

Supporting Information

Artificial Thiophdiyne Ultrathin Layer as Enhanced Solid Electrolyte Interphase for the Aluminum Foil of Dual-Ion Batteries

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Experimental Section

Reagents

Commercial aluminium (Al) was obtained from Shenzhen Kejing technology Co., Ltd. Copper iodide (CuI), trans-dichlorobis (triphenyl-phosphine) palladium(II) ($\text{PdCl}_2(\text{PPh}_3)_2$) and triphenylphosphine (Ph_3P) was obtained from Sigma-Aldrich Co., Ltd. Tetrabromothiophene was purchased from aladin. Tetrabutylammonium fluoride (TBAF) were obtained from AcrosOrganics. Copper foil and trimethylsilylacetylene were purchased from Sinopharm Chemical Reagent Co., Ltd. Tetrahydrofuran (THF), pyridine was pretreated as our previous reported to remove the moisture and oxygen.¹

The pretreated operation for copper substrates and Al foil were carried out as follow. Firstly, the copper foil was cut into square with 12×6 cm and immersed in 1 M hydrochloric acid under ultrasonic more than 4 hour. Meanwhile, the Al foil was cut into a smaller square with 5×5 cm and cleaned in 0.1 M hydrochloric acid for less than 5 minutes under ultrasonic. Then, both copper and Al foil was washed by water and acetone several times and dried under argon atmosphere. The Al foil were put into a folded copper envelope and used immediately.² The synthetic process of tetra(trimethylsilyl) ethynyl thiophene, tetraethynylthiophene monomer was described in supporting information.

Preparation of Thi-Dy modified Al foil

Thi-Dy modified Al was prepared through the synthetic route of Glaser-Hay reaction as suggested in Figure 1a. Several pieces of pretreated Al foil contained copper envelope were immersing into pyridine solution. Then, 34 mg of

tetraethynylthiophene monmer was dissolved in pyridine and added gradually under water-free and oxygen-free conditions. The reaction was carried out at 50°C for 12 hours. Finally the solution was removed and the obtained Thi-Dy coated copper and Al foil were washed and dried as our previous work. ²

Assembly of DIB batteries

The typical DIB cell was assembled in standard CR2032 coin cells with graphite (GS360, BTR New Energy Materials Inc) as positive active materials. GS360, Super P and polytetrafluoroethylene (PTFE, 10 wt % in water suspension) were mixed and grinded with weight ratio of 80:10:10 to form a slurry. Then the slurry was rolled onto Al current collector and punched into 10 mm diameter. The graphite positive electrode was dired and weighted with a mass loading around 2.4 mg/cm². The current densities for cell were calculated based on the mass loading of graphite active materials. The obtained Thi-Dy modified Al foil was cut into 14 mm diameter and used as negative electrode. The glass fiber separator was punched into 16 mm diameter and applied between the positive and negative electrode.

The synthetic of tetra (trimethylsilyl) ethynyl thiophene, tetraethynylthiophene

2g (5mmol) of 2, 3, 4, 5-tetrabromothiophene, 6.2 ml (45mmol) of (CH₃)₃SiC≡CH, 0.351 g (0.500 mmol) of PdCl₂(PPh₃)₂, 0.152 g (0.8 mmol) of CuI, and 0.2096 g (0.8 mmol) of Ph₃P were added into mixture of 80 mL TEA. The mixture was stirred under a argon atmosphere at 60 °C for 3 days in a tube sealing. The solvent was evaporated and the residue was then purified by columnchromatography to yield tetra (trimethylsilyl) ethynyl thiophene as pale yellow powder (1.85 g, 85.6 %).

The synthetic of tetraethynylthiophene

To a solution of 43.2 mg (0.1 mmol) tetra (trimethylsilyl) ethynyl thiophene in 15 mL THF was added 0.4 mL TBAF (1M in THF, 0.4 mmol) and stirred at 0 °C for 30 min. The solution was then diluted with CH₂Cl₂ and washed with distilled water and dried with anhydrous Na₂SO₄. The solvent was removed in vacuum rotary evaporation to yield tetraethynylthiophene.

Materials characterization

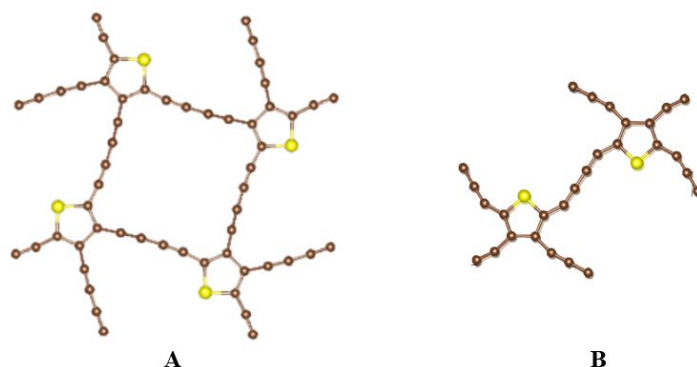
The Al and as-prepared Thi-Dy modified Al were characterized using field emission scanning electron microscopy (FESEM, HITACHI S-4800). The TEM image of exfoliated Thi-Dy after as-prepared Thi-Dy modified Al dissolved in a 1M hydrochloric acid solution to remove the metal aluminum base, and was measured by transmission electron microscopy (TEM, H-7650) apparatus. The ¹H and ¹³C NMR spectra were obtained by a Bruker AVANCE-III 600 MHz spectrometer. Nitrogen adsorption/desorption measurements were performed at 77 K using a Micromeritics ASAP2020 gas-sorption system, and the Barret-Joyner-Halenda (BJH) method was used for pore size distribution assessment. The XRD pattern was obtained by Bruker D8 ADVANCE diffractometer with Cu K α irradiation at $\lambda = 1.5406 \text{ \AA}$. The X-Ray photo electron spectrometer (XPS) was tested based on VG Scientific ESCA Lab220i-XL X-Ray photo electron spectrometer, using Al K α radiation as the excitation sources. FT-IR results were obtained through Fourier transform infrared spectroscopy (FT-IR, Thermo-Fisher Nicolet iN10). UV-vis absorption spectroscopy was performed on a HITACHI U-4100. The Raman spectra were recorded at room temperature using a Thermo Scientific DXRXI system with excitation from an Ar laser at 532 nm. The ex-situ XRD patterns, the ex-situ Raman spectra of the charged samples were prepared through the disassembled DIB which charged to a certain potential in glove box, washed with EMC, and protect from being oxidized by air.

Galvanostatic charge/discharge tests were measurement using a LAND-CT2001

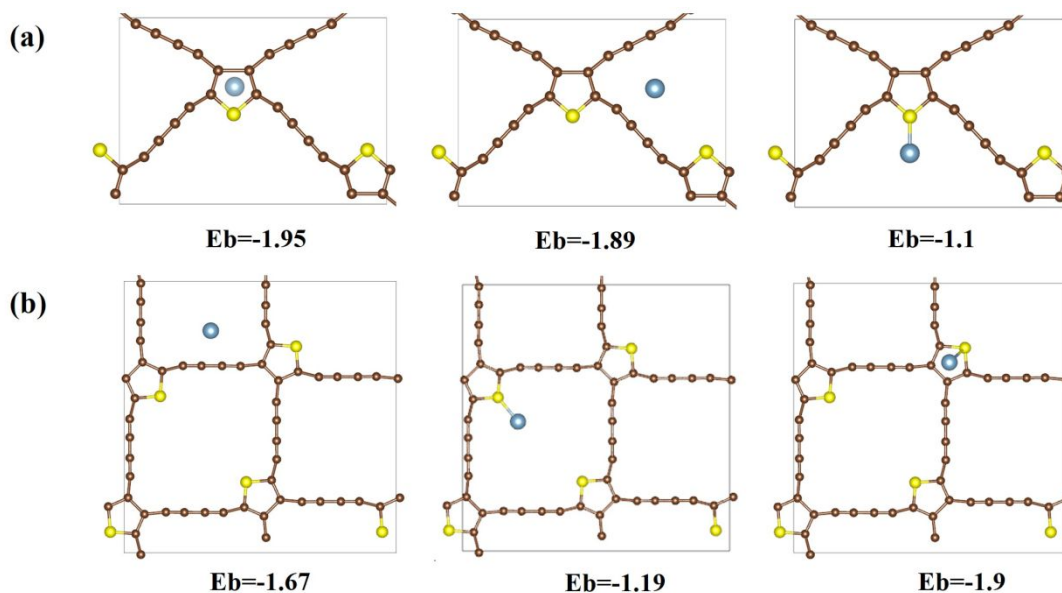
instrument. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) was performed by using a CHI660 electrochemical work-station at each measurement condition.

DFT calculations for the possible stable configurations of Thi–Dy

Scheme S1. The possible two stable configurations of Thi–Dy.



Scheme S2. The calculated adsorption energies of a single Al atom at different sites for (a) rhombus conformation and (b) tetragon conformation on the selected Thi–Dy repeating unit.



All the theoretical calculations were performed by first principle energy calculations based on generalized gradient approximation of Perdew, Burke, and

Ernzerhof (GGAPBE) functional. To simulate monolayer structure of Thi-Dy, slab models with tetragon-like structures in Thi-Dy were used. The convergence threshold for self-consistent iteration is 10^{-6} eV. We chose the typical bond lengths for both of the structures and let $C\equiv C-C\equiv C$ perfectly in a straight line to build our models. The structure of Thi-Dy(B) is unique under this condition, while that of Thi-Dy (A) is not. We adjust the S-C-C and C-C-C angles to be 93.20 and 96.57, respectively, to make the energy approach the minimum. Considering ground state and crystalline parameter optimizations are not performed in current calculations, the discrepancy between the current energies and that of ground state minimum must exist, but the results are reasonable for a preliminary analysis. The combining calculations between Al atom and Thi-Dy were performed within the framework of the dispersion-corrected density functional theory, as implemented in the VASP package with the projector-augmented-wave50 (PAW) basis set and the PBE exchange-correlation functional within a generalized gradient approximation (GGA). The geometry optimizations of the combining systems were carried out with the cell parameters remaining the same as those of the pristine system. The convergence tolerance of the total energy was set to 0.03 eV.

Assembly of Li half cell

The Al and Thi-Dy modified Al foil for Li half cells were assembled in standard CR2032 cells inside an argon filled glove box with oxygen and water levels lower than 2 ppm. The Al and Thi-Dy modified Al applied as working electrode was cut into a small square (1×1 cm) to prevent excessive Al. Then, the square was assembled

with Li metal foil as counter and reference separated by a glass fiber separator (Whatman) in an electrolyte (1 M LiPF₆ dissolved in ethylene carbonate and diethyl carbonate with a ratio of 1:2).

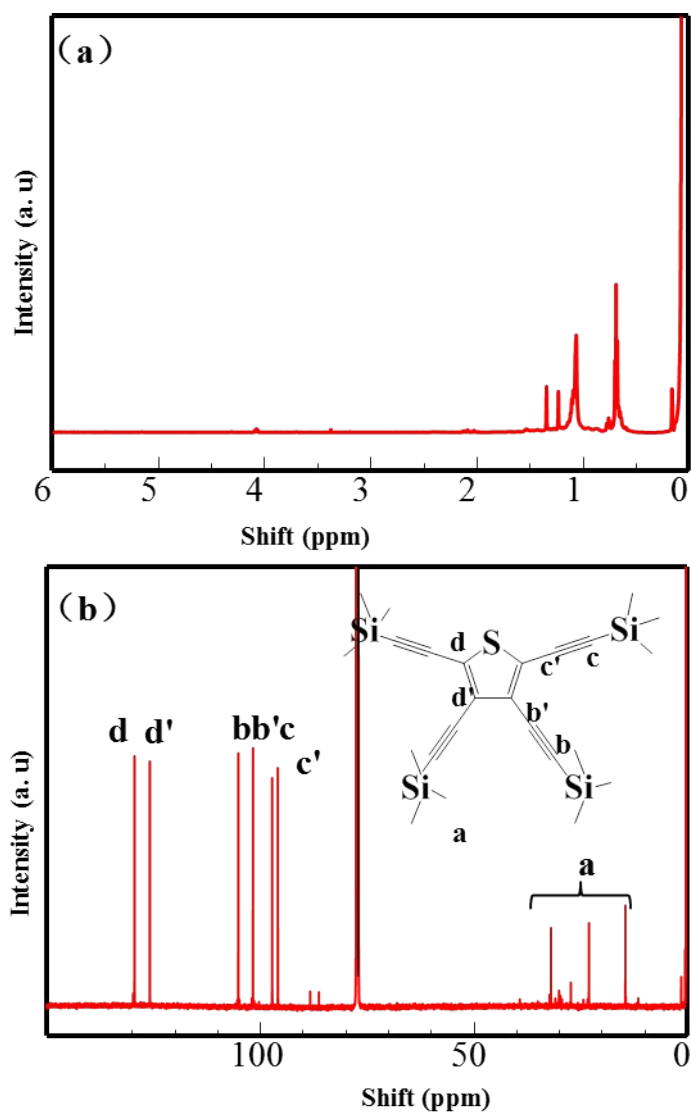


Figure S1. ¹H (a) and ¹³C (b) NMR spectra of Tetra [(trimethylsilyl) ethynyl] thiophene monomer.

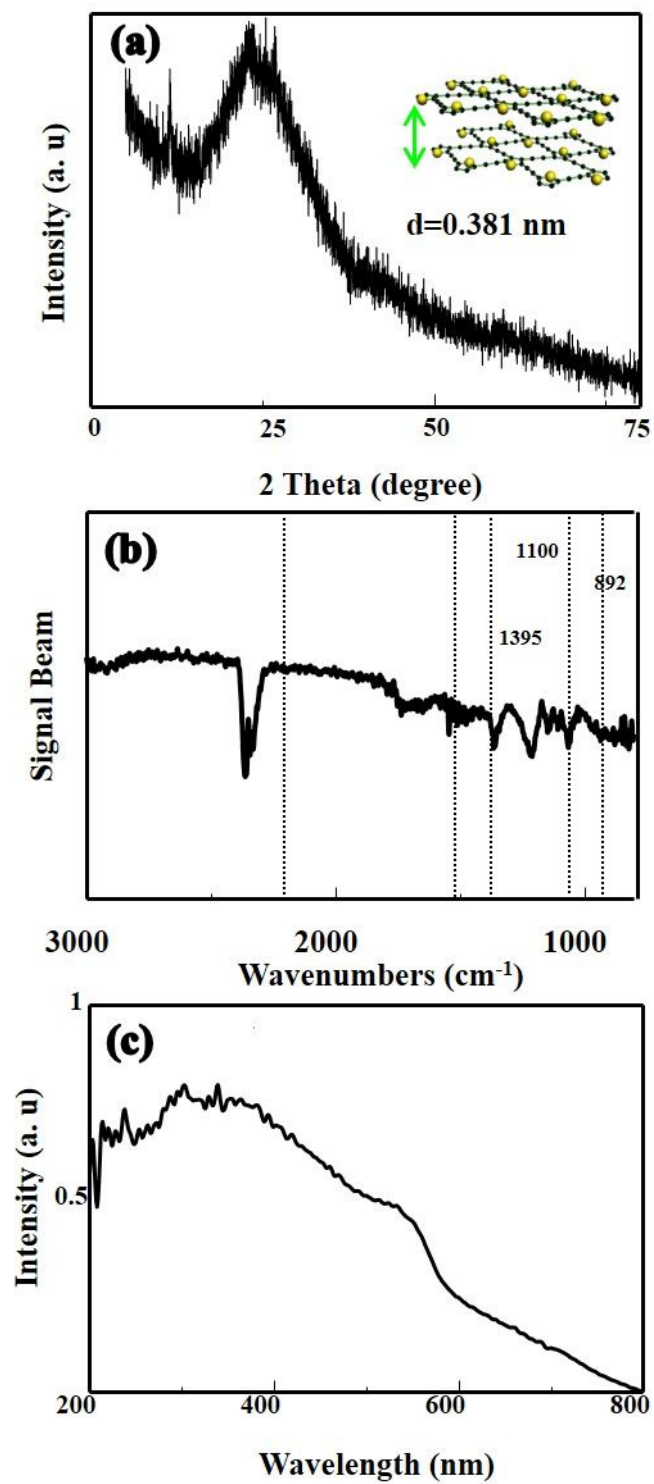


Figure S2. (a) XRD patterns of Thi-Dy layers as an exfoliated sample; (b) FT-IR spectra of Thi-Dy modified Al foil; (c) UV-vis spectrum of Thi-Dy modified Al.

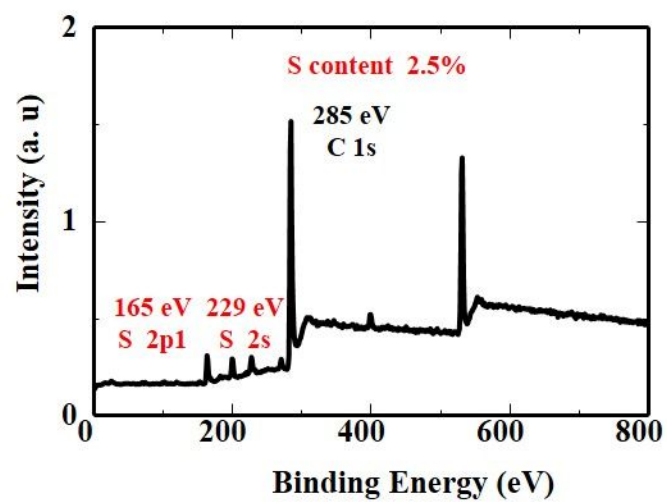


Figure S3. XPS survey of Thi-Dy modified Al samples.

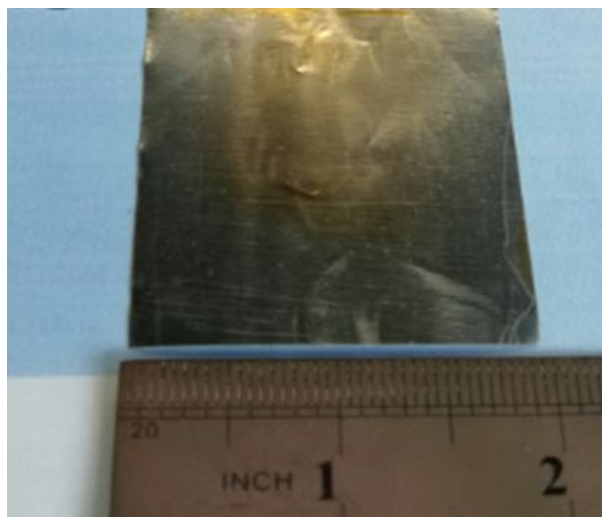


Figure S4. The obtained Thi–Dy layers on aluminum foil at large scale with 2×2 cm.

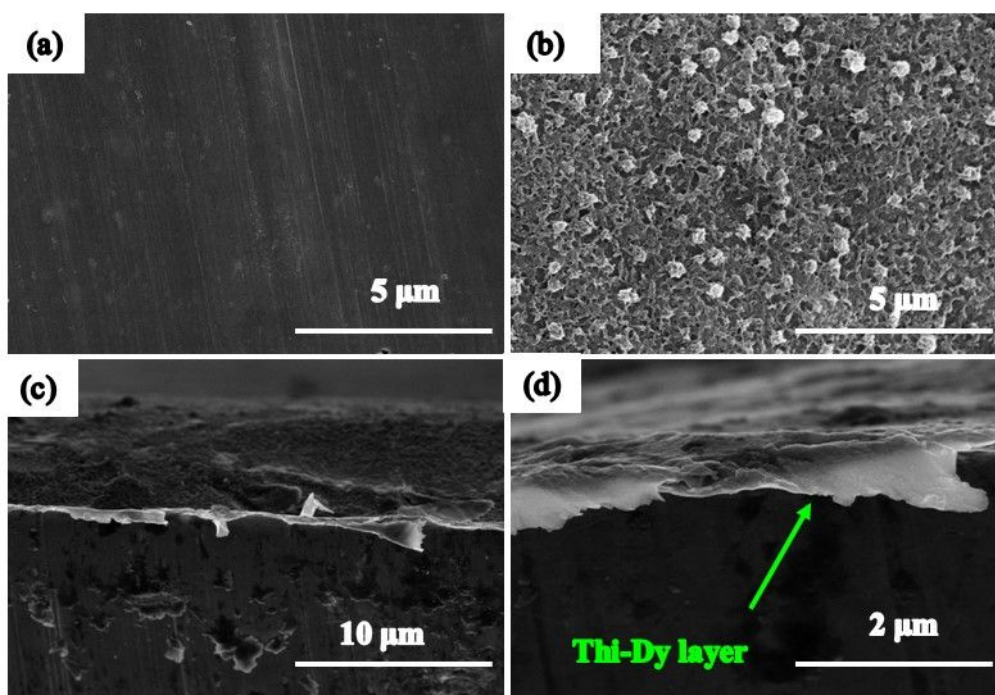


Figure S5. Surface morphologies of Al (a) and Thi-Dy modified Al (b) samples; The cross-sectional SEM image of Thi-Dy modified Al foil (c and d).

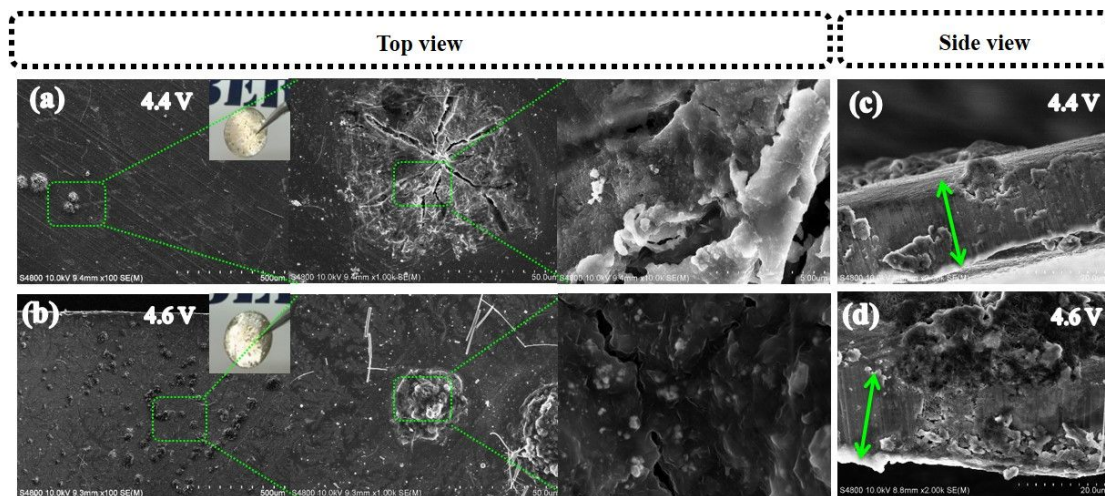


Figure S6. Morphologies of Thi-Dy modified Al electrode at potential from 4.4V (a) and 4.6 V (b) during the initial charge process with a different resolution. (c) and (d) The cross-sectional SEM image of Thi-Dy modified Al electrode at each potential.

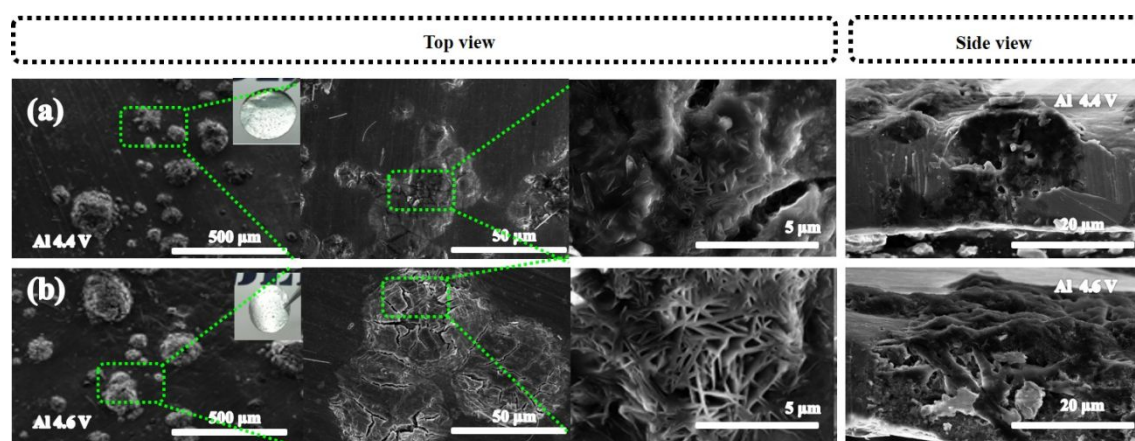


Figure S7. Morphologies of Al foil at potential from 4.4V (a) to 4.6 V(b) during the initial charge process with different resolution.

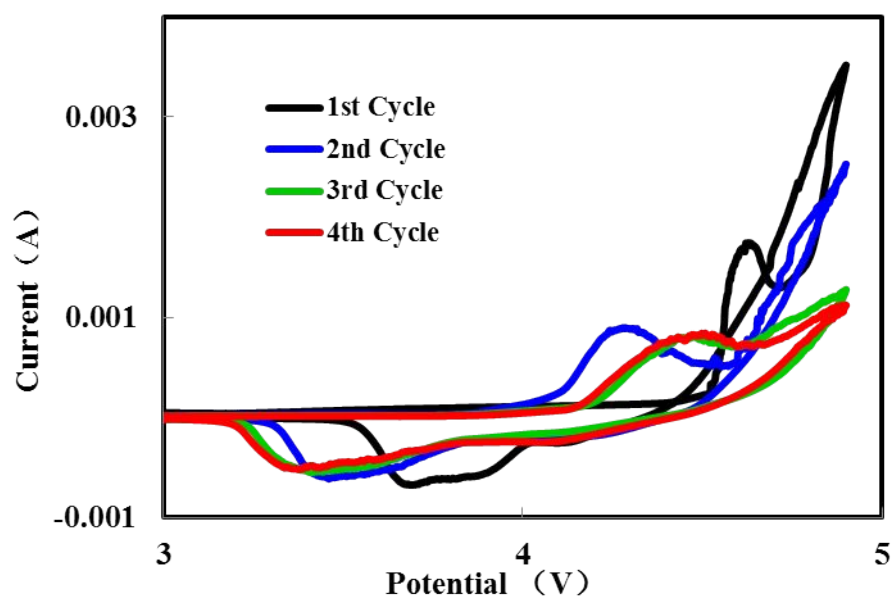


Figure S8. CV profiles of Al based cells for the initial four cycles with scan rate as 0.1 mV s^{-1} .

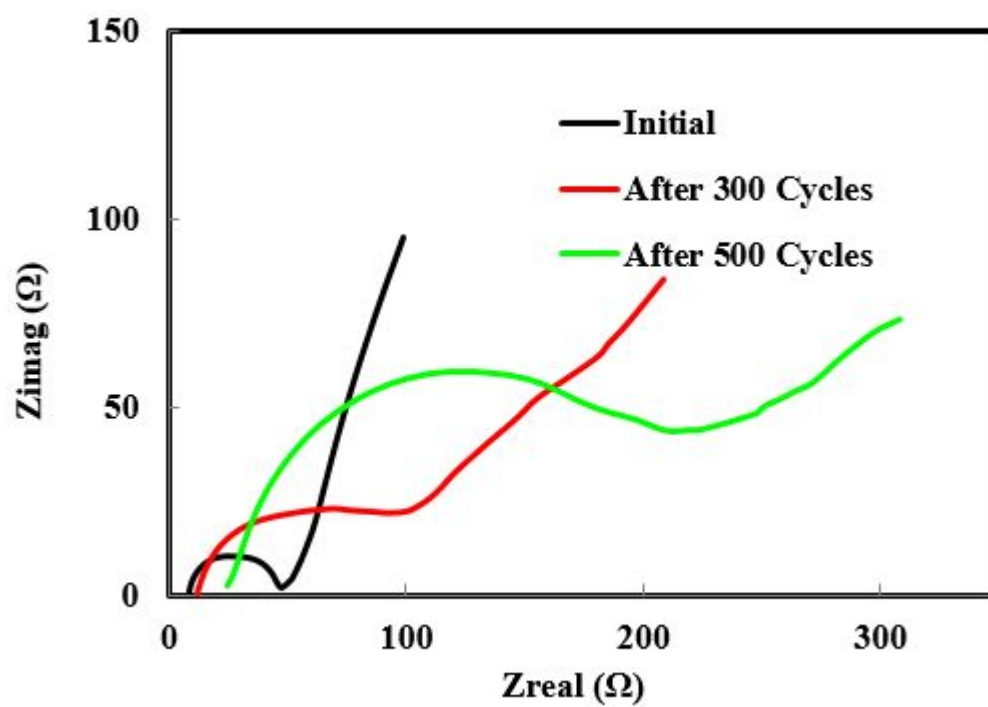


Figure S9. Nyquist plots of as-prepared Thi-Dy based cells with different cycles, respectively.

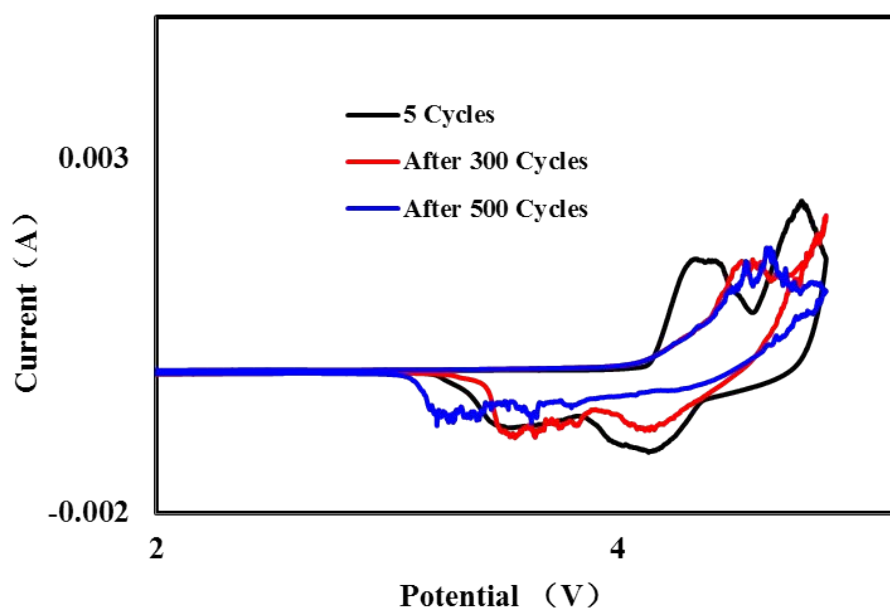


Figure S10. CV profiles of Thi-Dy based DIB cells after different charging-discharging cycles with scan rate as 1 mV s^{-1} .

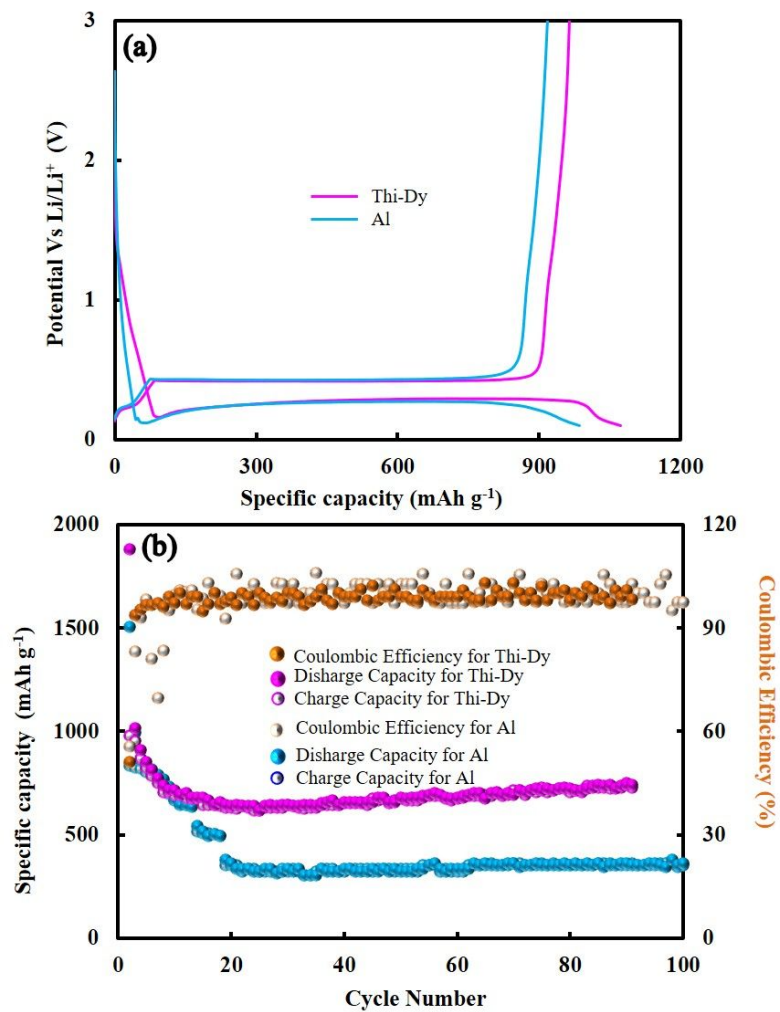


Figure S11. (a) The charge–discharge curves of Al and Thi–Dy modified Al foil based Li half cells at the current rate of 0.1 mA g⁻¹ at first cycle; (b) The cycle performance of the Al and Thi–Dy modified Al foil based Li half cells with a current density of 0.5 mA g⁻¹, respectively.

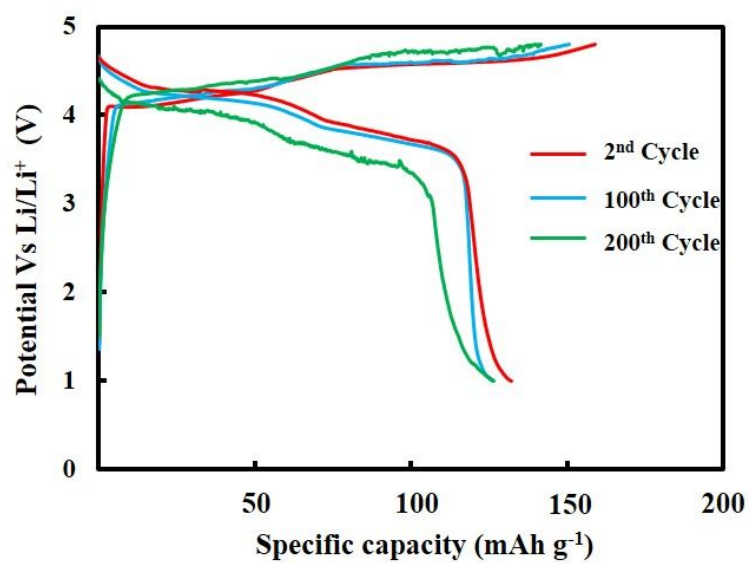


Figure S12. The charge–discharge curves of Thi–Dy modified Al foil based cells at the current rate of 100 mA g⁻¹ at 2nd, 100th, 200th cycles, respectively.

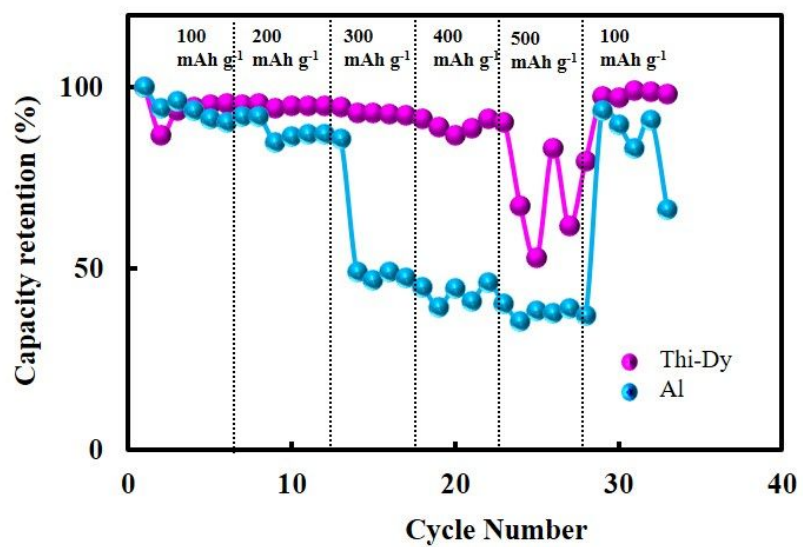


Figure S13. The capacity retention of Al and Thi–Dy modified Al foil based foil for each current density.

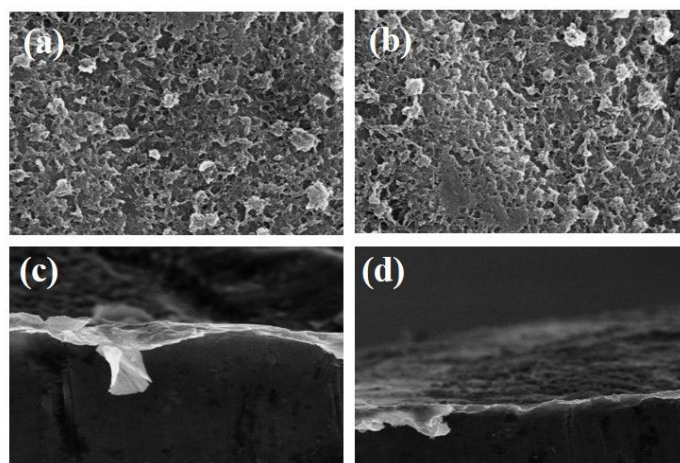


Figure S14. Top view images of Thi–Dy prepared with 2(a) and 4 (b) times HBE monomer, Scale bar: 2 μm ; Cross–sectional view of Thi–Dy based Al foil prepared with 2(c) and 4 (d) times tetraethynylthiophene monomer , Scale bar: 2 μm .

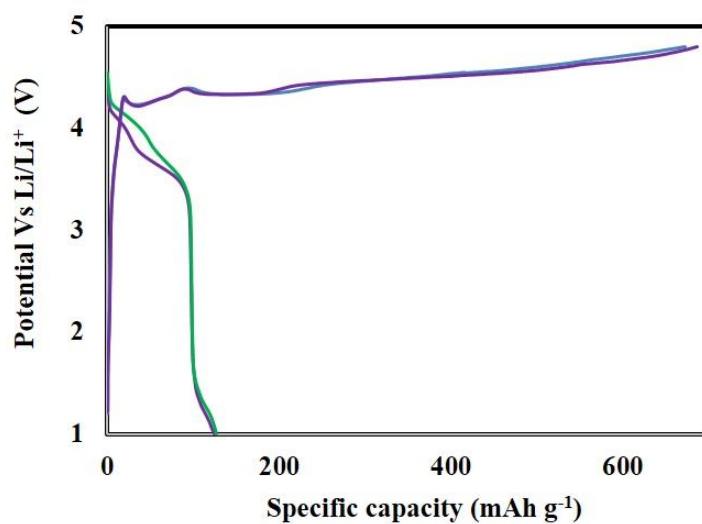


Figure S15. The charge–discharge curves of Thi–Dy prepared with 2(blue) and 4 (purple) times monomer based cells at the current rate of 1C at first cycle.

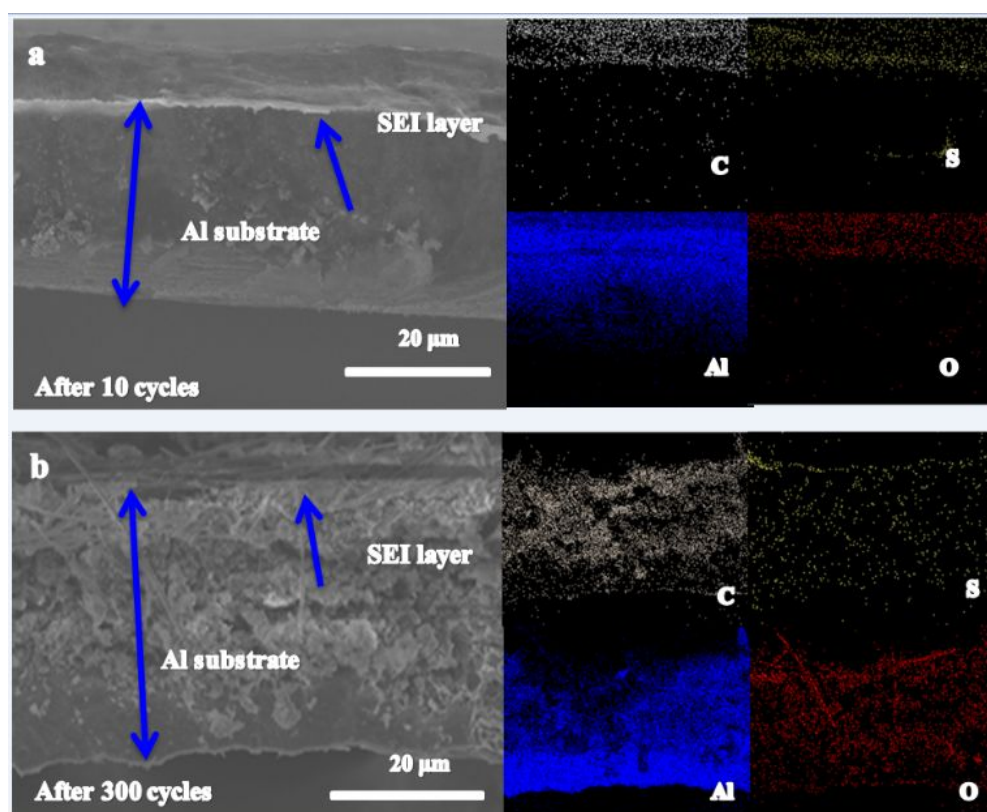


Figure S16. Cross-sectional view of Thi–Dy modified Al foil at potential of 0 V after 10 (a) and 300 (b) charge cycles with a different resolution (the images on the right are element distribution for each sample).

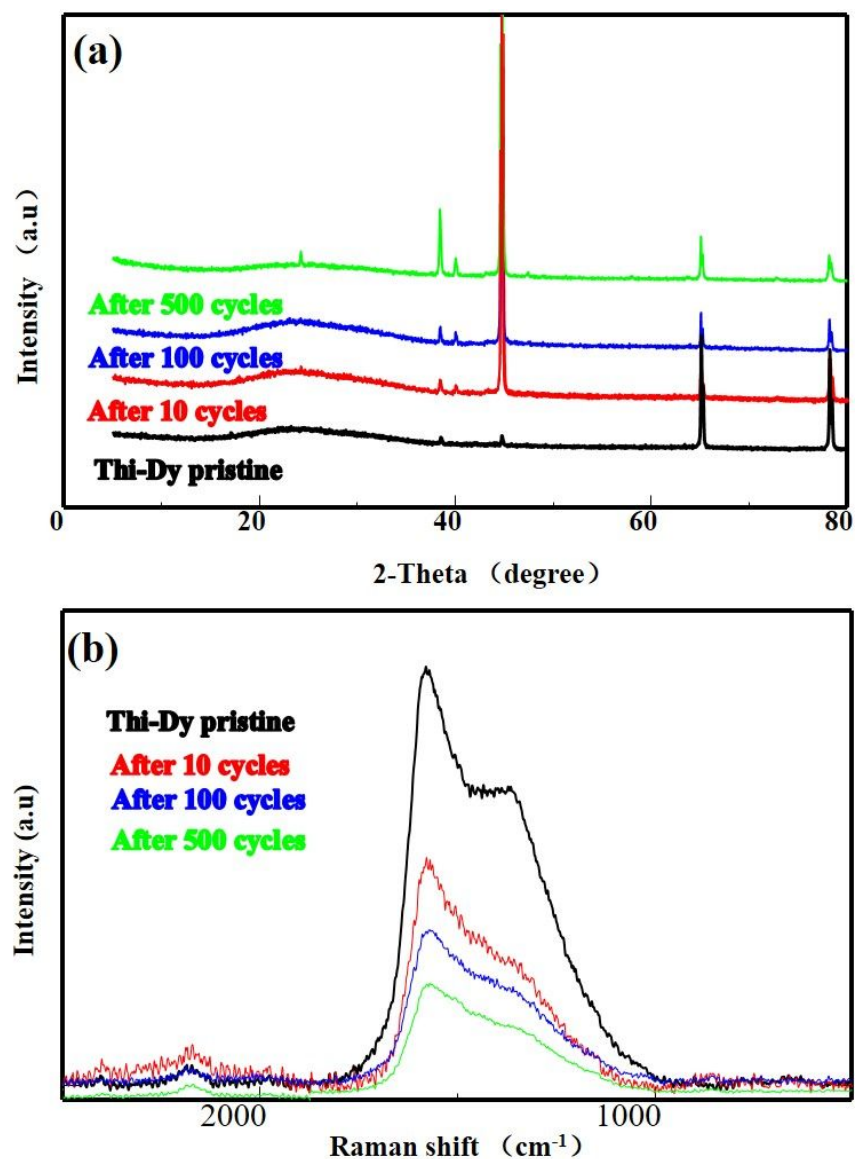


Figure S17. The *ex-situ* XRD patterns (a) and Raman spectra (b) of the Thi-Dy electrode at different cycles with a current rate of 100 mA g⁻¹.

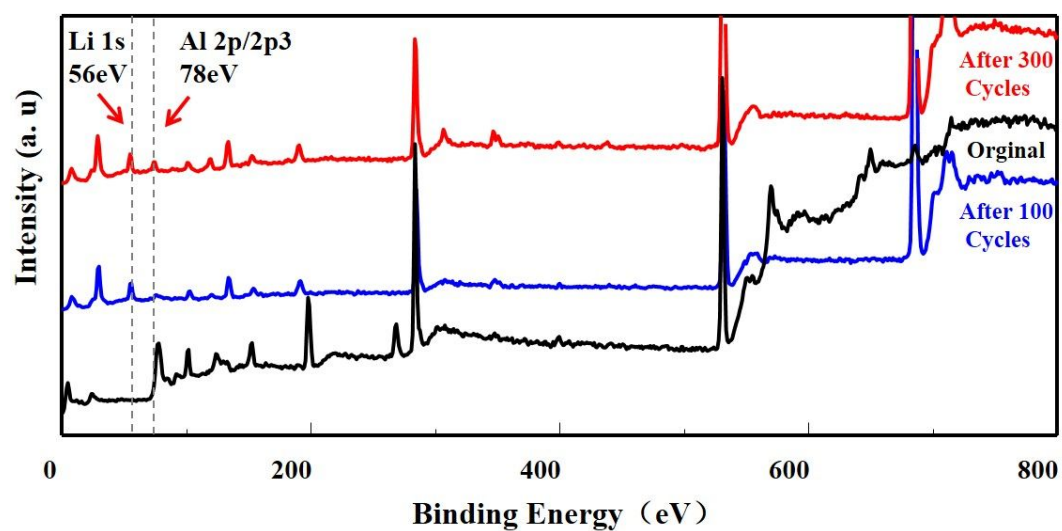


Figure S18. XPS survey of Thi-Dy modified Al foil based foil with different cycles, respectively.

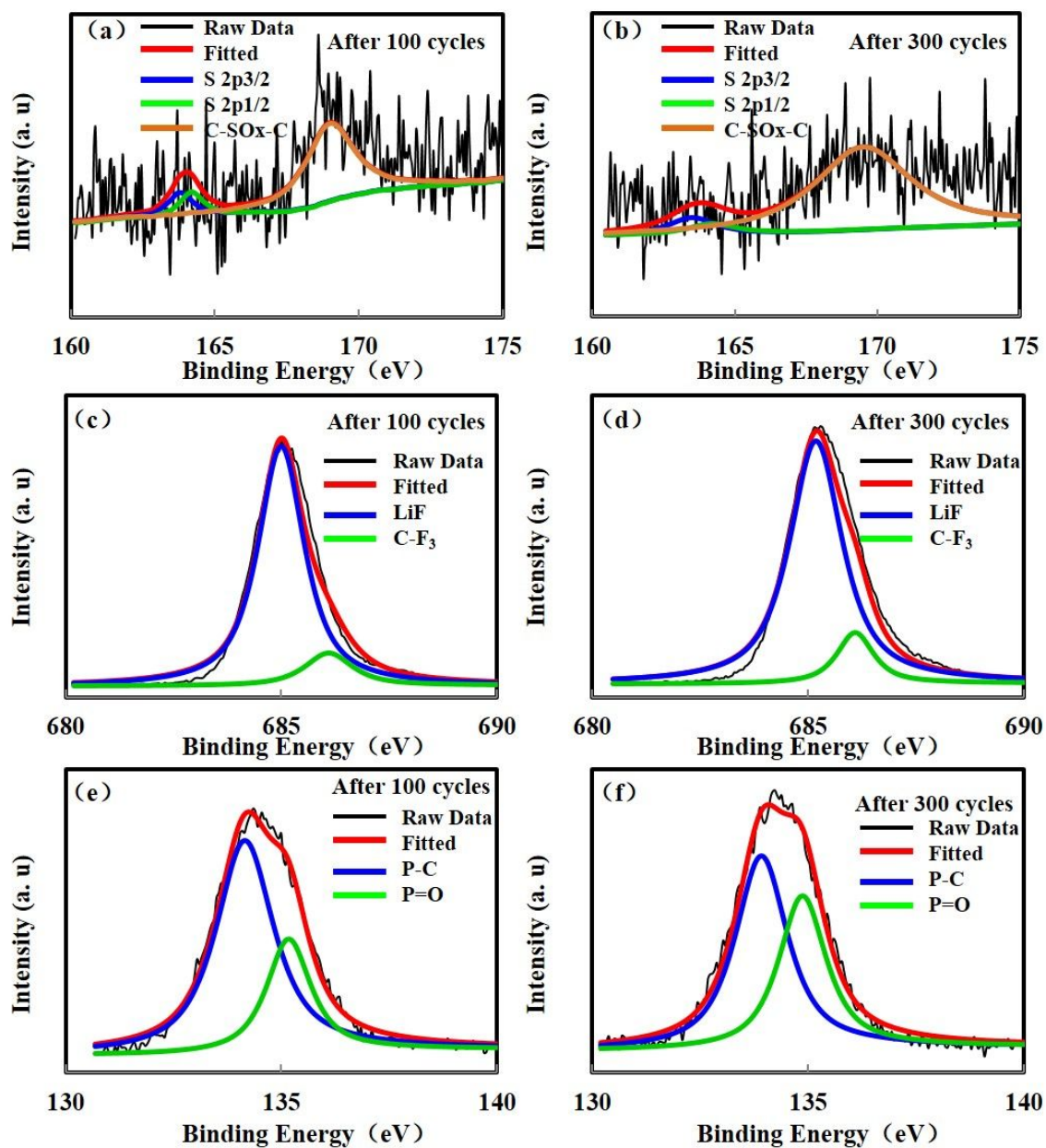


Figure S19. Chemical composition analysis of Thi-Dy modified Al foil based cells by XPS for S element (a, b), F element (c, d), and P element (e, f) after different cycles, respectively.

References

1. Wang, K.; Wang, N.; He, J.; Yang, Z.; Shen, X.; Huang, C. Preparation of 3D Architecture Graphdiyne Nanosheets for High-Performance Sodium-Ion Batteries and Capacitors. *ACS Appl. Mater. Interfaces* **2017**, *9*, 40604–40613.
2. Wang, K.; Wang, N.; He, J.; Yang, Z.; Shen, X.; Huang, C S. In-Situ Preparation of Ultrathin Graphdiyne Layer Decorated Aluminum Foil with Improved Cycling Stability for Dual-Ion Batteries. *Carbon*. **2019**, *142*, 401–410.