

Supporting Information

Trace Ethanol as an Efficient Electrolyte Additive to Reduce Activation Voltage of Li₂S Cathode in Lithium-Ion-Sulfur Batteries

Xin Liang^a, Jufeng Yun^a, Kun Xu^a, Pengcheng Shi^a, Yi Sun^a, Chunhua Chen^b, and
Hongfa Xiang^{*a}

*^aSchool of Materials Science and Engineering, Anhui Provincial Key Laboratory of
Advanced Functional Materials and Devices, Hefei University of Technology, Hefei
230009, Anhui, China.*

Email: hfxiang@hfut.edu.cn

*^bCAS Key Laboratory of Materials for Energy Conversions, Department of Materials
Science and Engineering, University of Science and Technology of China, Anhui
Hefei 230026, China*

Experimental Section

Preparation of the electrolyte and the electrodes

The standard lithium-sulfur battery electrolyte consisted of 1 M lithium bis (trifluoromethane sulfonyl) imide (LiTFSI) in 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) (1:1 by volume) with 2 wt% LiNO₃ as an additive. To prepare electrolytes capable of reducing the activation voltage of Li₂S, different amounts of ethanol (1000 ppm, 500 ppm, 250 ppm) are added to the standard lithium-sulfur battery electrolyte.

The graphene (The Six Element Inc.) were mixed with commercial Li₂S powder with a mass ratio of 4:6 and ball milled for 3 hours under Ar protection at 400 rpm using a planetary ball mill. After that, the Li₂S/Graphene composite was obtained. The slurry was prepared by mixing Li₂S/graphene composite, Super P (SP), and poly (vinylidene fluoride) (PVDF, 5130) in a ratio of 70:20:10 and distributing it in an N-methyl-2-pyrrolidinone (NMP, Aladdin Bio-Chem Technology Co. Ltd) solution. After that, the slurry was casted onto an aluminum foil and dried for 6 hours. Finally, it was punched into a disk with a diameter of 14 mm. The Li₂S loading amount of the electrode was 1.2~2 mg cm⁻².

Electrochemical measurements

The half cells were assembled to use CR2032 coin cells with Li foils as the counter and apply Celgard 2400 polypropylene membrane as separator. To standard the test, the electrolyte amount is relative to the active mass with 30 μL per mg of Li₂S in coin. Charge-discharge tests were performed on a LANHE cycler in a voltage range from 1.8 to 2.8 V after initial activating to 3.2 V (with ethanol added) and 3.8 V (without ethanol added). 1 C is donated as 1166 mA g⁻¹.

Material Characterizations

Cyclic voltammograms of Li₂S electrodes with and without ethanol added were performed on a CHI 604 electrochemical workstation (Shanghai Chenhua). Electrochemical impedance spectroscopy (EIS) of cells were also measured on the electrochemical workstation above, with a frequency range from 100 kHz to 0.1 Hz. The morphologies of the Li₂S electrodes were observed by field-emission scanning

electron microscopy (FE-SEM, Germany Zeiss). Since Li_2S is sensitive to air and moisture, it is sampled in a glove box filled with argon gas (M-Braun) and protected with Kapton tapes before the characterization. Transmission electron microscope (TEM) investigations were performed on JEM-2100F. X-ray photoelectron spectrometry (XPS) spectrum was measured on an X-ray Photoelectron Spectrometer (ESCALAB250Xi). In order to compare the solubility of Li_2S in ethanol and electrolyte, 10 mg Li_2S was added to 4 mL ethanol and 4 mL electrolyte, respectively. The photographs were taken one minute later.

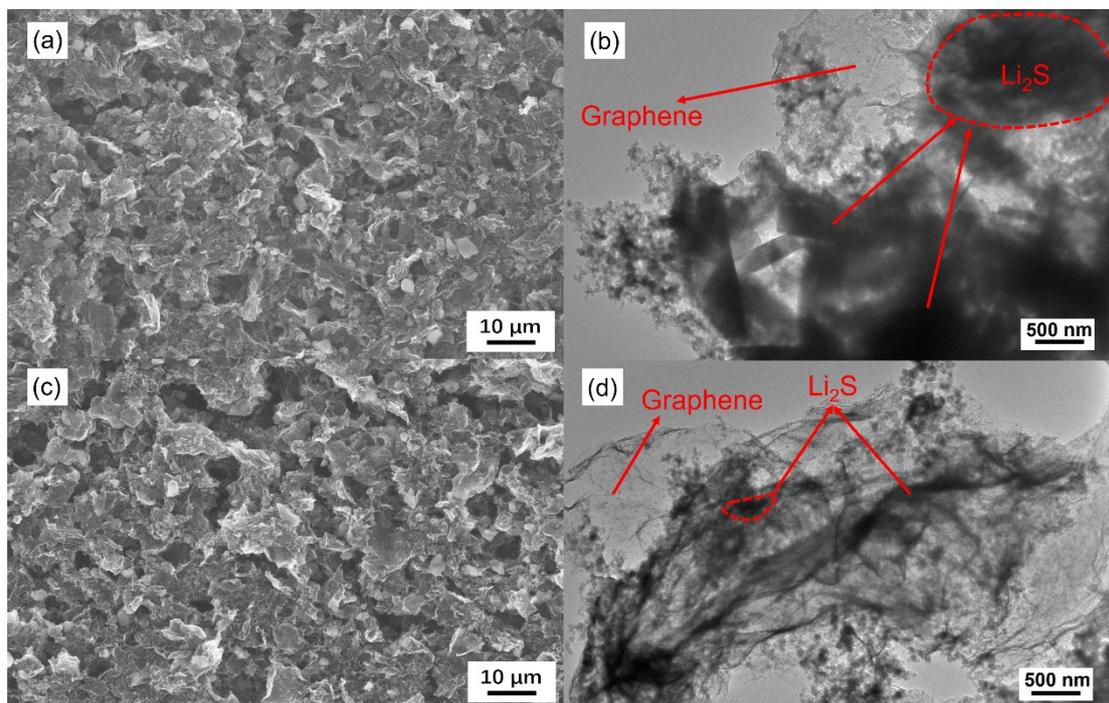


Fig. S1 (a) SEM and (b) TEM images of Li_2S cathodes without ethanol modification; (c) SEM and (d) TEM with ethanol modification at low magnification.

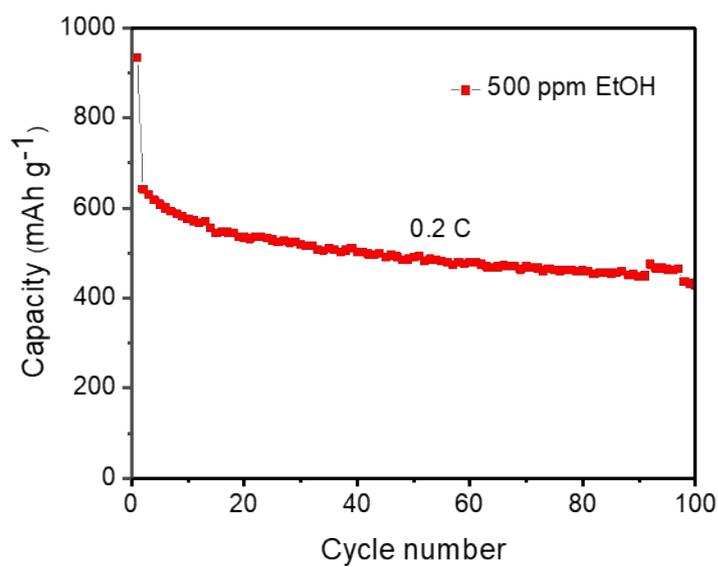


Fig. S2 Cycling performances of Li_2S electrode with high Li_2S loading (2.5 mg cm^{-2}) cycled in the electrolyte with 500 ppm ethanol.

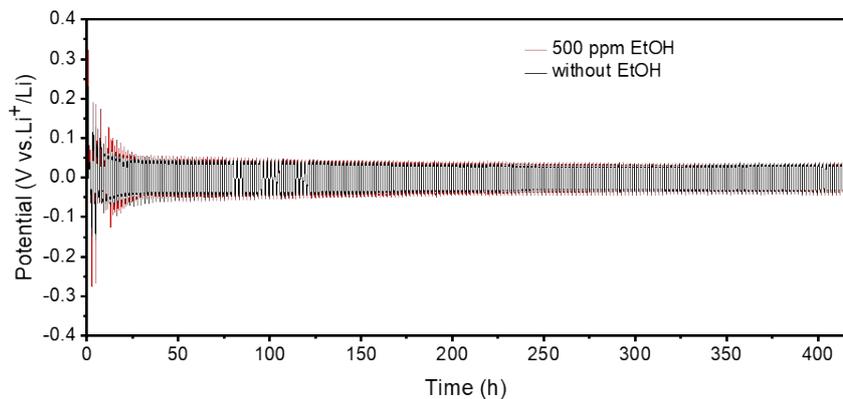


Fig. S3 Cycling stability of Li||Li symmetric cells in the electrolytes without and with 500 ppm ethanol at the current density of 1.0 mA cm^{-2} with 1 h plating/stripping time at $25 \text{ }^\circ\text{C}$.

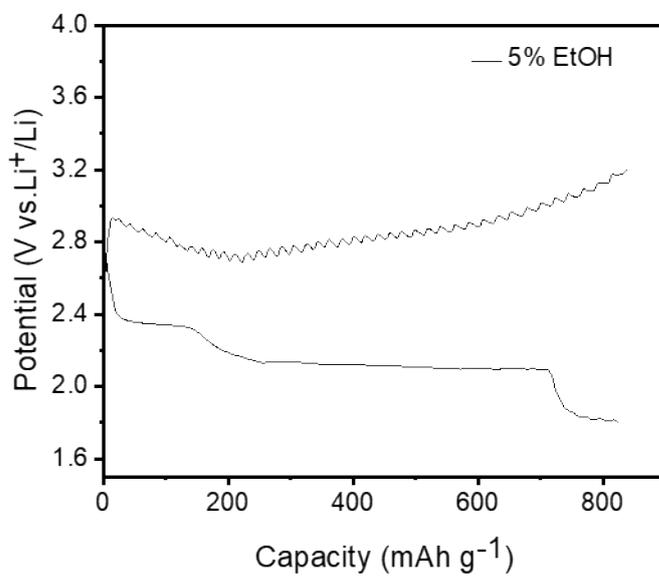


Fig. S4 The first charge–discharge profiles of the electrode modified by $6 \mu\text{l}$ DME solution contained 5% ethanol.

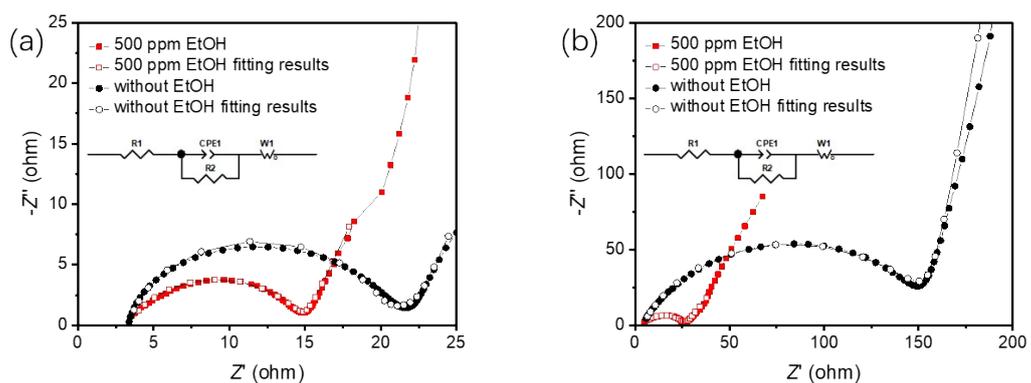


Fig. S5 Electrochemical impedance spectroscopy and the relevant fitting results of cells cycled in the electrolyte: (a) with 500 ppm ethanol and without ethanol before cycling; and (b) with 500 ppm ethanol and without ethanol after 100 cycles.

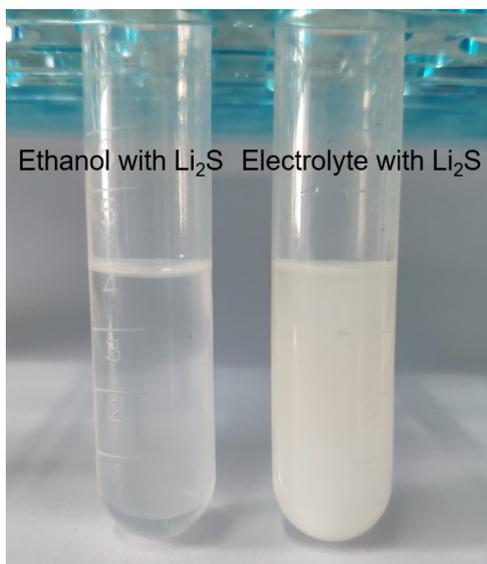


Fig. S6 The comparison of solubility of Li₂S in ethanol and electrolyte (photos taken after one minute).

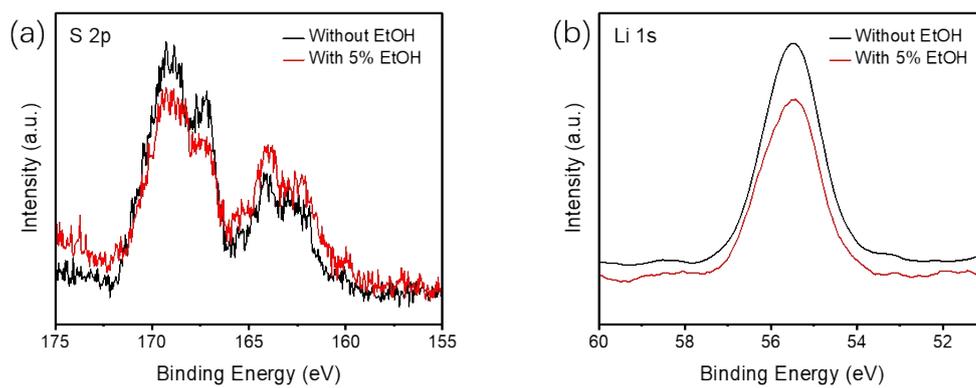


Fig. S7 XPS spectra of $\text{Li}_2\text{S}/\text{Graphene}$ cathodes with and without ethanol modification: (a) S 2p and (b) Li 1s.

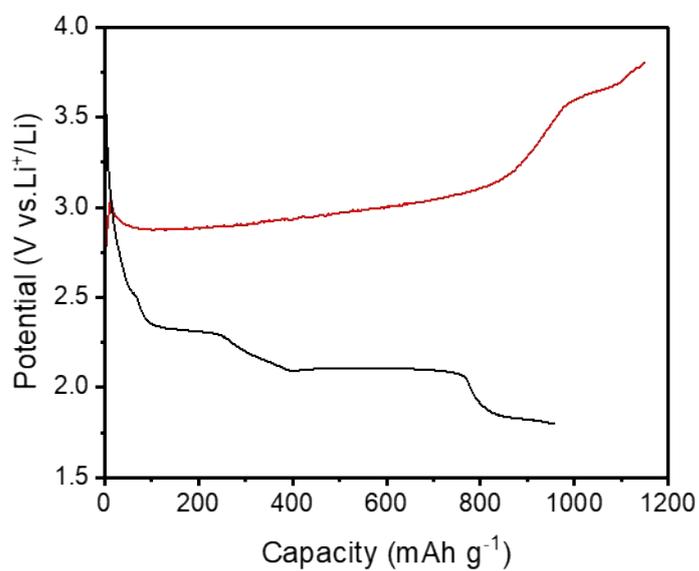


Fig. S8 The first charge–discharge profiles of electrolytes with 5000 ppm acetonitrile added at 0.05 C.

Table.1. Current work on reducing the activation voltage of Li₂S.

Electrode	Basic electrolyte	Additive	Activation Voltage	Principle	Ref
Li ₂ S in carbonized commercial wipe	1 M LiTFSI+ + 1 wt% LiNO ₃ in DOL:DME (1:1)	InI ₃	2.4 V	I ⁻ /I ³⁻ redox couple react Li ₂ S	24
P ₂ S ₅ +Li ₂ S in CNF current collector	1 M LiCF ₃ SO ₃ +1 M LiNO ₃ +TEGDME	P ₂ S ₅	2.4 V	React Li ₂ S to Li ₂ S _x	25
Li ₂ S+SP+PVDF on Al current collector.	10 % LiTFSI + 2 % LiNO ₃ in DOL:DME (1:1)	Redox Mediators	2.9 V	RM/RM ⁺ react Li ₂ S to (Li ₂ S) _x	23
Li ₂ S/Graphene+SP+PVDF on Al current collector.	1 M LiTFSI + 2 wt% LiNO ₃ in DOL:DME (1:1)	Ethanol	2.9 V	Dissolved Li ₂ S	This work