electrochemical evolution will be investigated using *in-situ* spectroscopic techniques.

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References: 1) S.-D. Han *et al.* **2018** in preparation. 2) M. Gauthier *et al. J. Phys. Chem. Lett.* **2015**, *6*, 4653; B. Philippe *et al. Chem. Mater.* **2013**, *25*, 394; T. Jaumann *et al. Phys. Chem. Chem. Phys.* **2015**, *17*, 24956. 3) N. Jiang *et al. Phys. Rev. B* **2004**, *69*, 115112. 4) K. N. Wood *et al. Nat. Commun.* **2018**, *9*, 2490.

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