*Electronic Supplementary Information for*

# Soluble Single Atom Catalyst Promotes Lithium Polysulfides Conversion in Lithium Sulfur Batteries

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**Experimental Details**

*Synthesis of the catalyst*

CoPcCl were synthesized according to literature reports. [1] Tetrachlophthalonitrile and CoCl$_2$ were dissolved in 1,2−dichlorobenzene with a molar ratio of 4:1. The mixture was heated at 200 °C for 12 hours under stirring. Then, diethyl ether was added to reaction mixture followed by shaking. The resulting solid was filtered and washed with diethyl ether. CoPc was purchased from Aladdin and used as contrast sample.

*Preparation of the electrolyte*

Lithium bis(trifluoromethane−sulfonyl)imide (1.0 M, LiTFSI) and lithium nitrate (0.1 M, LiNO$_3$) dissolved in a mixed solvent of 1,3−dioxolane (DOL) and 1,2−dimethoxyethane (DME) (1:2 by volume) were used as standard electrolyte (donated as STD). The additive of CoPcCl and CoPc were added to the standard electrolyte in amounts of 0.1 wt%, and labeled as STD−CoPcCl and STD−CoPc, respectively. In addition, the liquid supernatant of the electrolytes were gathered after stirring and standing. The actual content of the additives in the electrolyte is less than 0.1 wt% because of the low solubility of phthalocyanine complexes. The electrolytes were prepared in an Ar−filled glovebox, in which H$_2$O and O$_2$ concentrations were controlled to be less than 0.1 ppm.

*Assembly of lithium sulfur batteries*

The sublimed sulfur, polyvinylidene fluoride (PVDF) binder and conductive agent of carbon nanotubes (CNTs slurry with a solid content of 5%) were mixed by a mass ratio of 60:10:30 in NMP. The mixture was ball milled at a rate of 900 rpm for 10 h. And then the homogeneous mixture was blade cast onto aluminum foil and dried at 60 °C for 12 h in a vacuum oven. The electrode disks with a diameter of 12 mm and an average sulfur loading amount of 1.16 mg cm$^{-2}$ were used. The thickness of the electrode

was controlled at 13.3 μm, as shown in Figure S1. CR2032 type coin cells were fabricated in an argon filled glove box which the $H_2O$ and $O_2$ content were controlled below 0.1 ppm. Lithium foil was used as the anode. 40 μL of the prepared electrolytes were used in each cell.

*Assembly of the Li$_2$S$_6$ symmetric cells*

CNTs and PVDF were mixed by a mass ratio of 9:1 in NMP to prepare the working electrode and counter electrode. The symmetric cells were assembled with $Li_2S_6$ contained electrolyte and the as prepared electrolytes. 30 μL 50 mM $Li_2S_6$ contained and 30 μL as prepared electrolytes were added into each coin cell.

*Nucleation and Precipitation of Li$_2$S*

CNTs and PVDF derived electrode was used as working electrode and Li foil was used as counter electrode. 40 μL 50 mM $Li_2S_6$ contained and 20 μL as prepared electrolytes were dropped on the cathode side and then 20 μL as prepared electrolytes were added in the anode side. For the nucleation of $Li_2S$, the cells were firstly galvanostatically discharged at 0.112 mA to 2.08V and then kept at 2.07V until the current was below $10^{-5}$ A. According to Faraday's law, the whole charge was gathered to evaluate the nucleation/growth rate of $Li_2S$ CNTs substrate. [2, 3]

*Quantitative analysis of CoPcCl*

The CoPcCl solubility in the electrolyte were analyzed using inductively coupled plasma optical emission spectrometry (ICP−OES, iCAP 7600 ICP−OES, ThemoFisher). 2 mL of the STD−CoPcCl electrolyte were dissolved in the mixed solution of concentrated nitric acid and hydrochloric acid (Guarantee reagent; Sinopharm Chemical Reagent Co., Ltd.) and diluted with di−deionized water to 100 mL. A cycled battery was disassembled and washed by DME in several times (with a total DME amount of 10 mL) in glove box in order to analyze the content of CoPcCl in the long term cycled

batteries. After that, the mixed acid solution was added to the DME solution and diluted to 50 mL. As contrast, 40 µL STD−CoPcCl electrolytes were used to confirm the CoPcCl content in fresh cells.

*Electrochemical measurements*

The galvanostatic charge/discharge tests were carried out on a Land CT2001A (Wuhan, China) battery test system between 1.8 and 2.8 V. Cyclic voltammetric (CV) was performed at a scan rate of 50 mV $s^{-1}$ in the voltage range of −0.8 − 0.8 V. Linear sweep voltammetry (LSV) measurements were performed using stainless steel as working electrode and lithium foil as counter electrode with a scan rate of 0.1 mV $s^{-1}$ from open circuit potential to 4.5 V.

*Theoretically calculation details*

All the DFT calculations were conducted using DMol3 module in Materials Studio software. [4] The generalized gradient approximation (GGA) and the Perdew−Burke−Ernzerhof scheme (PBE) was employed for the exchange−correlation potential to optimize geometrical structures and calculate properties. [5] The All−Electron Relativistic Kohn−Sham wave functions (AER) and double numeric plus polarization (DNP) basis set are used in the local atomic orbital basis set with the global orbital cutoff 4.4 Å. Linear synchronous transit/ quadratic synchronous transit (LST/QST) and nudged elastic band (NEB) tools of the DMol[3] module was used to determine the energy barrier and minimum energy path for diffusion. [6]
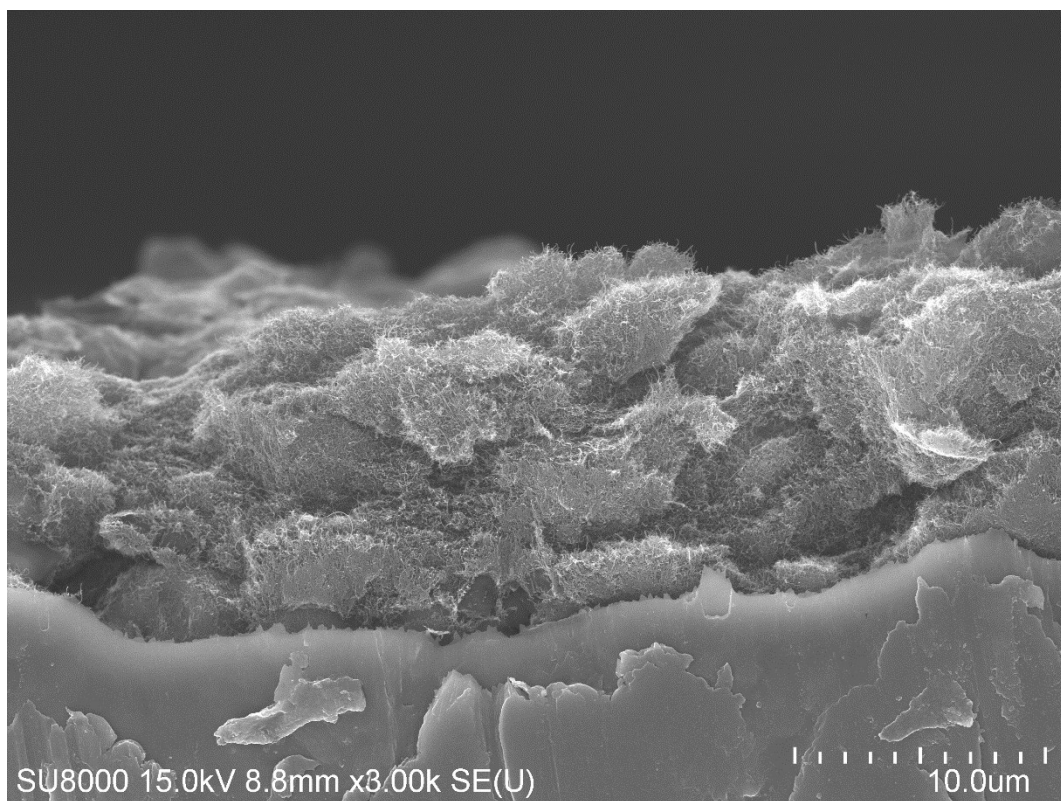
Figure S1. Cross section image of the sulfur cathode.

Table S1. ICP−OES results of the electrolytes

| Sample name | Ion concentration / ppm | |
| --- | --- | --- |
| | Co | Li |
| STD−CoPcCl | 0.4396 | 165.1 |
| Fresh battery | 0.0194 | 7.506 |
| Cycled battery | 0.0141 | 5.316 |

**References**

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