Supporting Information

Novel ALD Chemistry Enabled Low-Temperature Synthesis of Lithium Fluoride Coatings for Durable Lithium Anodes

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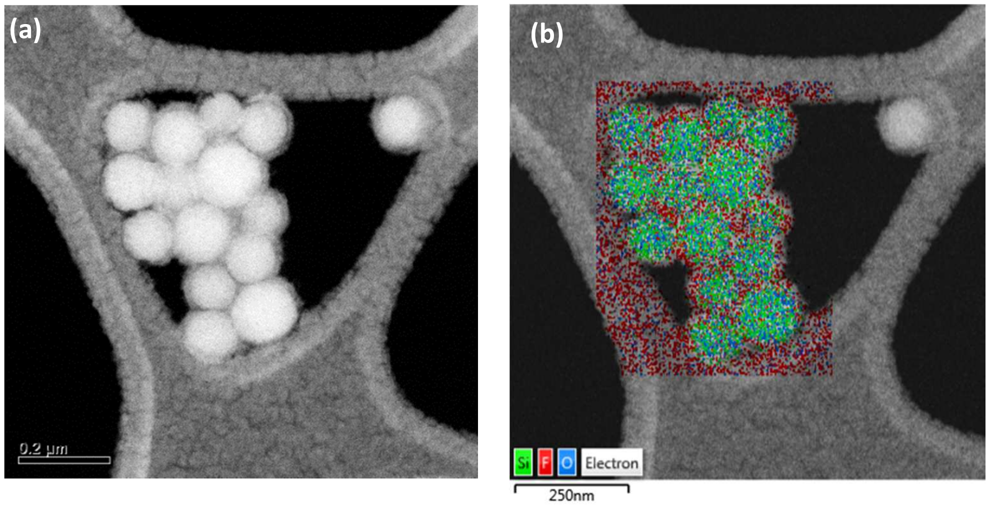

Figure S1. (a) High angle annular dark field (HAADF) transmission electron microscopy (TEM) image of 15 nm ALD LiF coating on 100 nm SiO_2 particles supported on a carbon TEM grid. (b) Energy-dispersive X-ray spectroscopy (EDX) map of Si, F, and O overlaid on the TEM image.

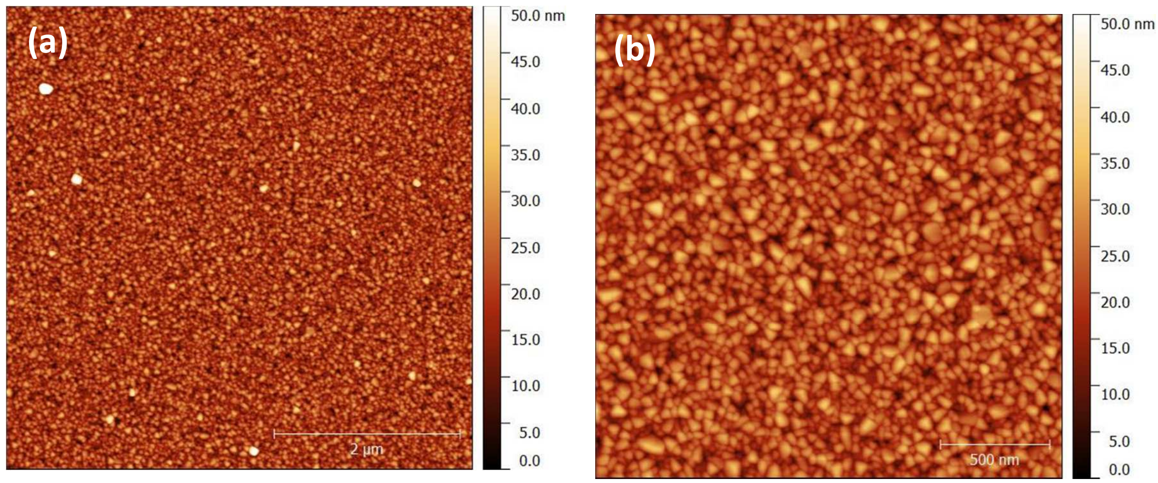

Figure S2. Atomic force microscopy (AFM) images of a 60 nm ALD LiF film on a silicon substrate using scan sizes of 5 µm x5 µm (a) and 2 µm x2 µm (b). These images have RMS roughness values of 6 and 7 nm, respectively.

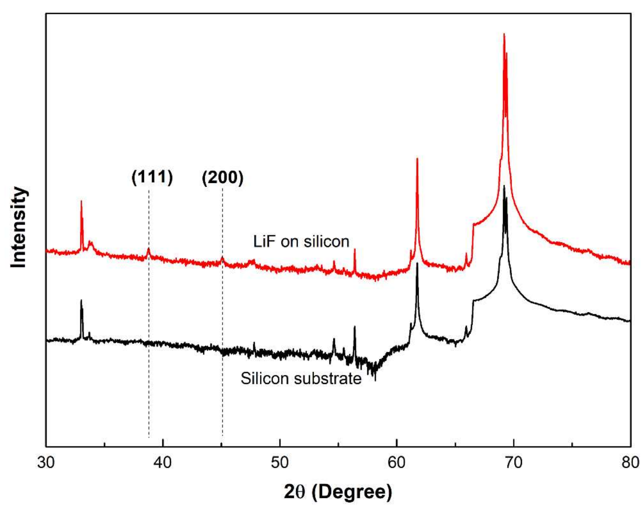

Figure S3. X-ray diffraction data for a 60 nm ALD LiF film on silicon (red) and uncoated silicon (black). The marked peaks correspond to the (111) and (200) reflections of cubic LiF. All other peaks are from the silicon substrate.

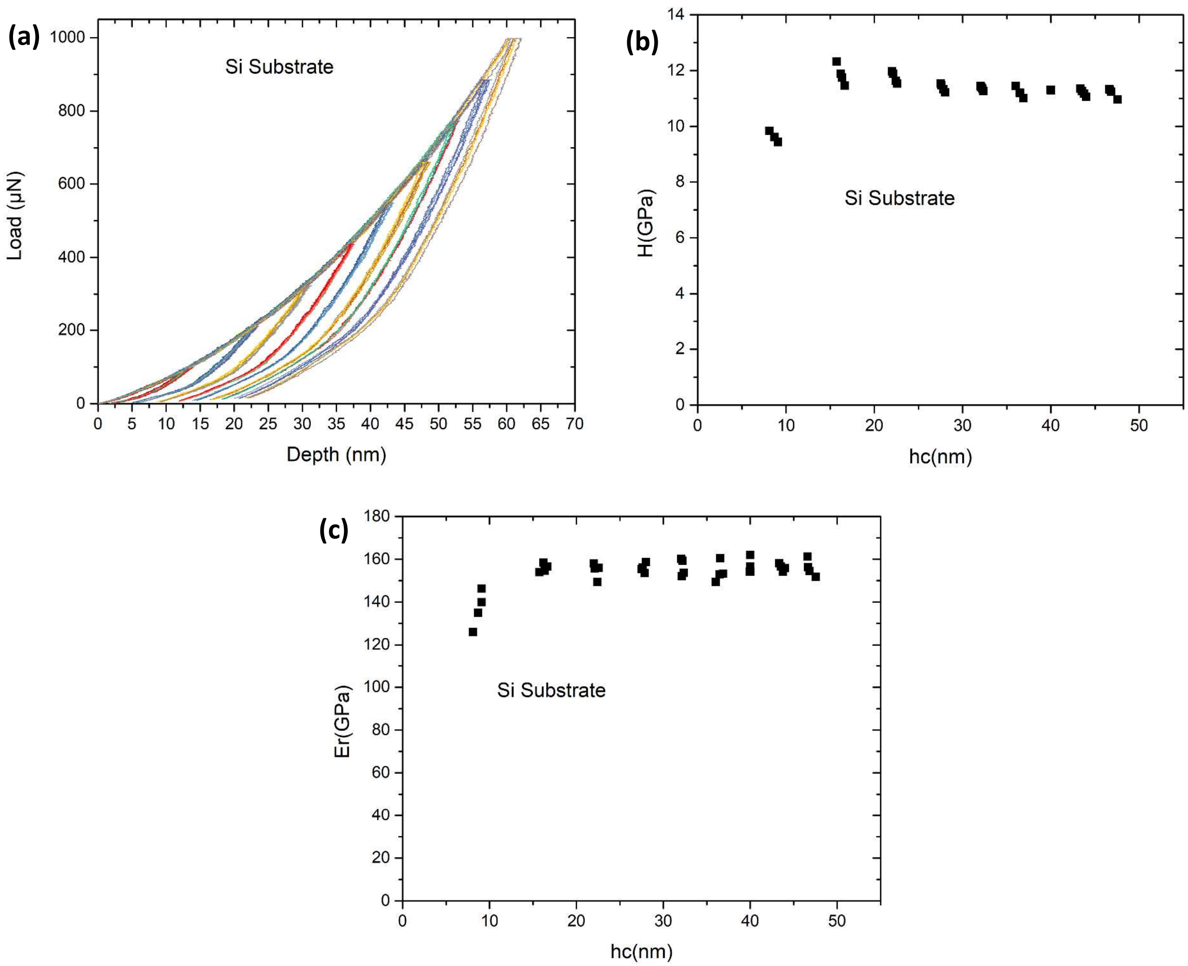

Figure S4. Nanoindentation testing of the Si(100) substrate. (a) Force-distance curves for the silicon substrate. (b) Hardness values for the silicon substrate. (c) Reduced modulus values for the silicon substrate.

Calculation of Elastic Properties: The force-distance curves (Fig. S4a and Fig. 3a) yield the reduced modulus values (Fig. S4c and Fig. 3b). The elastic modulus can then be calculated from:

$$1/E_r = (1-\upsilon_i^2)/E_i + (1-\upsilon_s^2)/E_s \quad \text{(S1)}$$

where E_r is the reduced modulus, E_i and ν_i are the Young's modulus and Poisson's ratio for the nanoindentor tip (diamond), and E_s and ν_s are the Young's modulus and Poisson's ratio for the substrate (silicon or LiF). Next, the shear modulus for the substrate (G_s) is calculated using:

$$2G_s(1+\upsilon_s) = E_s \quad \text{(S2)}$$

Table S1 shows the measured and calculated values, as well as the values for E_i, ν_i, and ν_s taken from the literature.

Table S1: Mechanical properties of silicon and ALD LiF determined from nanoindentation measurements.

	LiF	Silicon
E_r (GPa)	140	155
E_i (GPa)	1140	1140
ν_i	0.07	0.07
ν_s	0.27	0.17
E_s (GPa)	148	174
G_s (GPa)	58	74

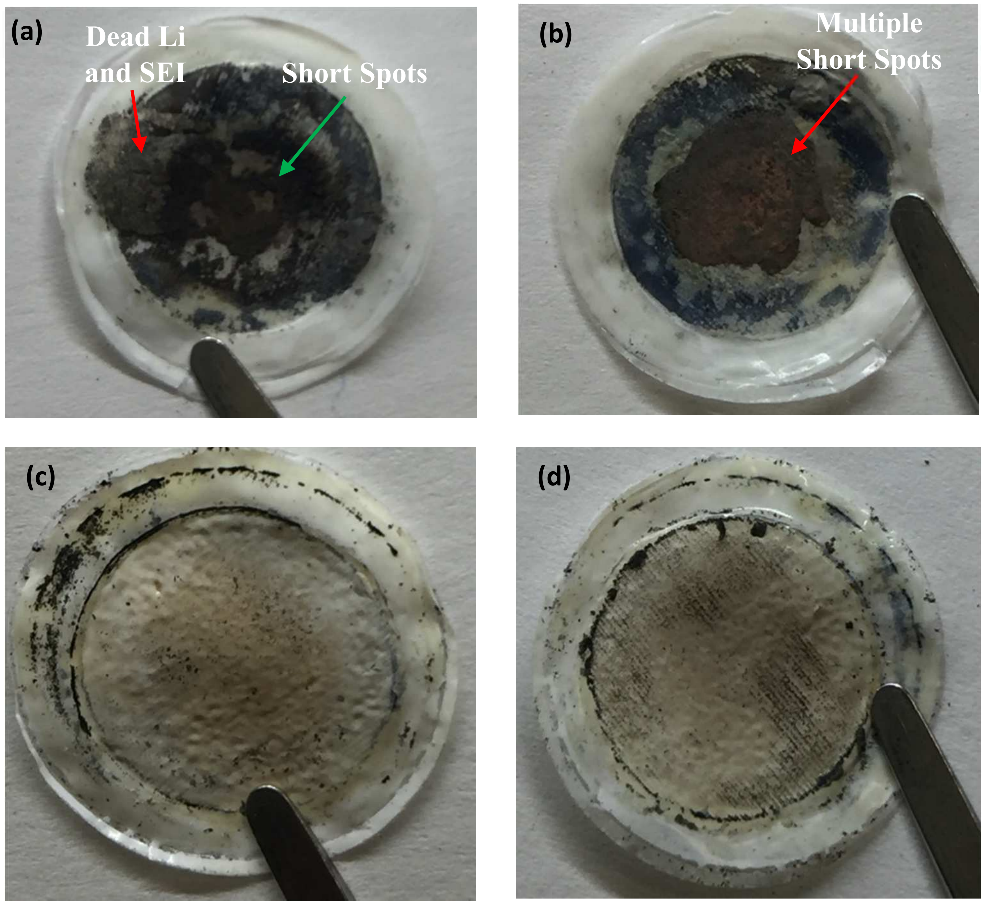

Figure S5. (a) One side of a separator used in Li symmetric cells with 5 μL electrolyte after 100 hours (multiple failures occurred before disassembly). (b) The other side of separator shown in (a). (c) One side of a separator used in LiF-coated Li symmetric cells after 200 hours. (d) The other side of the separator shown in (c).

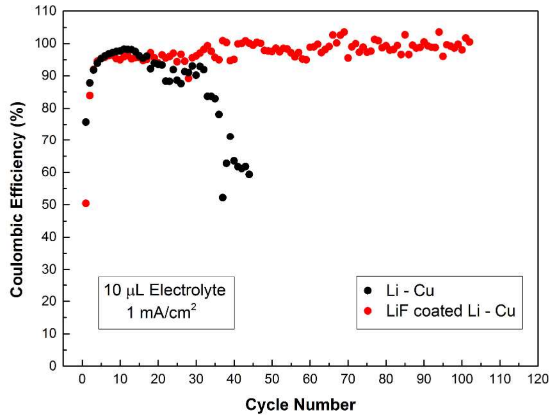

Figure S6. Lithium-copper cells with ether electrolyte of 10 μL at a current density of 1 mA/cm^2. 8 nm ALD LiF was only coated on the lithium metal.

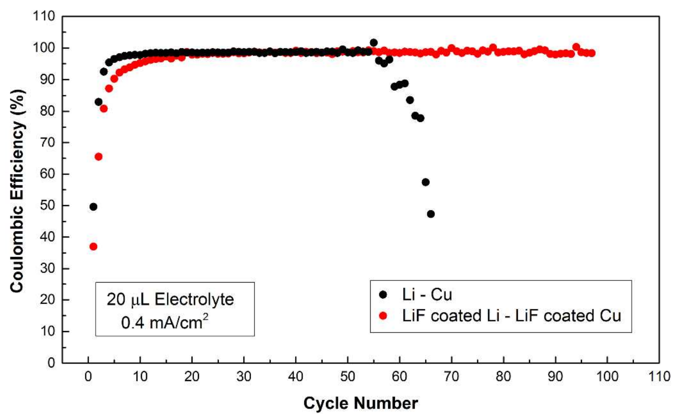

Figure S7. Lithium-copper cells with ether electrolyte of 20 μL at a current density of 0.4 mA/cm^2. 8 nm ALD LiF was coated on lithium metal and 6 nm ALD LiF was coated on Cu.

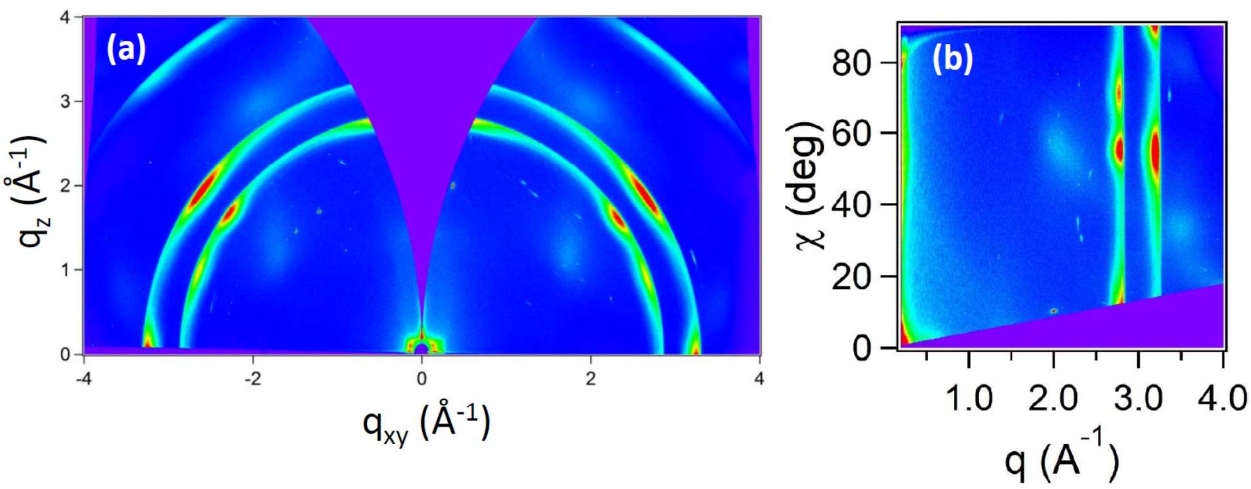

Figure S8. Grazing incidence wide angle X-ray scattering (GIWAXS) characterization for 118nm ALD LiF film on silicon. Stray sharp peaks are due to contamination from silicon dust resulting from cleaving Si substrate (a) 2D GIWAXS pattern of intensity as a function of q_{xy} (the in-plane component of the scattering vector) and q_z (the out-of-plane component). (b) Intensity vs azimuthal angle (χ) and total the scattering vector (q) from the GIWAXS pattern in (a). The intensity changes along chi shows the (111) and (200) texturing of the ALD LiF. The (111) texture can be seen from the (111) peak near 75° and the (200) peak near 54°. The (200) texture is seen as the (111) peak near 54° and the (200) peak near 90°.