

## Electronic Supplementary Information

### 1. Experimental section

#### 1.1 Preparation of $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$ powders

The powders of lithium sulfide ( $\text{Li}_2\text{S}$ , 99.98%, GanFeng Lithium Co., Ltd.), phosphorus pentasulfide ( $\text{P}_2\text{S}_5$ , 99%,  $\text{P} \geq 27\%$ , Shanghai Macklin Biochemical CO., LTD.), lithium chloride ( $\text{LiCl}$ , AR, 99%, Shanghai Aladdin Bio-Chem Technology Co., LTD.) were used as the starting material.  $\text{Li}_2\text{S}$  was pre-heated at 600 °C for 4 h and  $\text{LiCl}$  was pre-heated at 250 °C for 2 h. Then, 50 g precursor powder were weighted by the molar ratio of  $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$  and pulverized/mixed by a powder-mixing machine (DaDeYaoJi) at ultra-high speed of 25000 rpm, the mixing time is 25 s one time and the precursor powder was pulverized/mixed for 6 times. The as-prepared precursor powder was sintered in a quartz crucible with ground mouth at desired temperature for 16 h, and the heating rate is 3 °C/min, and the atmosphere of sintering is  $\text{N}_2$ -filled glovebox. After the temperature returned to room temperature, the  $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$  solid-state electrolyte (SSE) was pulverized by another powder-mixing machine and collected.

#### 1.2 Moisture exposure experiment and re-sintering

Fig. S1 exhibits the process of moisture exposure experiment, two 22 cm-diameter glass petri dishes and glass airtight bottle with 8 g  $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$  were transferred into a glovebox whose atmosphere was RH 1.2%-1.5%, and placed for one night. Then, SSE powder was transferred into two petri dishes and placed uniformly. After 1 h and 10 h, SSE powder was returned to the glass bottle and encapsulated by the cap. Finally, the moisture exposed  $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$  in glass bottles were moved back to  $\text{N}_2$ -filled glovebox to do further measurement and re-sintering. In case of the reaction between air and SSE is not uniform, when the glass bottles were moved back the glovebox, the caps were removed to release the residual air and the powders were well mixed again before use.

The re-sintering process is the same to the synthesis of  $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$  powder except the heating rate raises from 3 °C/min to 5 °C/min and the mass of air-exposed  $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$  powder is 4 g.

#### 1.3 Characterization

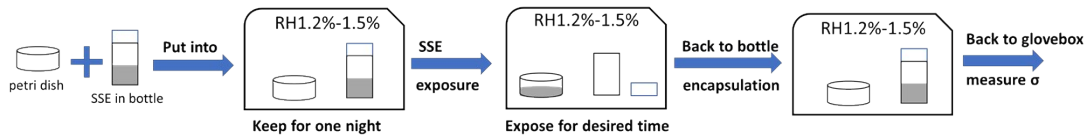
In case of moisture and oxygen reaction, X-ray diffraction (XRD) patterns were obtained by sealing the powders in a quartz substrate with a D 2.3 cm and H 0.1 cm hole in center, and the sealing material is double sides tape and 0.05mm thick polyimide (PI) film. The XRD (Bruker, D2) measurements parameters are Cu  $\text{K}\alpha$  radiation ( $\lambda=1.5418 \text{ \AA}$ ) and scan  $2\theta$  range of 10 ° to 70 °. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) is connected to an Ar-filled glovebox, and the samples are prepared in glovebox and directly transferred to XPS without any exposure to the ambient air.

#### 1.4 Electrochemical Testing

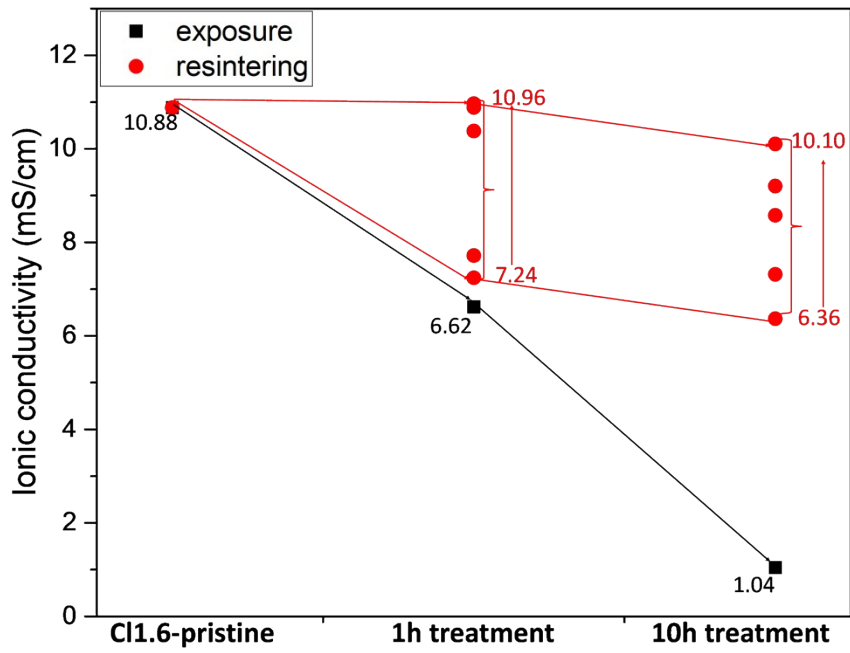
Impedance spectroscopy is employed to evaluate the ionic conductivity, the DC voltage of impedance is 0.2 V, the AC excitation amplitude is 20 mV, and the frequency range is 1 Hz to 1 M Hz. The process of impedance is as follow: 200 mg  $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$  powder was put into the 10 mm diameter cylinder hole of a 30 mm diameter  $\text{Al}_2\text{O}_3$  cylinder, then was pressed into pellet under a pressure of 1.25 tons, the thickness of the pellet was recorded to calculate the ionic/electronic conductivity later. Carbon-coated aluminum foil disks were attached to the both sides of SSE pellet as blocking electrode. During measurement, the pellet was pressed at 3-6 M Pa to guarantee the contact between SSE pellet and blocking electrode.

Before all solid-state lithium battery fabrication, the NCM811 cathode and graphite anode powders were heated at 120 °C for 2 h and 500 °C for 3 h, respectively. The weight ratio of cathode mixture and anode mixture are 7:3 (NCM811: SSE) and 6:4 (graphite: SSE). Both mixtures are prepared by a Thinky mixer ARE310, the mixing speed are 1000 rpm and mixing time are 10 min. Then, 100 mg SSE was pressed into pellet by using the above  $\text{Al}_2\text{O}_3$  cylinder at the pressure of 4 M Pa, 21 mg cathode mixture and 17 mg anode mixture were pressed at the two sides of SSE pellet at the pressure of 8 Pa and 12 M Pa, respectively. Finally, the ASSLBs were tested by the Neware battery cyclers at room temperature (25 °C -30 °C).

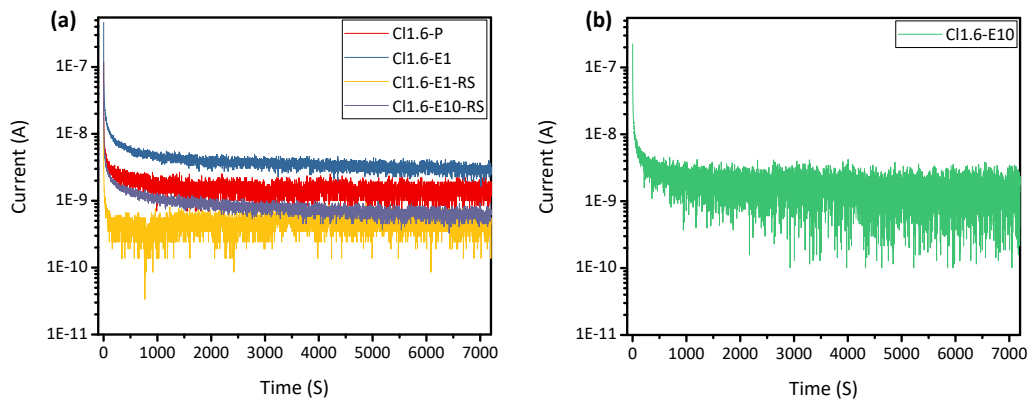
## 2. Supplementary Data



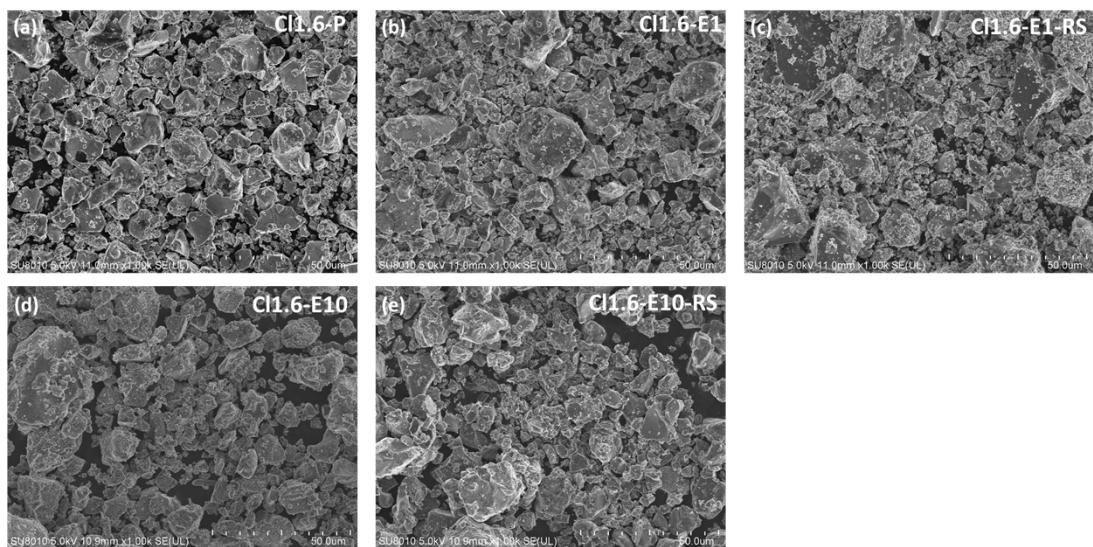
**Fig. S1.** Schematic diagram of the process for moisture exposure experiment.



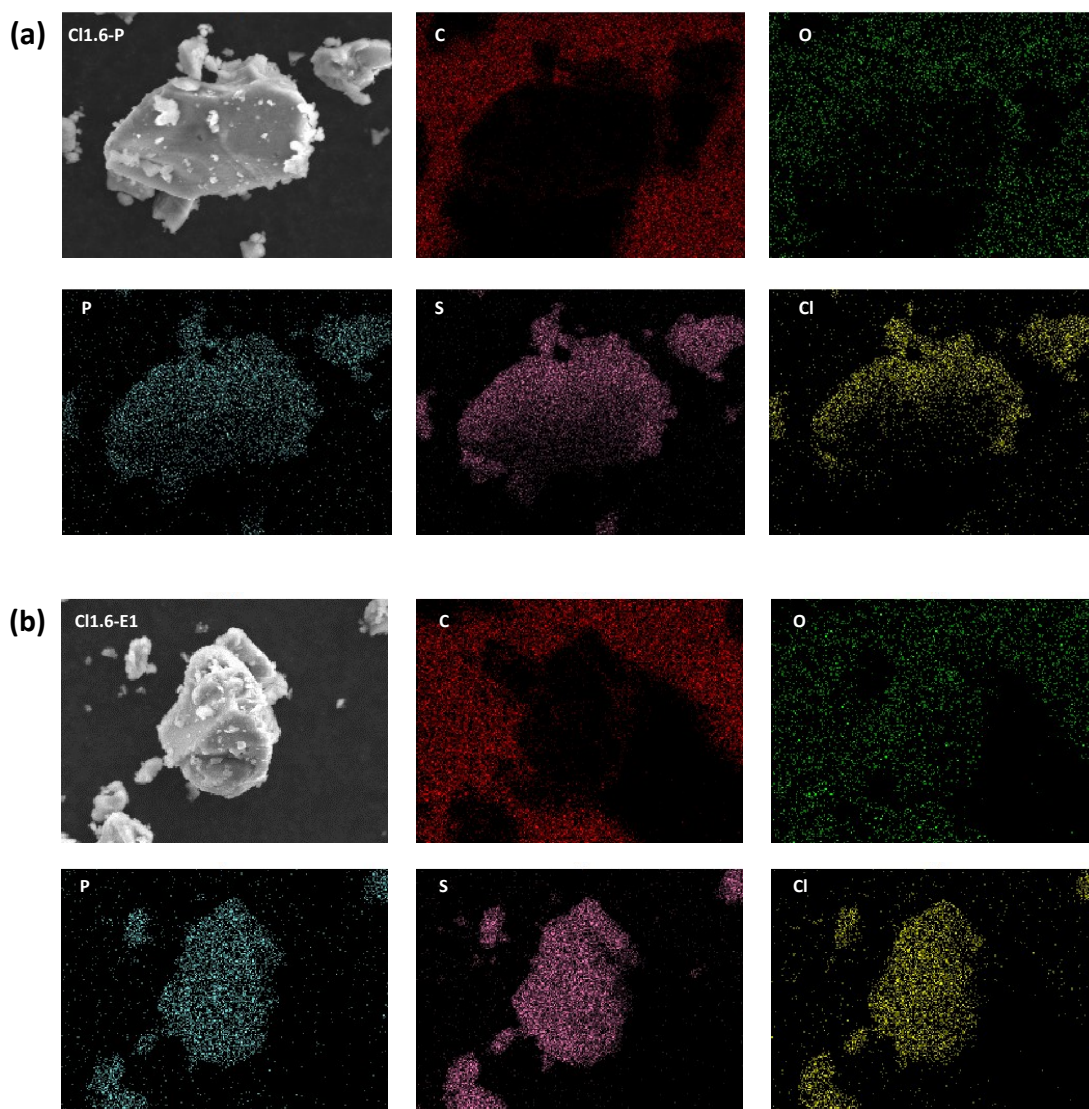
**Fig. S2.** Repeating the air-exposure and re-sintering experiments, and the mass for air-exposure and re-sintering experiments are 8 g and 1 g, respectively.

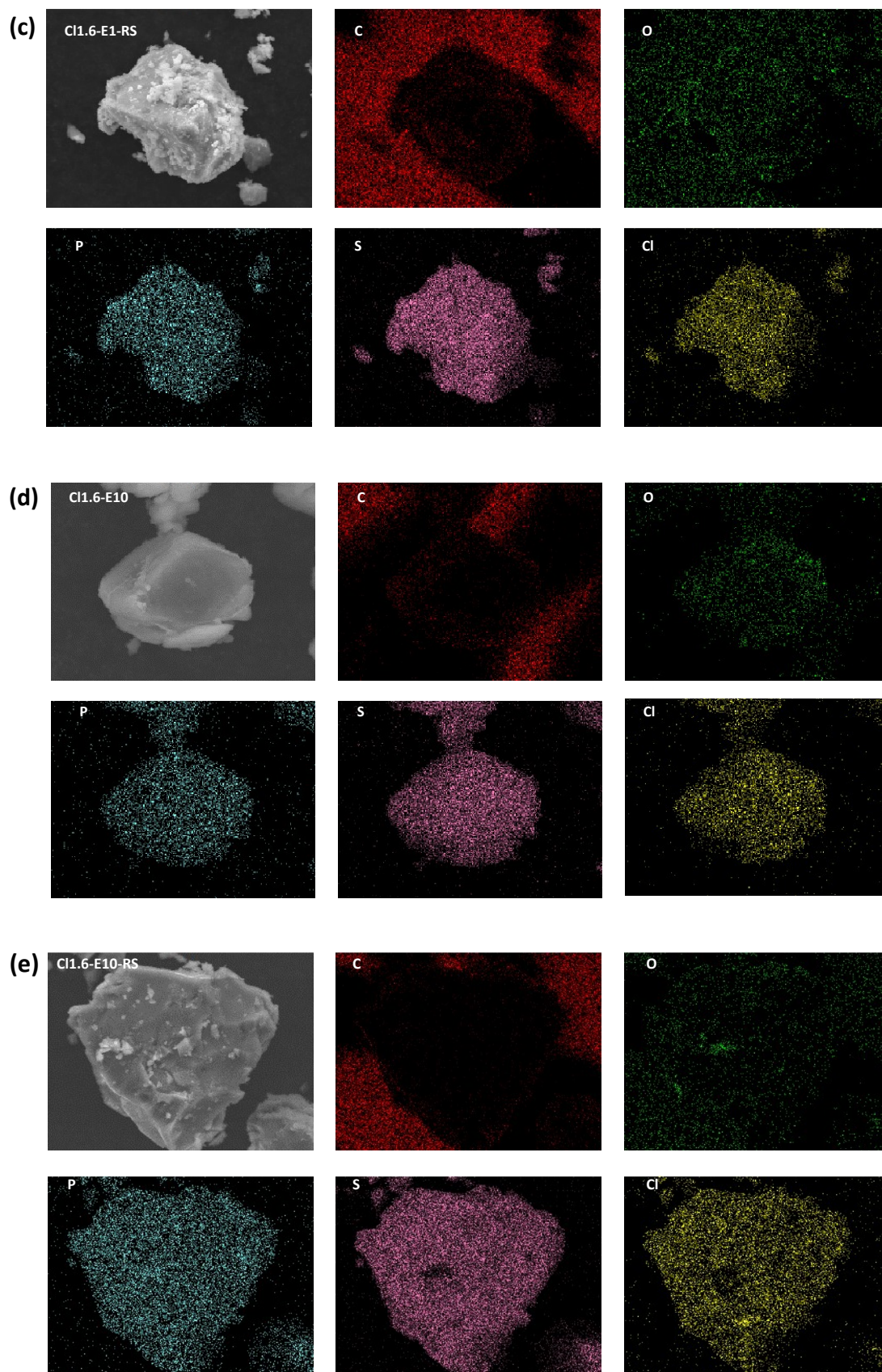


**Fig. S3.** The electronic conductivity evaluation for Cl1.6-P, Cl.16-E1, Cl1.6-E1-RS, Cl1.6-E10-RS (a) and Cl1.6-E10 (b), the DC bias is 0.4V and the testing time is 2h.

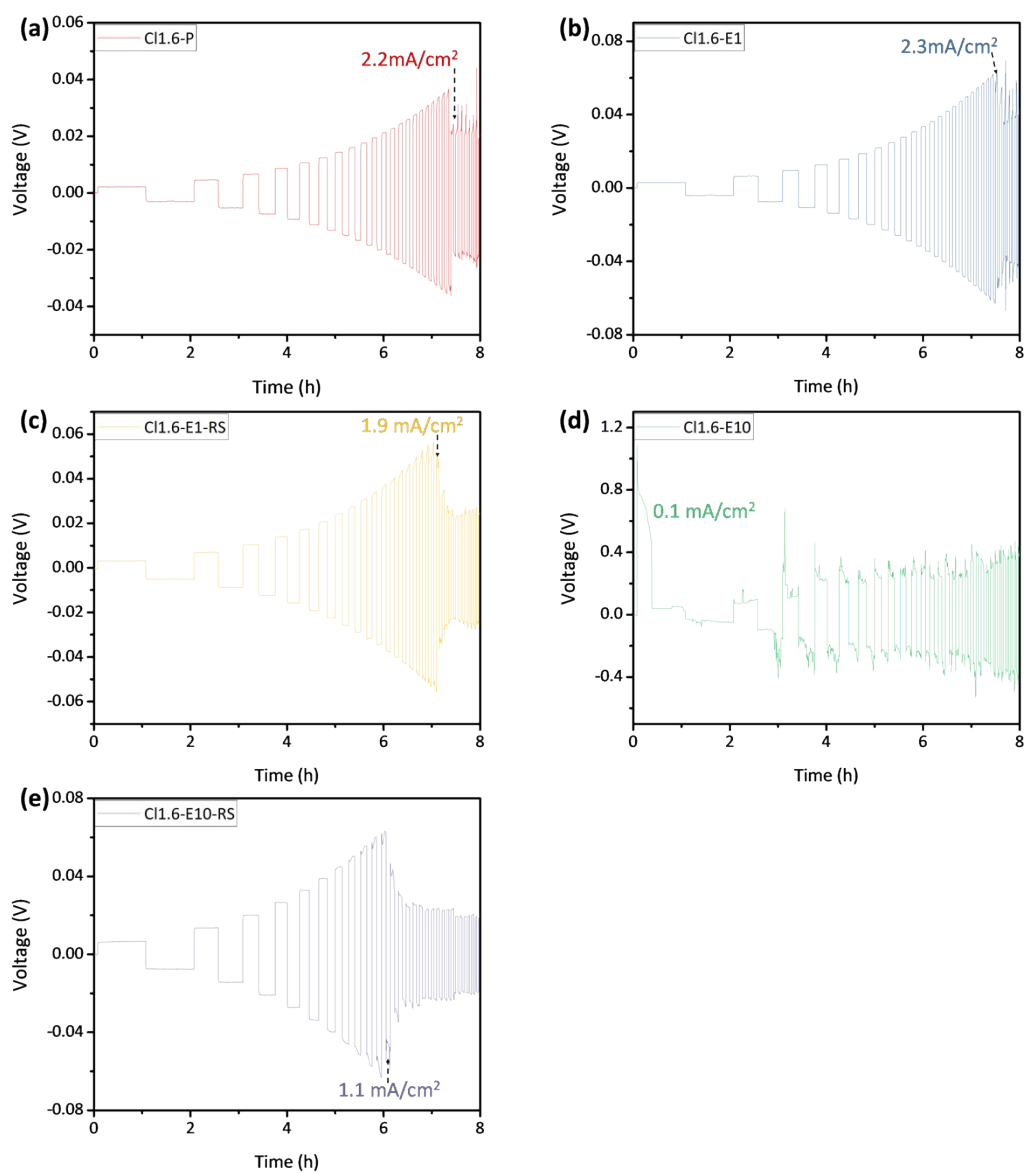


**Fig. S4.** SEM images of CI1.6 (a), CI1.6-E1 (b), CI1.6-E1-RS (c), CI1.6-E10 (d), CI1.6-E10-RS (e).

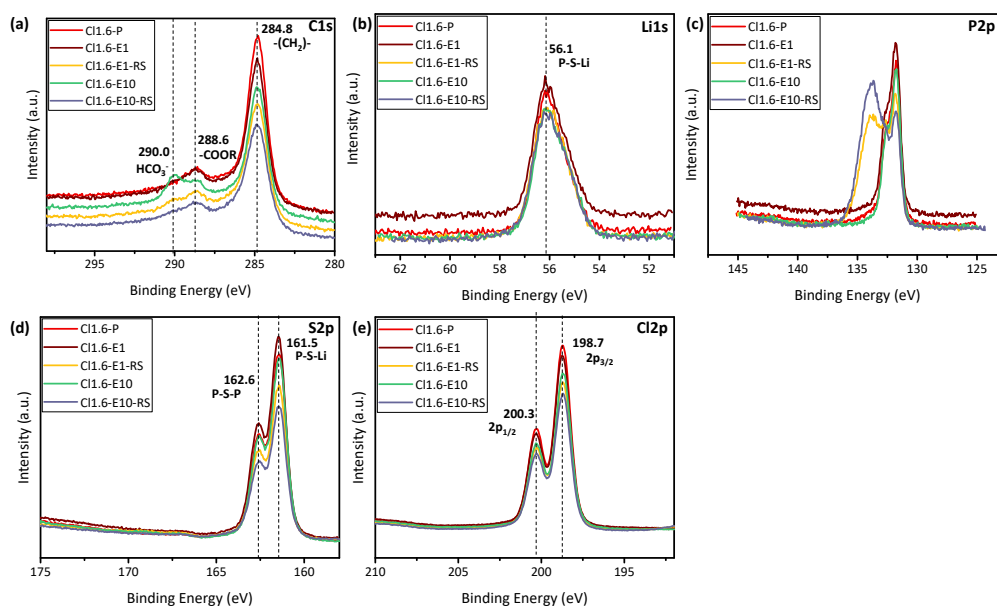




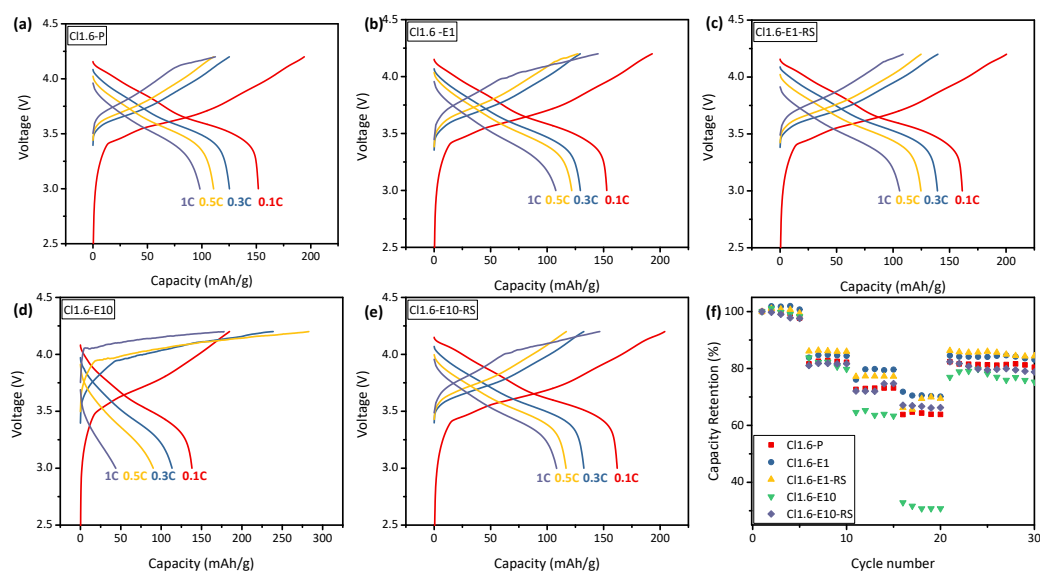
**Fig. S5.** EDS elemental mapping images of Cl1.6-P (a), Cl1.6-E1 (b), Cl1.6-E1-RS (c), Cl1.6-E10 (d), Cl1.6-E10-RS (e).



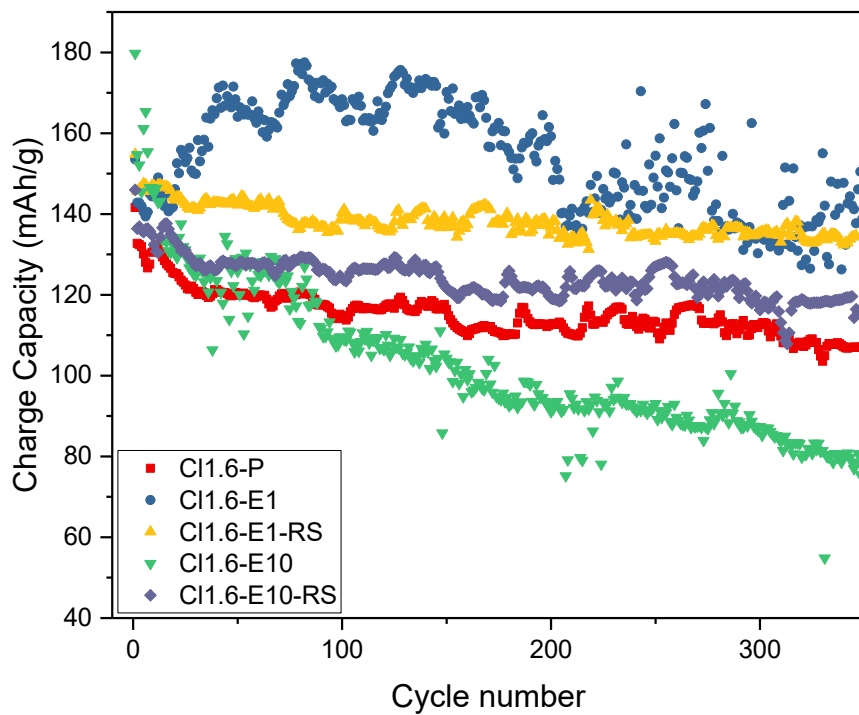
**Fig. S6.** galvanostatic cycling of Cl1.6-P (a), Cl1.6-E1 (b), Cl1.6-E1-RS (c), Cl1.6-E10 (d), Cl1.6-E10-RS (e). The critical current density of Cl1.6-P, Cl1.6-E1, Cl1.6-E1-RS, Cl1.6-E10 and Cl1.6-E10-RS are 2.2 mA/cm<sup>2</sup>, 2.3 mA/cm<sup>2</sup>, 1.9 mA/cm<sup>2</sup>, 0.1 mA/cm<sup>2</sup> and 1.1 mA/cm<sup>2</sup>.



**Fig. S7.** XPS spectra of C1s (a), Li1s (b), P2p (c), S2p (d), Cl2p (e) for the Cl1.6-P, Cl1.6-E1, Cl1.6-E1-RS, Cl1.6-E10, Cl1.6-E10-RS SSE powders.

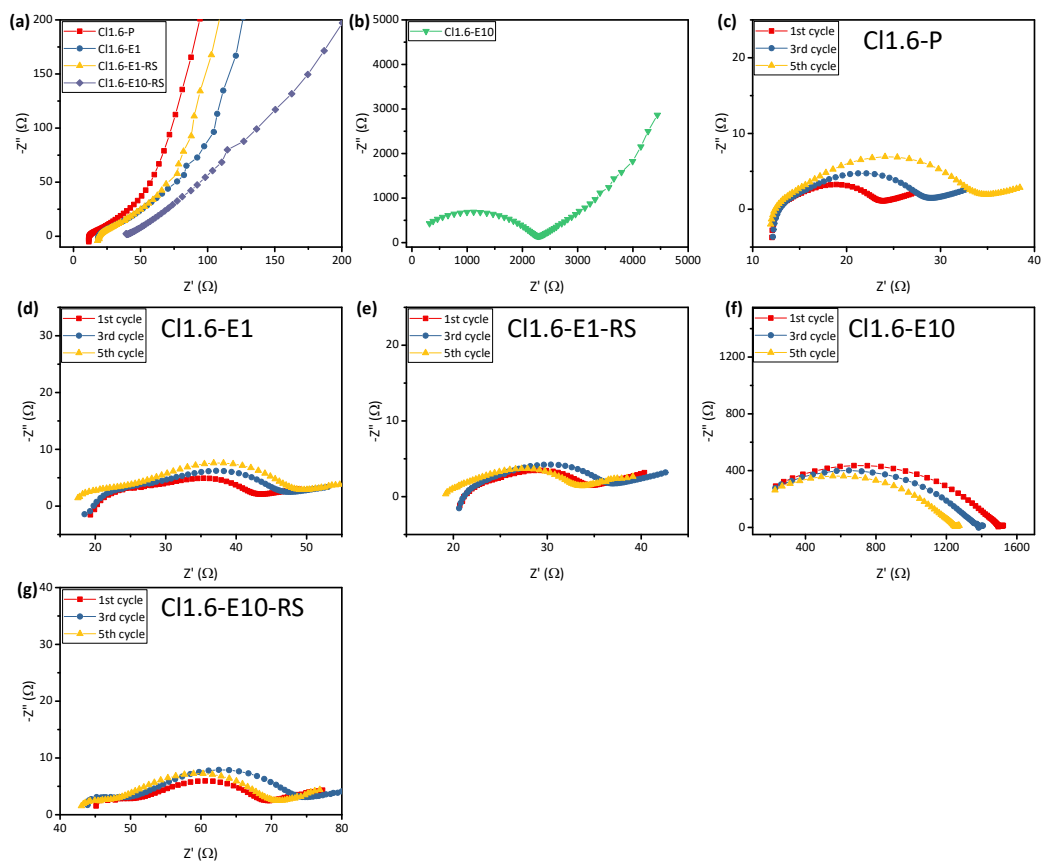


**Fig. S8.** Rate performance charge/discharge curve of the batteries which employed Cl1.6-P (a), Cl1.6-E1 (b), Cl1.6-E1-RS (c), Cl1.6-E10 (d), Cl1.6-E10-RS (e). And the curves for 0.1C, 0.3C, 0.5C, 1C are the 1<sup>st</sup>, 7<sup>th</sup>, 12<sup>th</sup>, 17<sup>th</sup> charge/discharge curves. (f) The rate performance of discharge capacity retention.



**Fig. S9.** The charge capacity of all the batteries, which shows the Cl1.6-E1 battery suffered from a low coulombic efficiency.





**Fig. S10.** The Nyquist plots of Cl1.6-P, Cl1.6-E1, Cl1.6-E1-RS, Cl1.6-E10-RS (a) and Cl1.6-E10 (b) before cycling, and the Nyquist plot of 1<sup>st</sup>, 3<sup>rd</sup>, 5<sup>th</sup> cycle of full charged to 4.2V for the NCM811/SSE/graphite ASSLBs using Cl1.6-P (c), Cl1.6-E1 (d), Cl1.6-E1-RS (e), Cl1.6-E10 (f) and Cl1.6-E10-RS (g). The cycling rate is 0.1 C.