

# Supporting Information

## Synergetic Effects of Inorganic Components in Solid Electrolyte Interphase on High Cycle Efficiency of Lithium Ion Batteries

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## 1. Experimental Details

Si thin-film electrodes (~100 nm) were prepared by RF magnetron sputtering on copper current collectors, and tested in coin cells for electrochemical characterizations. Surface coatings were also prepared by RF magnetron co-sputtering of lithium fluoride and lithium carbonate targets on as-prepared Si thin-film electrodes. The ratio of the coatings were controlled by sputtering rates (power control).

The Si electrodes (or coated Si electrodes) were used as working electrodes, and pure lithium metal foil as counter and reference electrodes in CR2032 coin cells. A separator (Celgard, USA) was placed between working electrode and lithium foil, and 1M LiPF<sub>6</sub> in ethylene carbonate and dimethyl carbonate (EC:DMC 1:1 volume ratio, BASF) was employed for the electrolyte. The Arbin battery test system (BT-2000) was used to cycle the coin cells, using the constant-current method (with a rate of C/3) and a voltage window between 0.05 V to 1.5 V. The EIS study was conducted in two-electrode coin cells at the assigned voltage. The coin cells were rested for 24 hours until they were stabilized.<sup>1</sup> The high-frequency (Ohmic) resistance of the coin cells was ranged from 400 to 500 Ohms. The applied frequency range for EIS measurements was between 1 MHz to 10 mHz by VMP3 (Biologic).

Thermo Scientific K-Alpha XPS with a monochromated Al K $\alpha$  source (1486.6 eV) was used for chemical analysis of coatings SEI on the electrodes.

For the isotope exchange experiment, the as-prepared LiF/Li<sub>2</sub>CO<sub>3</sub> thin films (<1% LiF, 15% LiF, and 50% LiF, respectively) were soaked in 0.1M <sup>6</sup>LiClO<sub>4</sub> (95% <sup>6</sup>Li abundance, <sup>6</sup>Li<sup>+</sup>/<sup>7</sup>Li<sup>+</sup> ~ 20) dimethyl carbonate solution in an Ar glove box for 3 min. After the immersion, the specimens were rinsed thoroughly with dimethyl carbonate (DMC), dried in the glove box, and transferred under Ar in a special vessel to the analysis instrument.

The TOF SIMS (time-of-flight secondary ion mass spectrometry) analyses were performed on a PHI TRIFT V nanoTOF spectrometer (Physical Electronics, Chanhassen, MN). The analysis chamber of the instrument was maintained at a pressure of less than  $5 \times 10^{-7}$  Pa during analyses. A 30kV  $\text{Au}^+$  ion source was used for both sputtering and analysis. The analysis area was  $50 \mu\text{m} \times 50 \mu\text{m}$ , within a sputter area of  $200 \mu\text{m} \times 200 \mu\text{m}$ . A uniform sputter rate of 0.1 nm/s (calibrated with 100 nm  $\text{SiO}_2$ ) was used to calculate the sputter depth.

## 2. Model details:

The electrostatic potential (we take the infinite of  $\text{Li}_2\text{CO}_3$ :  $\phi_{\text{Li}_2\text{CO}_3}^\infty = 0 \text{ V}$ ) and net charge density can be related by the Poisson-Boltzmann relationship <sup>2</sup>

$$\frac{\partial^2 \phi(x)}{\partial x^2} = -\frac{e}{\varepsilon \varepsilon_r} \left( c_{\text{Li}_i}^\infty e^{-\frac{e\phi(x)}{k_B T}} - c_{e'}^\infty e^{\frac{e\phi(x)}{k_B T}} \right), \quad (S 1)$$

where  $\varepsilon$  is the permittivity of vacuum,  $\varepsilon_r$  (~4.9) is the relative permittivity of  $\text{Li}_2\text{CO}_3$ ,  $c_{\text{Li}_i}^\infty$  ( $c_{e'}^\infty$ ) is the bulk concentration of Li ion interstitial (free electrons) in  $\text{Li}_2\text{CO}_3$ .  $c_{\text{Li}_i}(x) = c_{\text{Li}_i}^\infty e^{-\frac{e\phi(x)}{k_B T}}$  ( $c_{e'} = c_{e'}^\infty e^{\frac{e\phi(x)}{k_B T}}$ ) is the defect concentration of Li ion interstitial (free electrons) in the space charge region of  $\text{Li}_2\text{CO}_3$ . In addition,  $\rho(x) = e \left( c_{\text{Li}_i}^\infty e^{-\frac{e\phi(x)}{k_B T}} - c_{e'}^\infty e^{\frac{e\phi(x)}{k_B T}} \right)$  is the net space charge density at a spatial point  $x$  with space charge potential  $\phi(x)$ . The defect concentration ( $\zeta = \frac{c_{\text{Li}_i}(x)}{c_{\text{Li}_i}(x=\infty)} = e^{-\frac{e\Delta\phi(x)}{k_B T}}$ ) in  $\text{Li}_2\text{CO}_3$  can be solved as <sup>2,4</sup>

$$\zeta = \left[ \frac{1 + \vartheta e^{-\xi}}{1 - \vartheta e^{-\xi}} \right]^2, \quad (S 2)$$

where  $\xi = x/\lambda_D$  (Debye length:  $\lambda_D = \sqrt{\frac{\epsilon\epsilon_r k_B T}{2e^2 C_{Li_i}^{bulk}}} \approx 9 \text{ nm}$ ), and  $\vartheta = \frac{1-\zeta^{-1/2}(\xi=0)}{1+\zeta^{-1/2}(\xi=0)}$ .

### 3. Surface Characterization of artificial SEIs by X-ray Photoelectron Spectroscopy

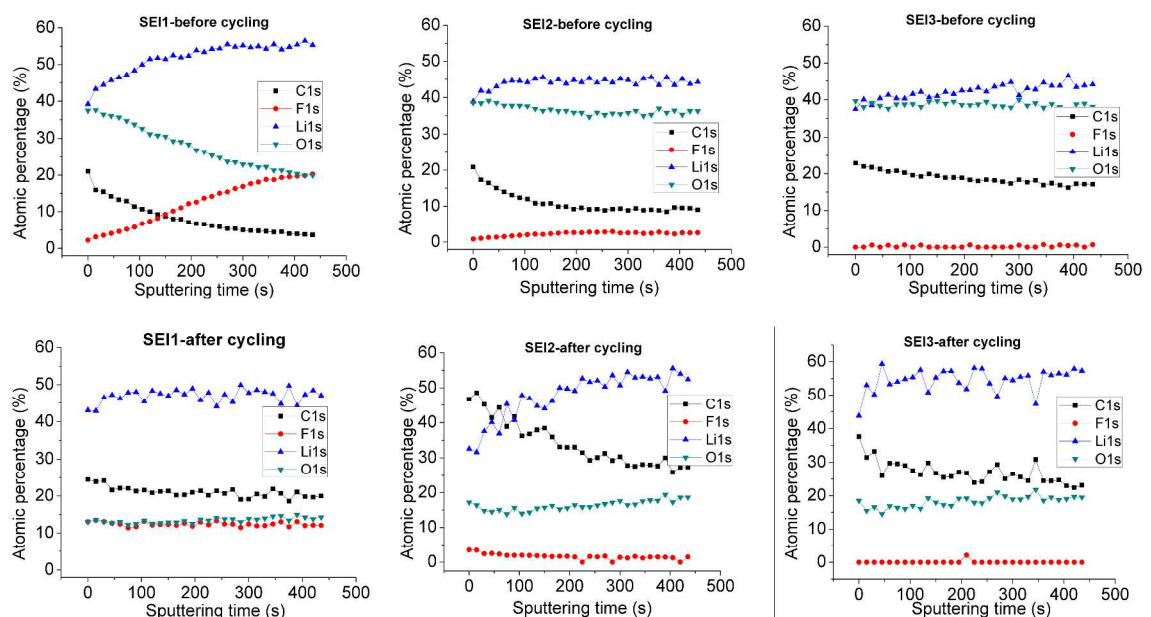
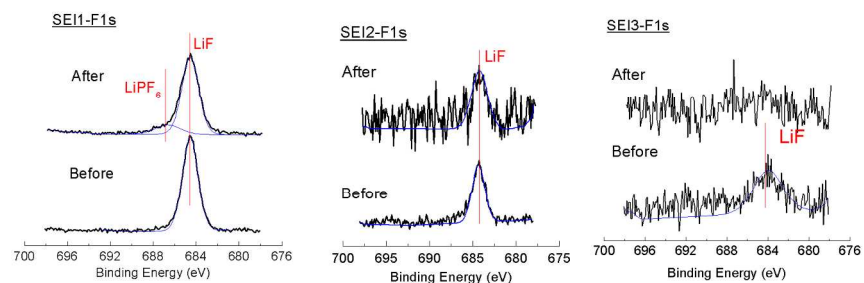


Figure S1 XPS depth profile for different SEI films before and after cycling.



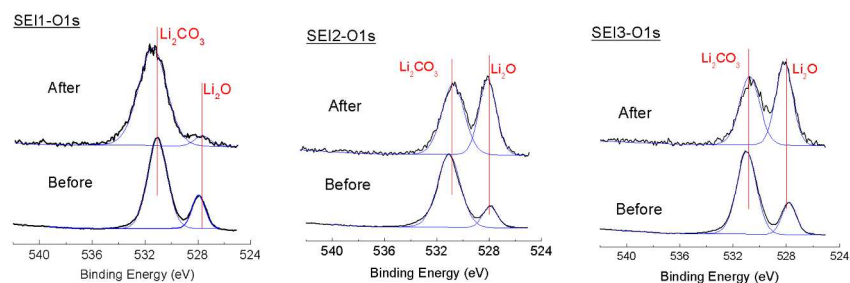


Figure S2 XPS spectra of SEI 1, 2 and 3, before and after cycling

#### 4. Composition and Mechanical Properties of artificial SEIs

Previous studies have shown that the elastic properties of SEIs can impact the cycling performance<sup>5-7</sup>. Therefore, we measured the hardness and elastic moduli of different SEIs by nanoindentation, as shown in Table S1. Among all three engineered SEI films, SEI1 has the highest modulus and hardness, which are 86 GPa and 2.2 GPa, respectively.

**Table S1 Composition of different artificial SEIs before and after cycling (\*counts as LiF, Li<sub>2</sub>CO<sub>3</sub> and Li<sub>2</sub>O), and elastic properties of SEIs before cycling**

| Artificial SEI | Estimate thickness | F atomic percentage before cycling | F atomic percentage after cycling | Approximate LiF percentage* | Hardness (GPa) | Modulus (GPa) |
|----------------|--------------------|------------------------------------|-----------------------------------|-----------------------------|----------------|---------------|
| SEI1           | 100 nm             | 15%                                | 15%                               | 50%                         | 2.22 ± 0.10    | 86.43 ± 1.28  |

|      |        |     |     |     |             |                 |
|------|--------|-----|-----|-----|-------------|-----------------|
| SEI2 | 100 nm | 3%  | 3%  | 15% | 1.02 ± 0.08 | 63.73 ±<br>3.49 |
| SEI3 | 100 nm | <1% | <1% | <1% | 0.65 ± 0.07 | 25.92 ±<br>1.05 |

## References for Supporting Information:

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