Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary information

Towards Reliable Li-metal-free $LiNO_3$-free Li-ion Polysulphide Full Cell via Parallel Interface Engineering

Ju Sun[a], Jiaxing Liang[a], Junnan Liu[b], Wenyan Shi[a], Neeraj Sharma[b], Wei Lv[c], Ruitao Lv[d, e], Quan-Hong Yang[f], Rose Amal[a], Da-Wei Wang[a*]

[a]Particles and Catalysis Research Group, School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

[b] School of Chemistry, The University of New South Wales, Sydney, NSW 2052, Australia

[c] Shenzhen Key Laboratory for Graphene-based materials and Engineering Laboratory for Functionalized Carbon Materials, Graduate School at Shenzhen, Tsinghua University, Shenzhen, 518055, China

[d] State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

[e] Key Laboratory of Advanced Materials (MOE), School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

[f] Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin, 300072, China

Corresponding author. Tel.: +61-2-9385-7355; e-mail: da-wei.wang@unsw.edu.au

Calculation of electron balance for Li-ion polysulphides full cell

Quantity of electrons at anode:

$$Q = I * t * \eta = 0.24\ mA * 7\ h * 75\ \% = 4.54\ C$$

I is the applied current; t means the alloy time; η represents the first Coulombic efficiency of alloy/de-alloy process.

Number of electrons at anode:

$$\mathrm{n} = \frac{Q}{q * N} = \frac{4.54\ C}{1.6 * 10^{-19} * 6.02 * 10^{23}} = 47.13\ \mu mol$$

According to the reaction at the cathode:

$Li_2S_4 + 6\ e^- + 6\ Li^+ \rightarrow 4\ Li_2S$

The polysulphides catholyte is 12 μL, 0.25 M Li_2S_4.

Therefore, the electrons needed for cathode reaction is 0.25 M *12 μL * 6 = 18 μmol.

The amount of electrons at anode (47.13 μmol) is around two times higher than that at the cathode (18 μmol), with a Li utilization of 38%. In most Li-S half cells, the mass of commercial Li chip is 30 to 40 mg, corresponding to >4 mmol Li. The Li utilization for commercial Li chip is less than 5%.

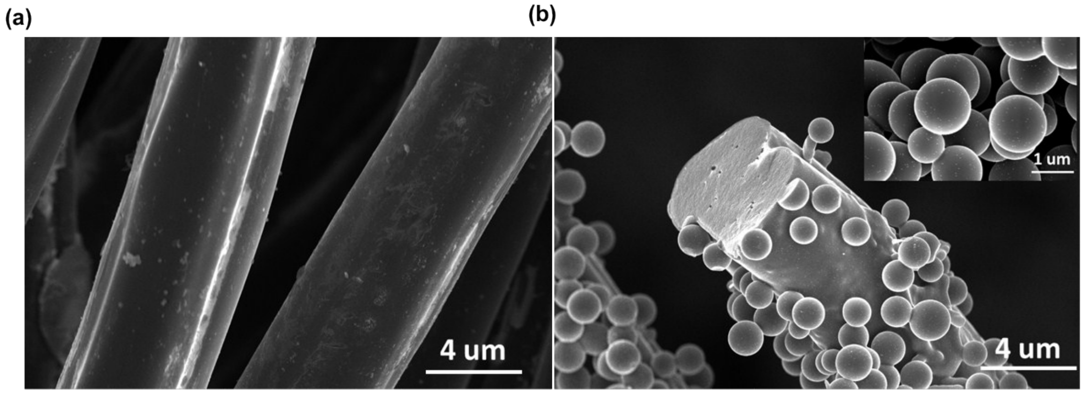

Fig. S1 SEM images of (a) CC and (b) HTC-CC, (insert is the high magnification picture of HTC)

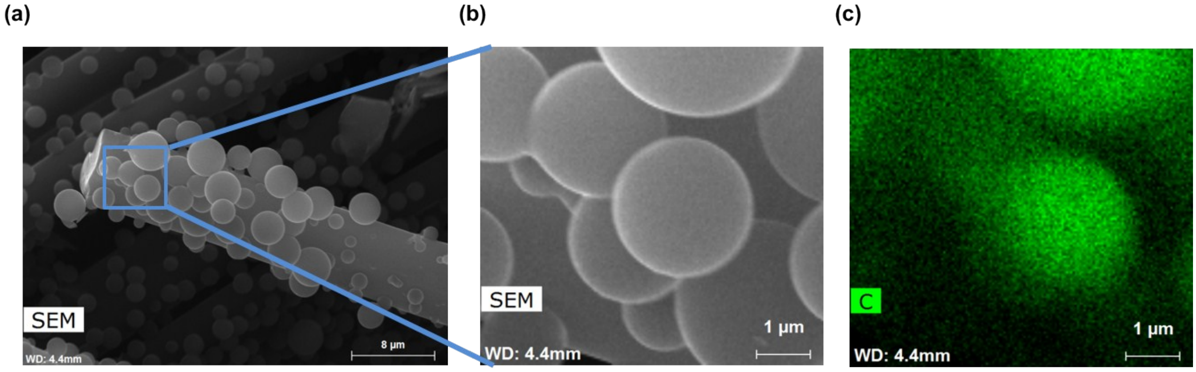

Fig. S2 SEM images of (a) HTC-CC, (b) enlarge SEM of HTC, (c) EDX of carbon element

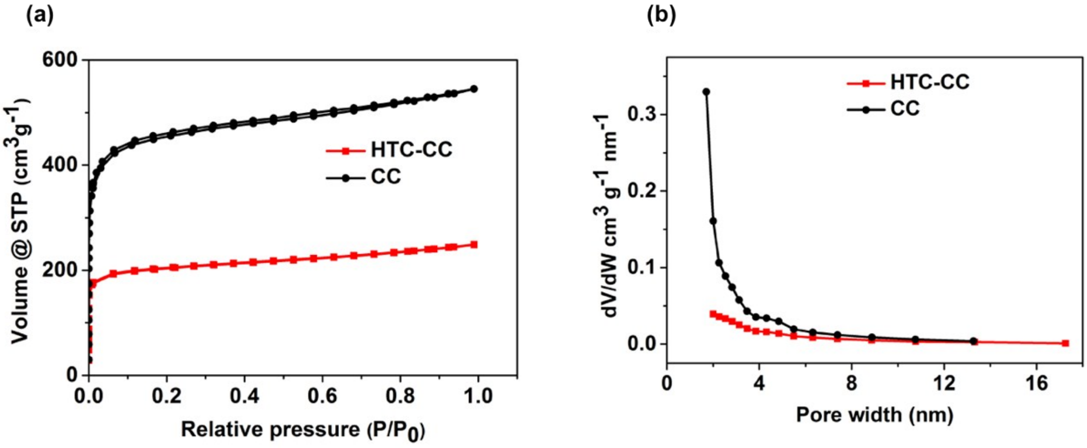

Fig. S3 (a) N_2 isothermal adsorption-desorption and (b) pore-size distribution of CC and HTC-CC current collectors

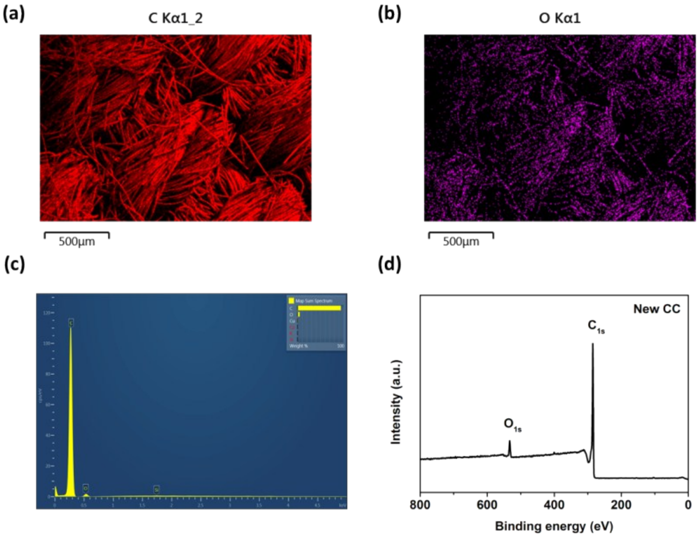

Fig. S4 (a, b) EDS element mapping of the new Kynol CC surface, (c) EDS spectrum of new CC; (d) XPS full spectra of new CC

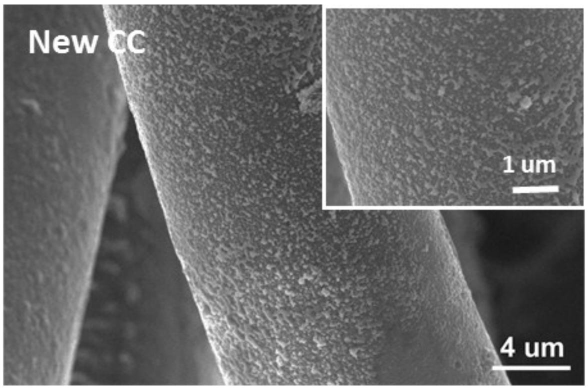

Fig. S5 SEM images of the Li_2S deposits on new Kynol CC surfaces after full discharge; inset is the corresponding high-magnification image

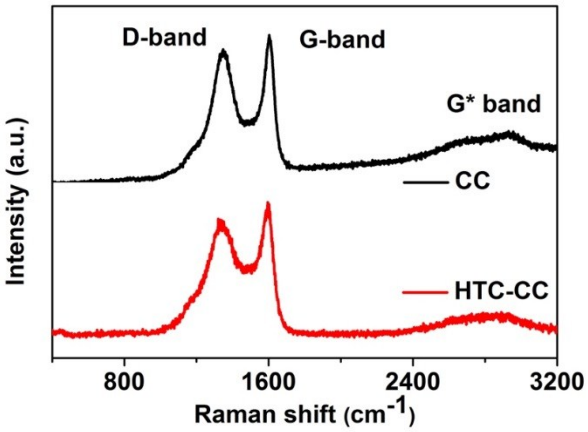

Fig. S6 Raman spectra of CC and HTC-CC current collectors

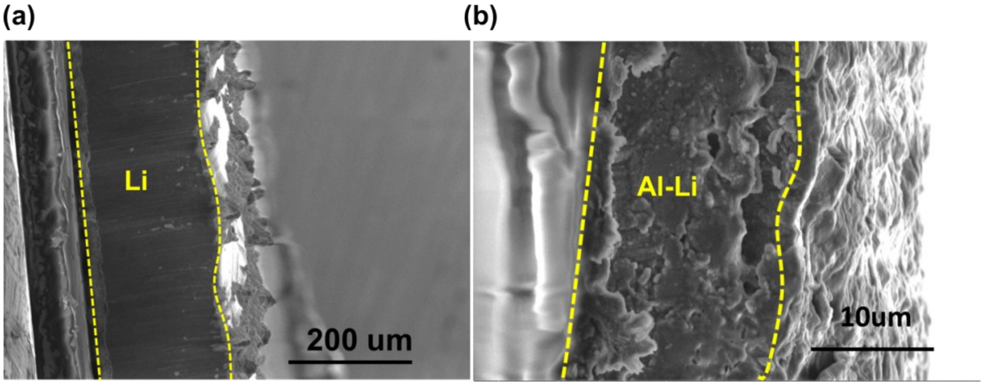

Fig. S7 Cross-sectional SEM images of fresh (a) Li metal; (b) Al-Li alloy

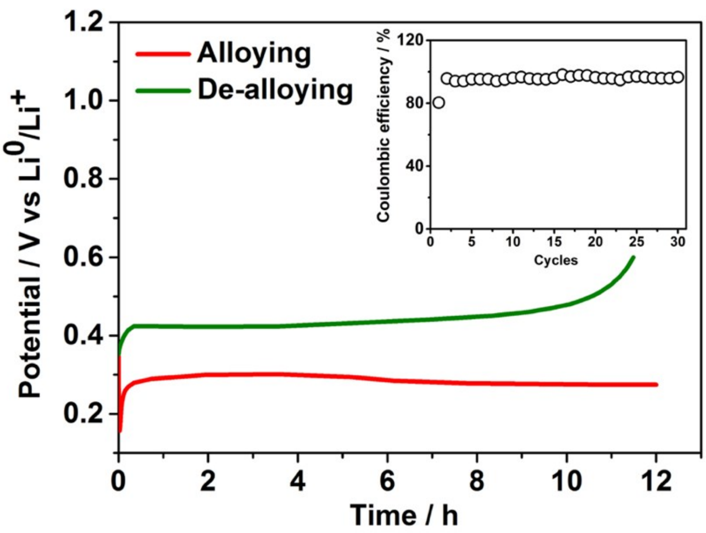

Fig. S8 The charge-discharge curve of Al-Li half-cell in 1M $LiPF_6$ + EC/EMC electrolyte; insert is Coulombic efficiency of alloying/de-alloying reactions

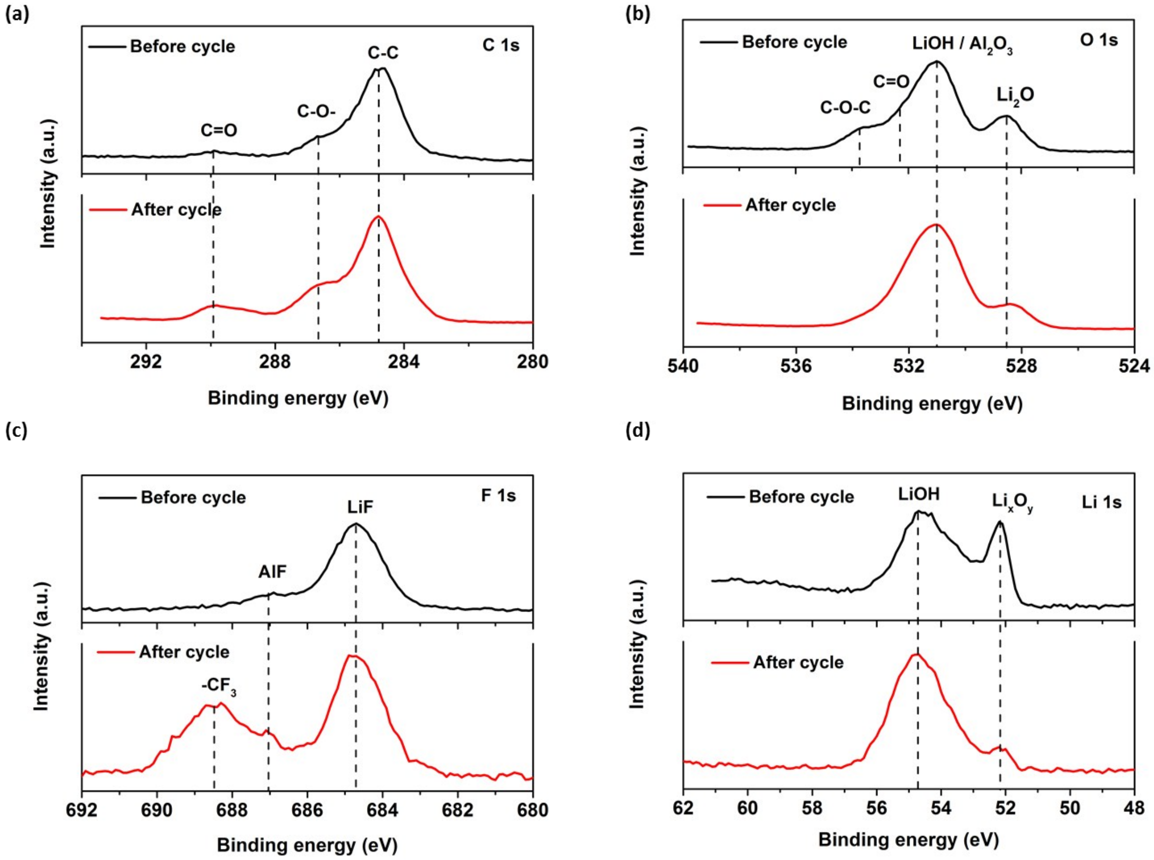

Fig. S9 XPS spectra of SEI component on the surface of Al-Li alloy prepared in $LiPF_6$+EC/EMC solvent and cycled in LiTFSI+TEGDME solvent, (a) C 1s, (b) O 1s, (c) F 1s and (d) Li 1s.

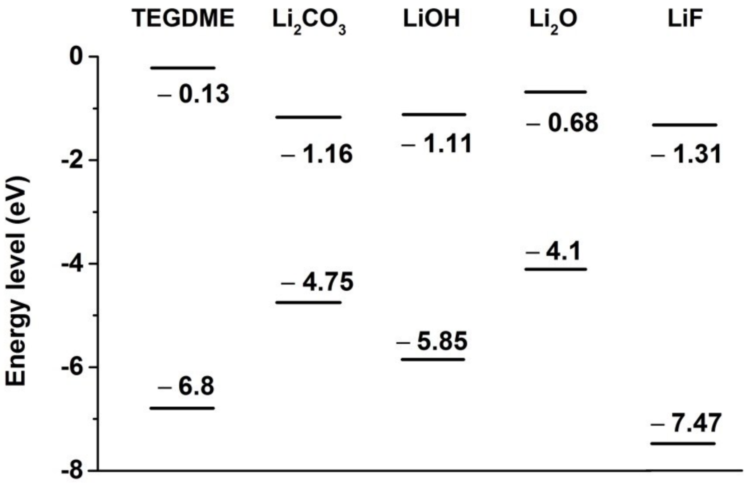

Fig. S10. HOMO and LUMO levels of SEI composition and electrolyte solvent

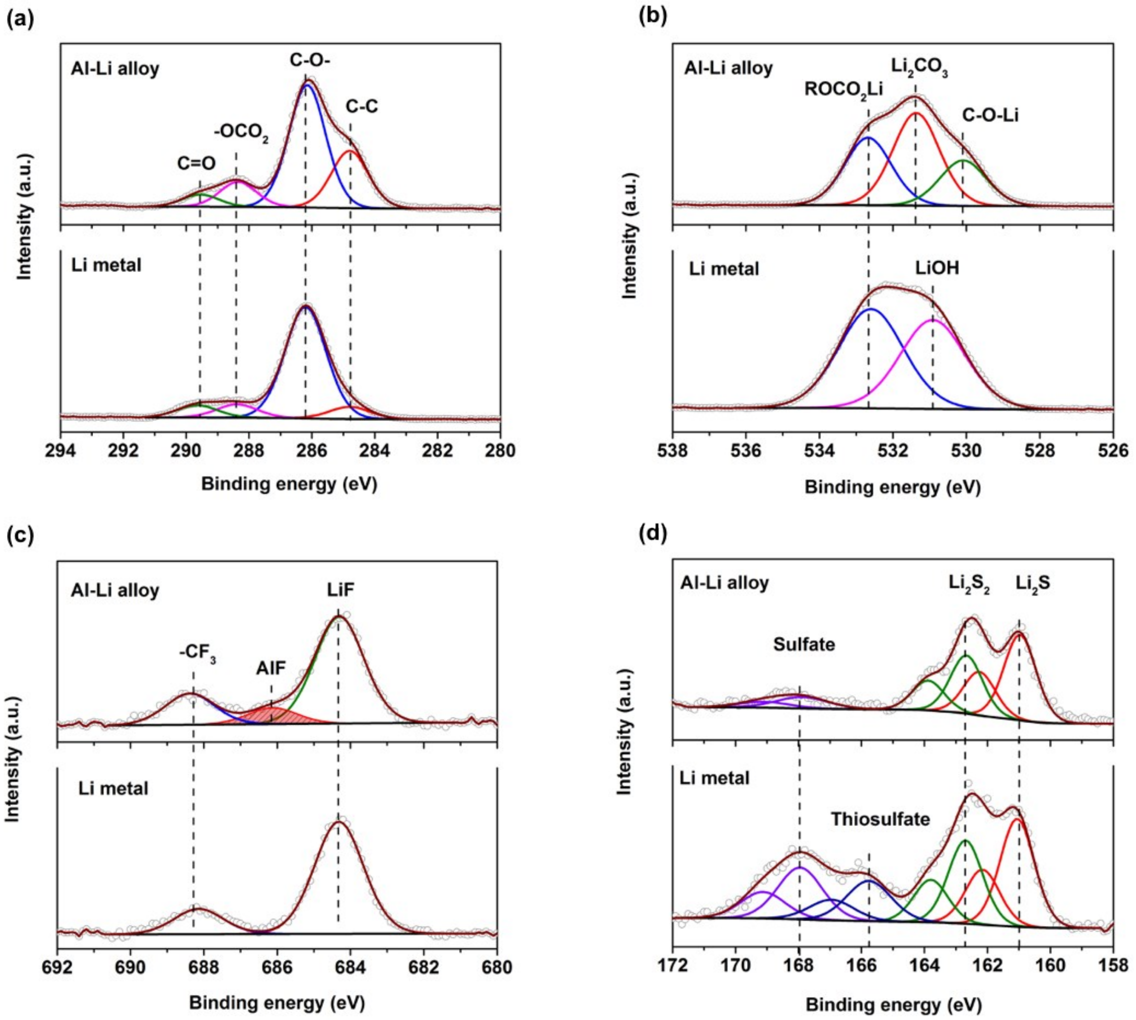

Fig. S11 The XPS profiles of the soaked surfaces of Li metal and Al-Li alloy (a) C 1s; (b) O 1s; (c) F 1s and (d) S 2p

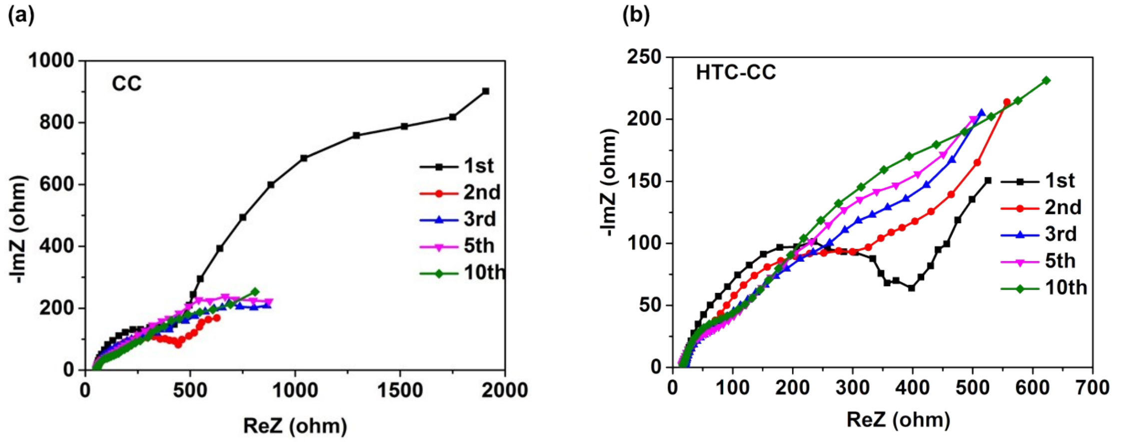

Fig. S12 EIS data of HTC-CC and CC current collector after 1st, 2nd, 3rd, 5th and 10th cycle of discharge state at 0.1 C

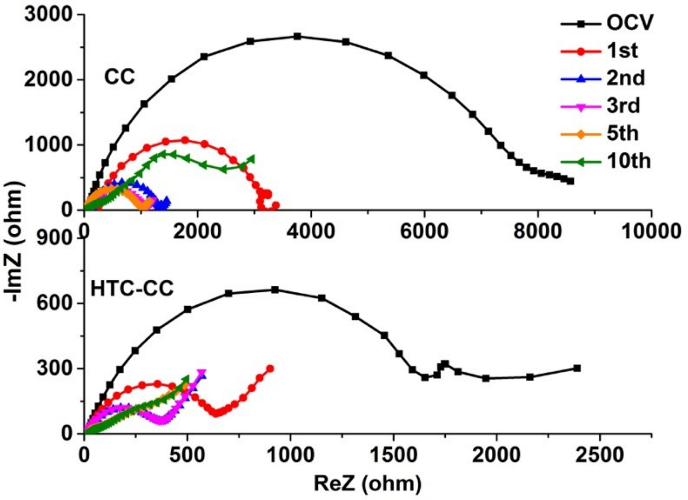

Fig. S13 EIS data of HTC-CC and CC current collector after 1st, 2nd, 3rd, 5th and 10th cycle of charge state at 0.1 C

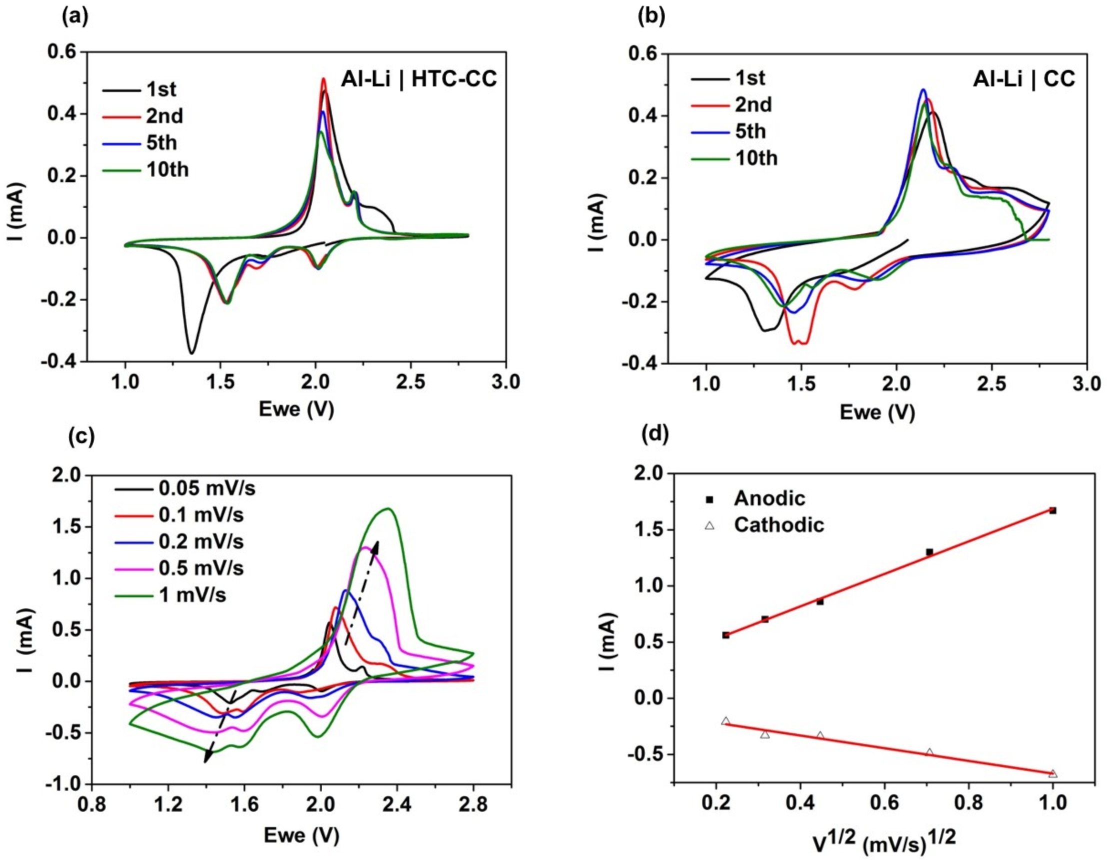

Fig. S14 Typical CV test of (a) Al-Li | HTC-CC and (b) Al-Li | CC full cell with Li_2S_4 catholyte at scan rate of 0.1 mV s^{-1}; (c) CVs at different scan rate of Al-Li | HTC-CC cell; (d) relationships between cathodic/anodic peak currents and scan rates from (c)