## **Support information**

## **Experimental section**

## Preparation of carbon-sulfur composite and Al<sub>2</sub>O<sub>3</sub> ALD coating on carbon-sulfur electrode

Commercial carbon black was mixed with sulfur powder and dried at 80 °C for 12 h to remove moisture. The mixture was then transferred to a sealed steel reactor and was heated at 150 °C for 9 h and then 300 °C for 3 h. The obtained sulfur-carbon black composites maintained 65 wt% sulfur load. The electrodes were prepared by slurry casting onto aluminum foil. The slurry mass ratio of active material, acetylene black, and polyvinylidene fluoride (PVDF) is 70:20:10. The as-prepared electrodes were finally dried at 80 °C over 12 h under vacuum. Atomic layer deposition was conducted in a Savannah 100 ALD system (Cambridge Nanotech, USA). ALD Al<sub>2</sub>O<sub>3</sub> coating was grown on the C/S electrode at 100 °C by using trimethylaluminium and H<sub>2</sub>O as precursors.

## Physical and electrochemical characterization

The morphologies of the samples were characterized by Hitachi S-4800 field emission scanning electron microscope (FE-SEM) operated at 5 KeV. CR-2032 type coin cells were assembled in argon filled glove box. The coin-type cells consisted of Li metal as anode, a separator, and as-prepared electrode as cathode. The electrolyte was composed of 1M LiTSFI salt dissolved in dioxolane (DOL): dimethoxyethane (DME) of 1:1 volume ratio. Cyclic voltammograms were collected on a versatile multichannel potentiostation 3/Z (VMP3) under scanning rate of 0.1 mV/s between 1.0 V- 3.0 V (vs. Li/Li<sup>+</sup>). Charge-discharge characteristics were galvanostatically tested in the range of 1.0 V-3.0 V (vs. Li/Li<sup>+</sup>) at room temperature using an Arbin BT-2000 Battery Tester. X-ray photoelectron spectroscopy (XPS) experiments on the Al 2p were conducted on the variable line spacing plane grating monochromator (VLS PGM) beamline at the Canadian Light Source (CLS), located at the University of Saskatchewan in Saskatoon. Thermogravimetric analysis (TGA) was carried out on a TA SDT Q600 in an N<sub>2</sub> atmosphere from room temperature to 700 °C at a rate of 10 °C/min.



**Fig. S1.** TGA curves of pristine carbon-sulfur composites, 2-cycle Al<sub>2</sub>O<sub>3</sub> C/S composites, and 20-cycle Al<sub>2</sub>O<sub>3</sub> C/S composites.



**Fig. S2.** FE-SEM and Al elemental mapping images of C/S electrode with 5-cycle (a, b, c), 10-cycle (d, e, f), and 20-cycle (g, h, i) ALD Al<sub>2</sub>O<sub>3</sub> coating.



Fig. S3. FE-SEM image of pristine carbon-sulfur electrode.



Fig. S4. Comparison of Al 2p peaks of AlF<sub>3</sub> with different ALD cycles