Supporting Information

Integrated cathode and solid electrolyte via in situ polymerization with significantly reduced interface resistance

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Experimental materials and instruments

The involved reactants including Polyethylene glycol (diol) diacrylate (PEGDA, MW 1000), tetrakis (3-mercaptopropionic acid) pentaerythritolester (PETMP, 90%), trifluoroethyl methacrylate (TFEMA, 98%), bistrifluoromethanesulfonimide lithium salt (LITFSI, 99%), succinonitrile (SN, 99.7%), ethanol, N-Methylpyrrolidone (NMP, 99.5%), sodium Alginate (SA, AR 90%)，polyvinylidene fluoride (PVDF, HSV900), poly vinylidenefluoride-hexafluoro propylene (PVDF-HFP, MW 455000), and polyvinyl pyrrolidone (PVP k30, MW 58000) were purchased from MACKLIN (Shanghai China). Lithium Iron Phosphate (LFP) was purchased from Ternary Materials Network (Shanghai China). Kochenhei (ECP-600JD) was purchased from Guangdong Canrd New Energy Technology Co., Ltd (Guangdong China). Carbon nanotube (MWCNT) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd (Shanghai China).

The experimental instruments involved include UV curing machine (G-T21-200,220V 2000W), Beijing Expert company; Glove box (GP25S), Chengdu Delix Industrial Co., Ltd; Mini tape casting coater (MSK-AFA-HC100), Shenzhen Kejing Co., Ltd; Ultrasonic cleaning machine

(JP-020S), Shenzhen Jiemeng Cleaning Equipment Co., Ltd; Double potentiostat (CS2350H), Wuhan Coster Instrument Co., Ltd; Battery testing system (CT-ZWJ-4'S-T-1U), Shenzhen Neware Electronics Co., Ltd; Shanghai Hengfeng scientific drying box Co., Ltd. (BPA-90A); Tungsten filament scanning electron microscope (VEGA3 SBH); Fourier infrared spectrometer (Thermo Fisher Nicolet IS5).

Preparation of the ICSE

The light-cured ICSE was quickly transferred to a glove box filled with argon (H2O and O2 contents below 0.1 ppm) and cut into a piece with a diameter of 16mm. Using tweezers to polish the surface of lithium metal. The polished lithium sheet was pressed on the pole piece, and no liquid electrolyte was added to assemble the 2025 battery case. TSSB was produced by rapidly transferring light-cured TSSE to a glove box filled with argon gas, cutting it into a piece with the same diameter of 16mm. The TSSE film was assembled with a 15mm diameter cathode sheet, lithium metal, and a 2025 battery case to form a button battery (TSSB). Additionally, liquid lithium ion battery (LIB) with the LiFePO4 cathode and commercial liquid electrolyte was also assembled. The electrochemical test was carried out at a voltage of 2.5-3.85V at a rate of 0.1, 0.2, 0.5, 1C at 25°C. The impedance spectrum of the ICSE//Li battery was measured before and after cycling. The infrared spectrum (FTIR) of ICSE was tested before and after cycling.

Preparation of cathode sheet

The cathode is prepared by mixing $LiFePO_4$ (active substance, 73 wt%) ($LiFePO_4$ accounts for 75.8% after PVP is dissolved), kochenhei (conductive material, 10%), carbon nanotubes (conductive material, 3.3%), polyvinylpyrrolidone (PVP) (dispersant, 3.7%), and sodium alginate (binder, 10%) in deionized water, and mixing them on the planet. Then, the uniform cathode slurry was coated on the aluminum foil with a spatula, dried in the air, and then baked at 85℃ for 2 hours. The effective mass load of the cathode is 0.6-0.7mg/cm^2.

Preparation of pure solid electrolyte membrane

The mixed solution of PVDF, PVDF-HFP, and PVDF was coated on a glass plate with a scraper, and the solvent NMP was volatilized at 85℃. After being completely dried, the polymer film will fall off the glass plate after being soaked in ethanol for 12 hours (the ethanol will be changed every 3 hours). Immersing the porous polymer membrane from which the PVP has been wholly removed into the ethanol solution of UV curable monomer, the ethanol volatilizes slowly and completely at 65℃. Then the film was spread on a glass plate. The solution on both sides of the film was peeled off and then cured under a 2000W UV lamp for 1 min to obtain a pure solid electrolyte film (Fig. S 1).

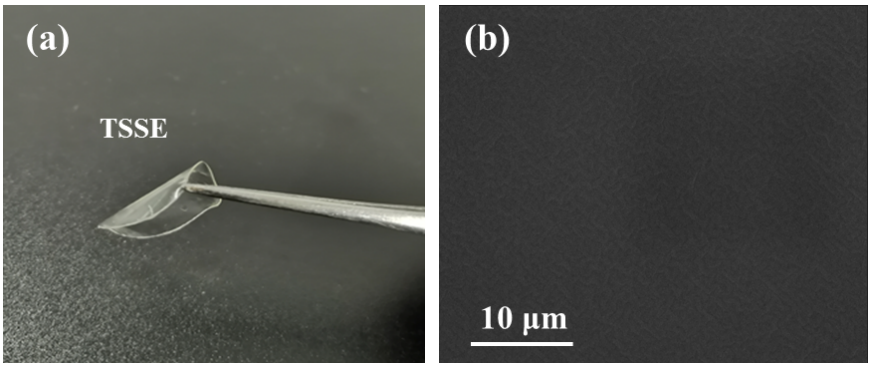

Fig. S1. (a) Photo of TSSE. (b) SEM images of TSSE surface.

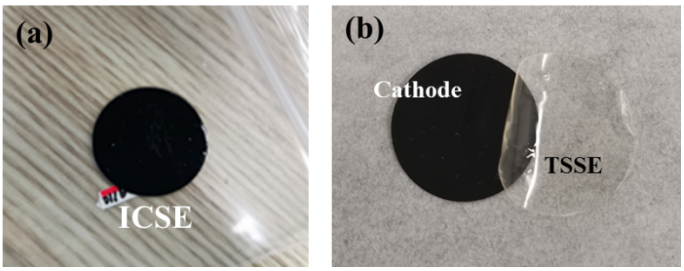

Fig. S2. (a) Photo of ICSE. (b) Photo of TSSE and cathode.

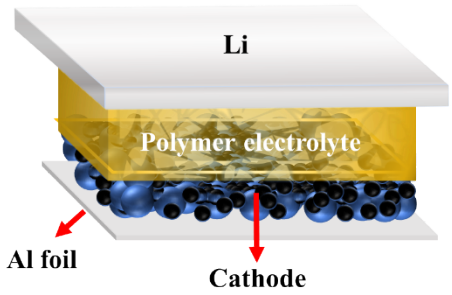

Fig. S3. Schematic diagram of TSSB

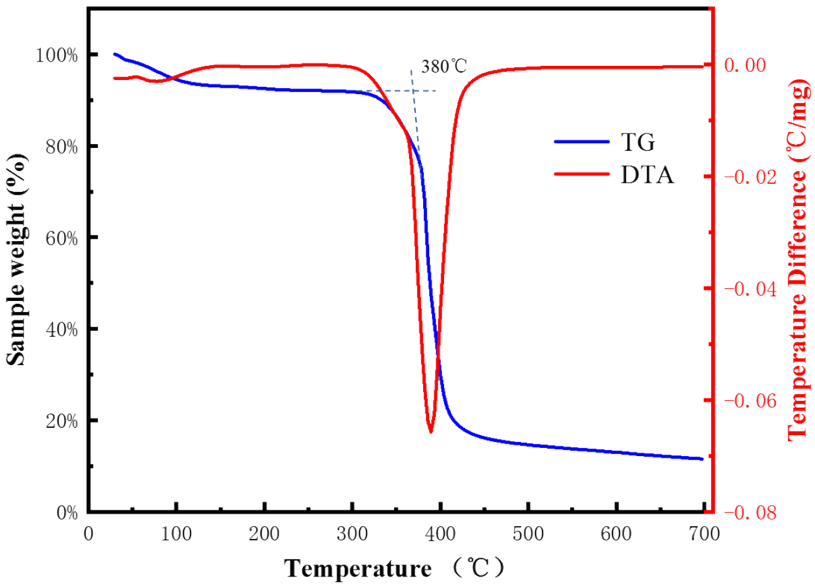

Fig. S4. The thermogravimetric (TG) curve and differential thermal analysis (DTA) curve of TSSE.

ICSE/Li Characterizations

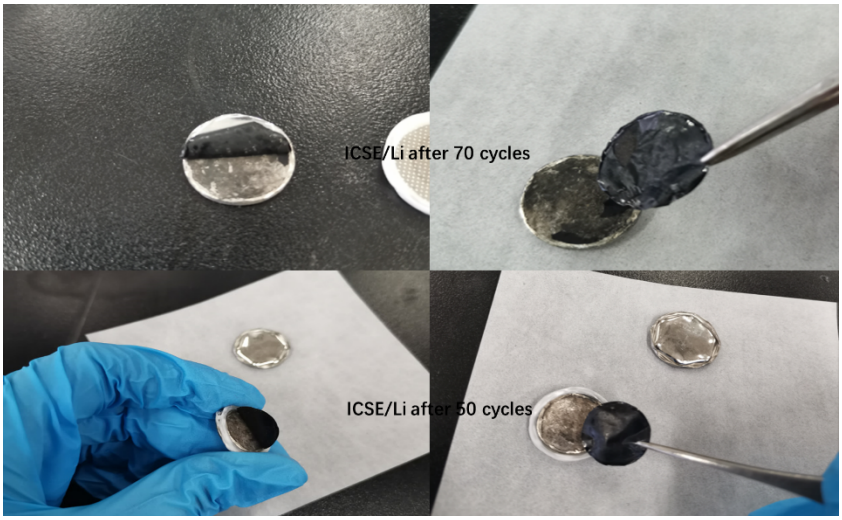

Fig. S5. Photos after 70 and 50 cycles of ICSE/Li. Lithium metal and ICSE maintain close contact after multiple cycles.

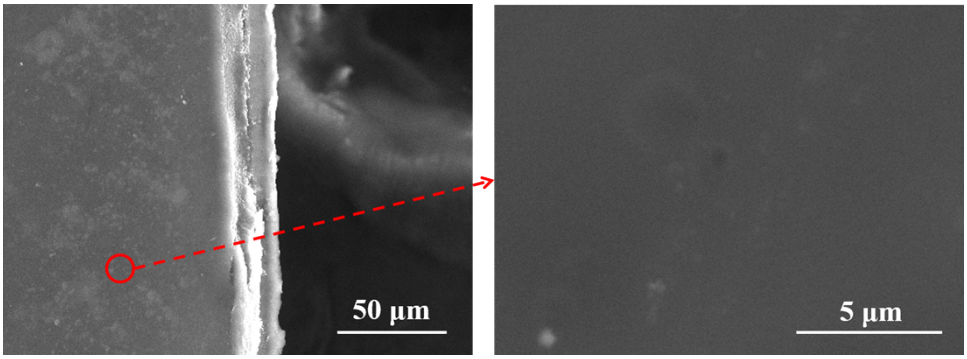

Fig. S6. SEM image of ICSE / Li after 200 cycles at 0.5C current.

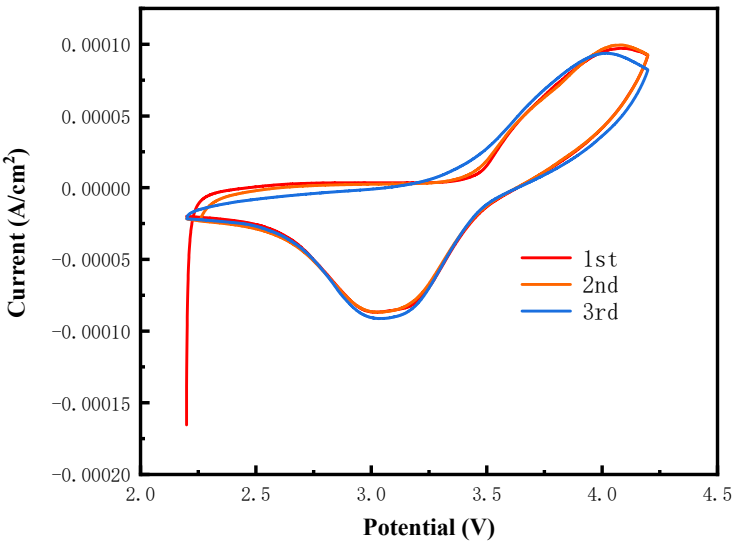

Fig. S7. Linear cyclic voltammetry curve of ICSE/Li. The scanning range is 2.2-4.2V, the scanning speed is 5mV/S.

Electrochemical stability of solid electrolyte membrane (TSSE)

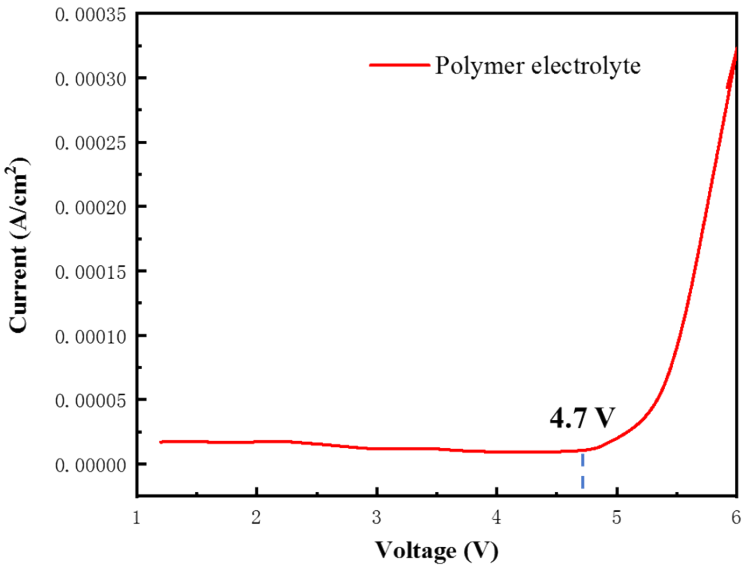

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Fig. S8. Linear sweep volt-ampere (LSV) curve of TSSE at 25℃. The scanning range is 1.2-6 V and the scanning speed is 5 mV/s.

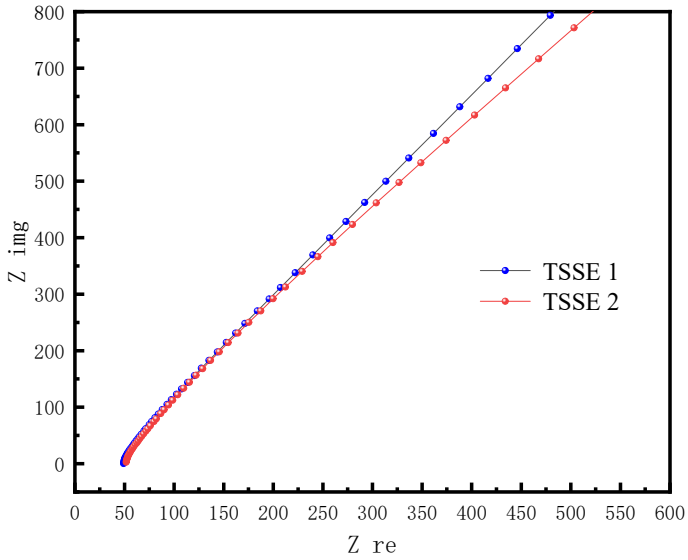

Fig. S9. Nyquist plot of SS/TSSE/SS at 25℃.

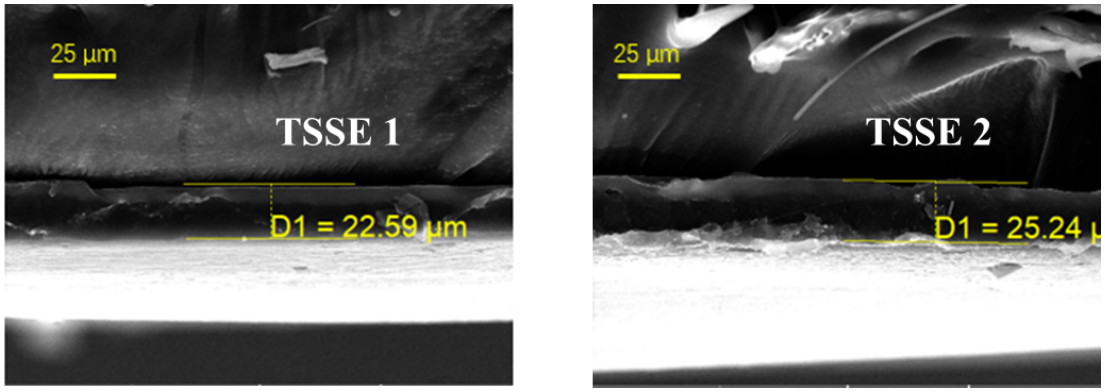

Fig. S10. The SEM image of TSSE.

The conductivity of the polymer electrolyte is calculated by formula (1-1):

$$\sigma = L/(RS) \quad (1\text{-}1)$$

In formula (1-1), σ represents the conductivity of the polymer electrolyte (S cm^{-1}), R is the impedance (Ω) of the obtained electrolyte, L represents the thickness of the electrolyte (cm), and S represents the test area of the electrolyte (cm^2). The calculated ion conductivity of TSSE at room temperature is about 2.5×10^{-5} S cm^{-1}.

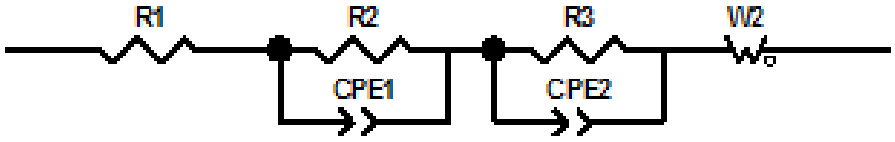

Fig. S11. Schematic diagram of equivalent circuit model for EIS spectrum fitting.

	R1(Ω)	Error (%)	**R2(Ω)**	Error (%)	**R3(Ω)**	Error (%)
ICSE/Li before the cycle	**63.49**	14.035	**85.98**	8.2508	**968.7**	1.4012
ICSE/Li after 150 cycles	**138.8**	0.65808	**37.38**	7.4567	**1101**	7.8381
TSSB before the cycle	**155.3**	0.99382	**189.9**	10.204	**1901**	2.2334
TSSB after 150 cycles	**172.2**	4.627	**23.43**	18.666	**1422**	0.60278

Table. S1. Nyquist impedance spectrum fitting results.

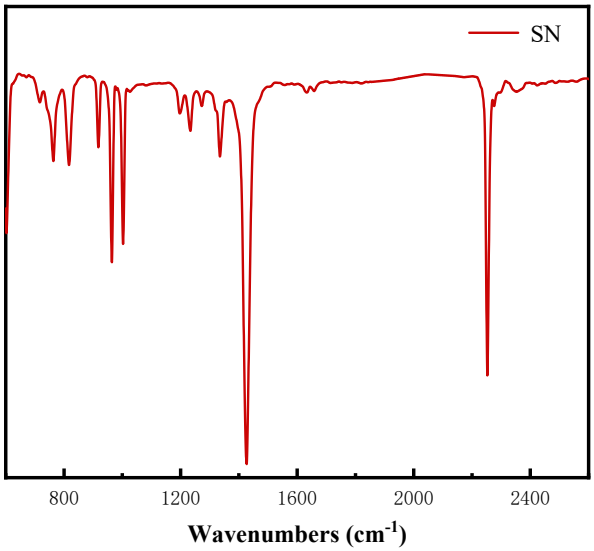

Fig. S12. FTIR spectra of SN

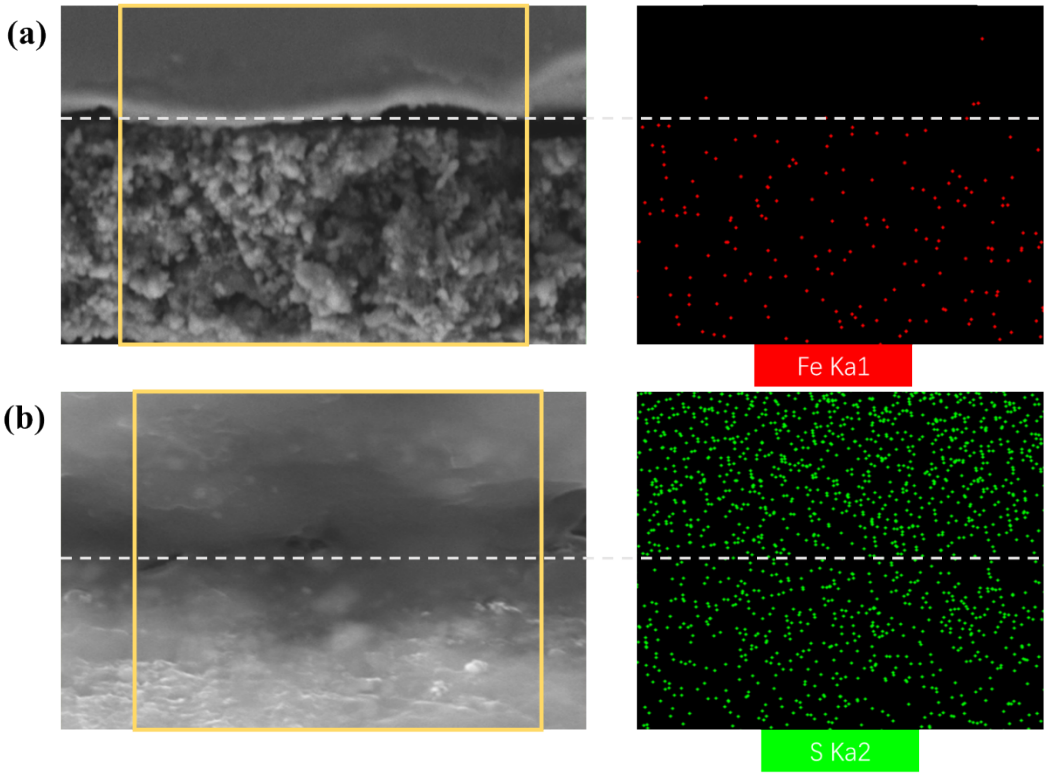

Fig. S13. (a) EDS maps of Fe in TSSB. (b) EDS maps of S in ICSE.

Element Fe belongs to $LiFePO_4$ cathode and element S belongs to lithium salt in electrolyte (LITFSI).

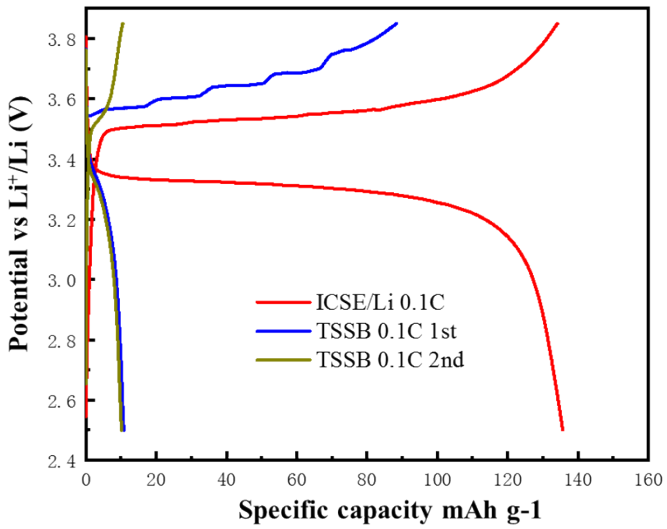

Fig. S14. ICSE / Li and TSSB charge discharge curves at room temperature with higher cathode load (ICSE 1.345mg/cm^2; TSSB 1.32mg/cm^2).

The discharge capacity of ICSE/Li at 0.1C current is 137mAh/g. The first charging capacity of TSSB reaches 90mAh/g, but the discharge capacity is only 11mAh/g.

Electrochemical performance of liquid lithium ion battery (LIB)

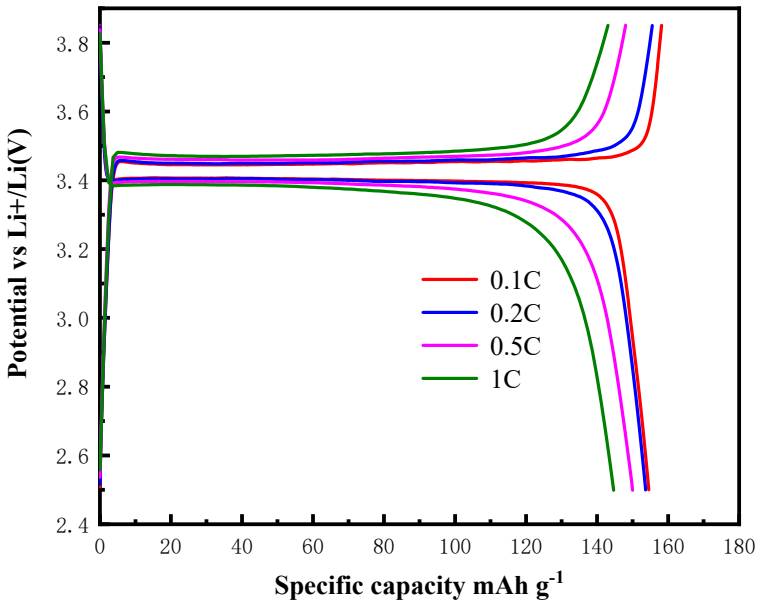

Fig. S15. Galvanostatic charge-discharge curves of a liquid LIB tested at 25℃.

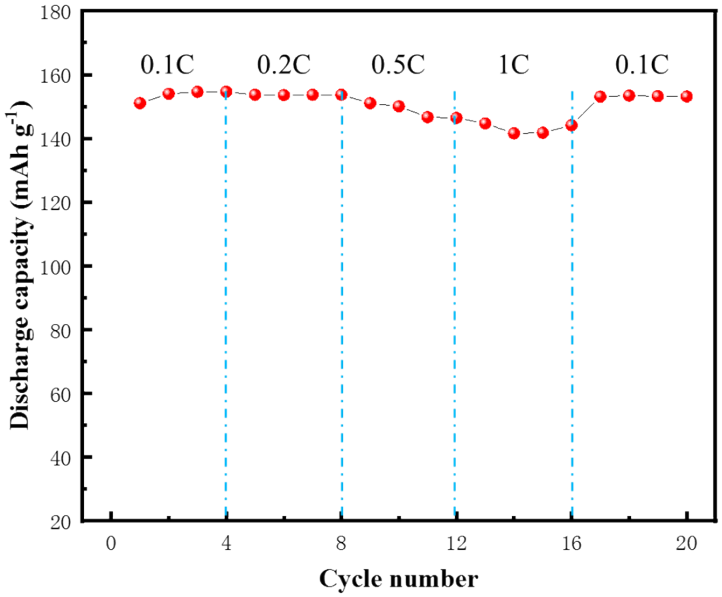

Fig. S16. Discharge capacities of a liquid LIB tested at 25°C.