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Sulfuryl Chloride as a Functional Additive towards Dendrite-Free and Long-Life Li Metal Anodes

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Experimental

Materials: The metallic Li foil (Φ15 mm) was obtained from China Energy Lithium Co., Ltd. The electrolyte composed of $LiPF_6$ (1.0 M) and EC/DMC (1:1 by volume) was purchased from DodoChem. Sulfonyl chloride (SO_2Cl_2) with purity of 99.5% was purchased from Macklin Co. Ltd.

Material characterization: The morphology and elemental distribution were observed by Field-emission scanning electron microscope (FE-SEM, Hitachi SU8010) with an energy dispersive X-ray spectroscope (EDS, JEOL JSM-6100LV). All the batteries after cycled were disassembled and flushed with anhydrous dimethyl carbonate (DMC) solvent three times to remove remnant lithium salts, and then dried until the solvent volatilized thoroughly in glovebox before operating. The elemental valence of the SEI layer was detected by X-ray photoelectron spectroscopy (XPS, ESCALab220i-XL) with 300 W Al Kα radiations under ambient temperature.

Electrochemical measurements: Two-electrode cells configuration using standard 2032 coin-type cells were employed and assembled in an Ar-filed glove box with H_2O and O_2 concentrations below 0.1 ppm. The electrolytes were prepared by dissolving 0.5%, 1%, 2%, 5% SO_2Cl_2 additives (by quality) into 1.0 M $LiPF_6$ in EC/DMC. For the symmetric cell tests, two identical electrodes were carried out at various current densities under different electrolytes with the deposition capacity of 1 mAh cm^{-2} or 4 mAh cm^{-2} to investigate the lithium stripping/plating processes. The electrodes used in contrast experimental were pretreated the Li with SO_2Cl_2 for 5 minutes and tested at 1 mA cm^{-2} under a fixed capacity of 1 mAh cm^{-2}. For the CE testing, 0.5 mAh cm^{-2} of Li

without or with 2% SO_2Cl_2 additive was deposited on Cu foil (Φ12 mm) and then stripped away up to 1.0 V at a current density of 0.5 mA cm^{-2} for every cycle. Li||$LiFePO_4$ full cells tests used $LiFePO_4$ as the cathode at 1 C in a voltage range of 2.5-4.2V, the mass loading of the $LiFePO_4$ cathode material is about 5 mg cm^{-2}. EIS tests were carried out on an electrochemical workstation (CHI660a, Shanghai Chenhua) in the frequency ranging from 10^5 to 10^{-2} Hz.

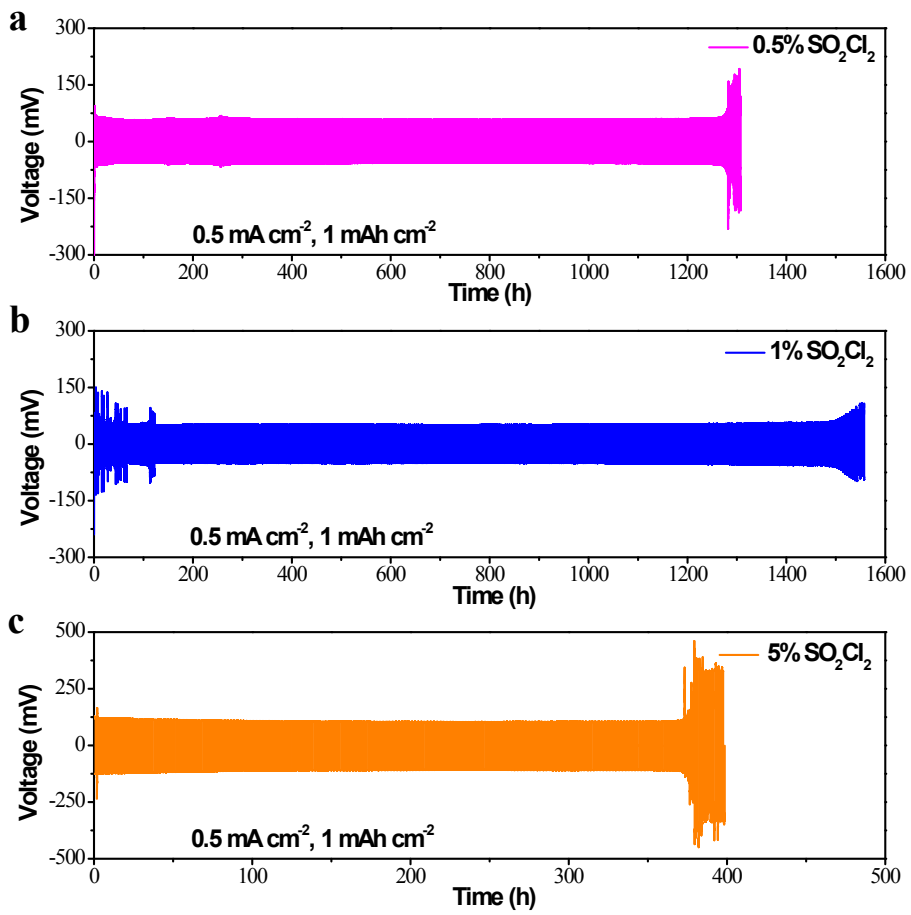

Fig. S1 Cycling stability of symmetrical cells using various ratios of electrolyte additives at 0.5 mA cm^{-2} under a fixed capacity of 1 mAh cm^{-2}.

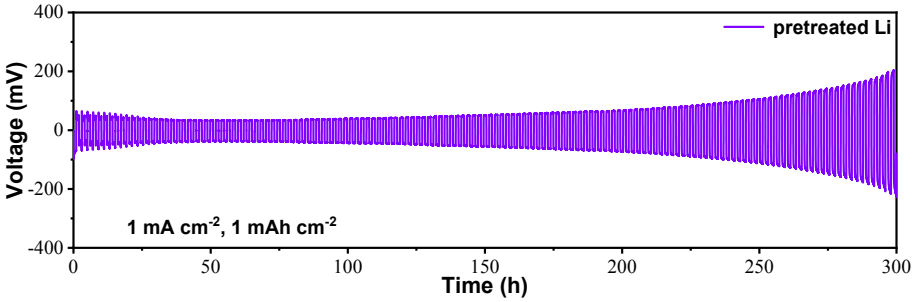

Fig. S2 Cycling stability of symmetrical cells using pretreat the Li with SO_2Cl_2 at 1 mA cm^{-2} under a fixed capacity of 1 mAh cm^{-2}.

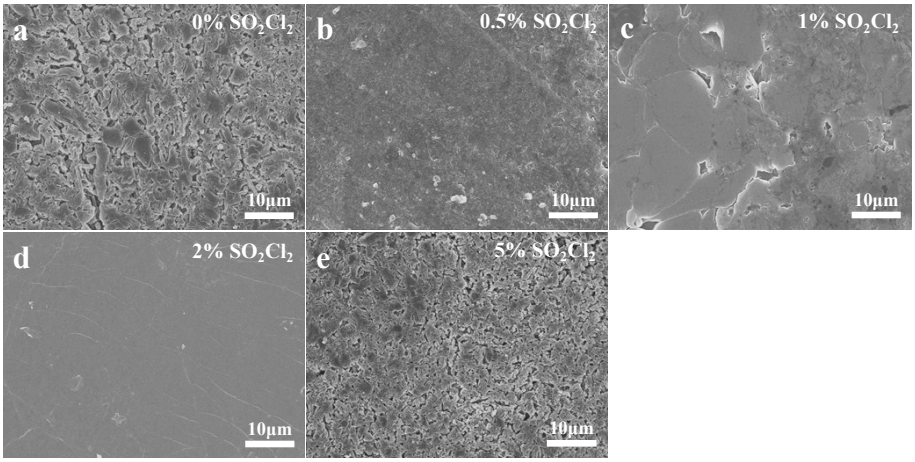

Fig. S3 SEM images of symmetrical cells after 100 cycles using various ratios of electrolyte additives at 0.5 mA cm^{-2} under a fixed capacity of 1 mAh cm^{-2}.

Table. S1 Cyclic stability comparison with previously reported works on Li metal anodes.

Current density (mA cm^{-2})	**Deposition capacity** (mAh cm^{-2})	**Overpotential** (mV)	**Cycle time** (h)	**Electrolyte**	**References**
0.1	0.2	~60	800	1M LiTFSI/(DOL+DME)	Ref.1
1	0.5	~100	900	1M $LiPF_6$/(EC+DMC+DEC)	Ref.2
1	1	43.4	520	1M LiTFSI/(DOL+DME)	Ref.3
0.5	1	55	650	1M LiTFSI/(DOL+DME)	Ref.4
0.5	0.5	52	300	1M LiTFSI/TEP	Ref.5
1	1	60	400	1M LiTFSI/(DOL+DME)	Ref.6
1	1	52	700	1M $LiPF_6$/(EC+DMC+DEC)	Ref.7
1	1	~100	250	1M $LiPF_6$/(EC+DMC+DEC)	Ref.8
0.5	1	32	2000	1M $LiPF_6$/(EC+DMC)	This work
1	1	~40	1200		

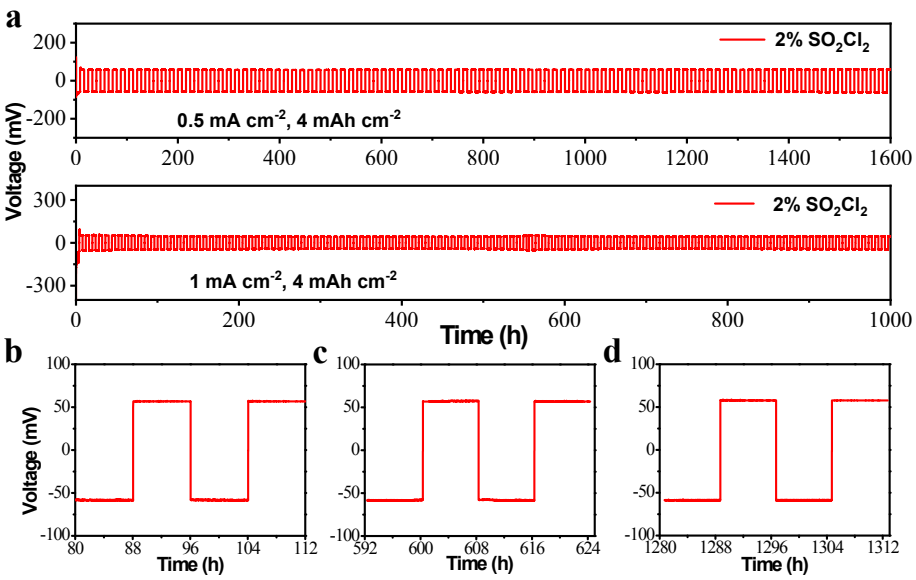

Fig. S4 Cycling stability of symmetrical cells using 2% SO_2Cl_2 as the electrolyte additive at 0.5 mA cm^{-2} and 1 mA cm^{-2} under a fixed capacity of 4 mAh cm^{-2}.

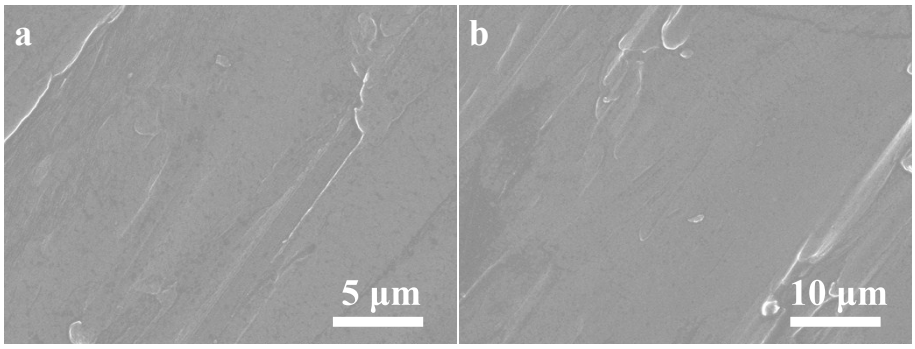

Fig. S5 SEM images of Li metal anode before cycling.

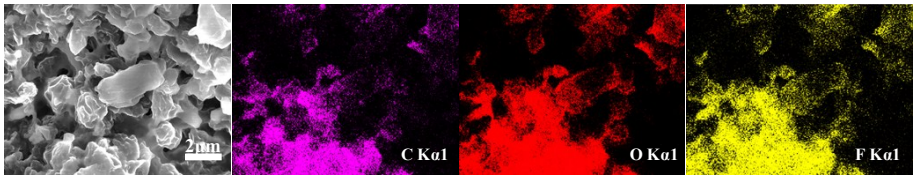

Fig. S6 EDS elemental distribution maps of bare Li metal.

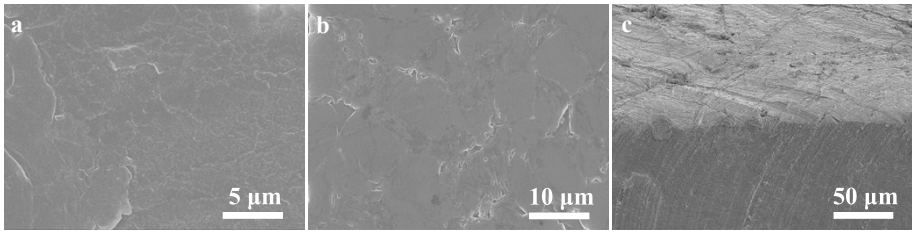

Fig. S7 SEM images of Li surface with SO_2Cl_2 additive after 200 cycles.

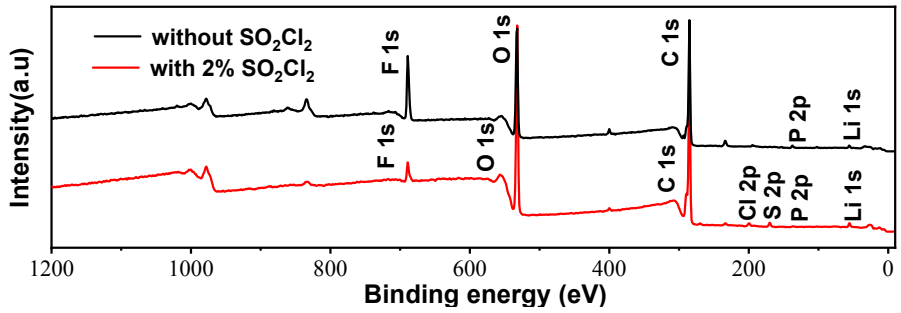

Fig. S8 XPS survey scans of Li metals surface statement after 10 cycles at the current density of 0.5 mA cm^{-2} in symmetrical cell.

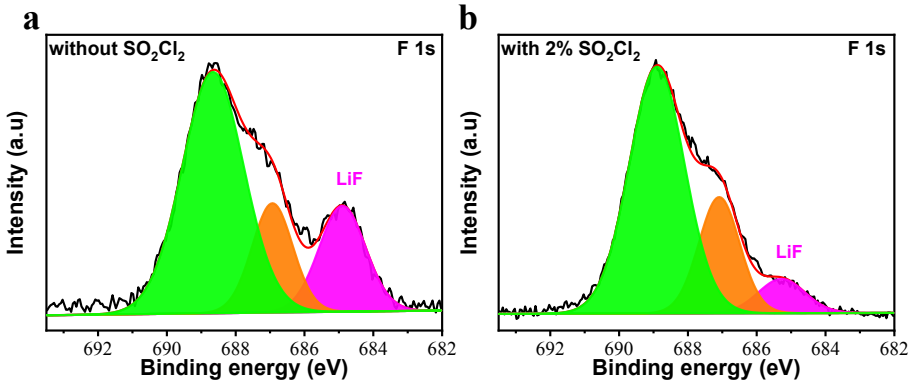

Fig. S9 The high-resolution XPS spectra of (a) F 1s for bare Li anode and (b) F 1s for 2% SO_2Cl_2 additive at the current density of 0.5 mA cm^{-2} after 10 cycles in symmetrical cells.

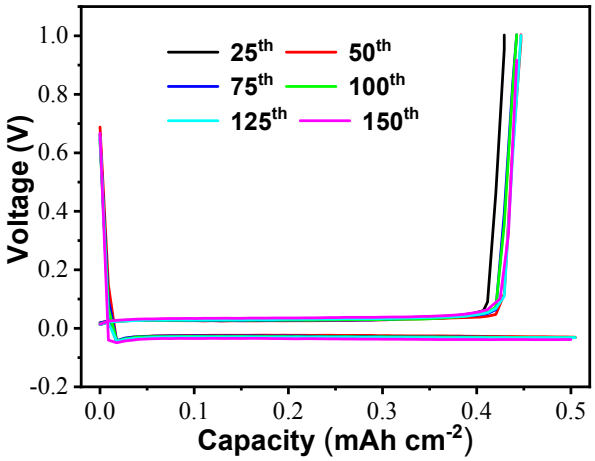

Fig. S10 Charge/discharge curves of Li||Cu cell with 2% SO_2Cl_2 at particular cycles.

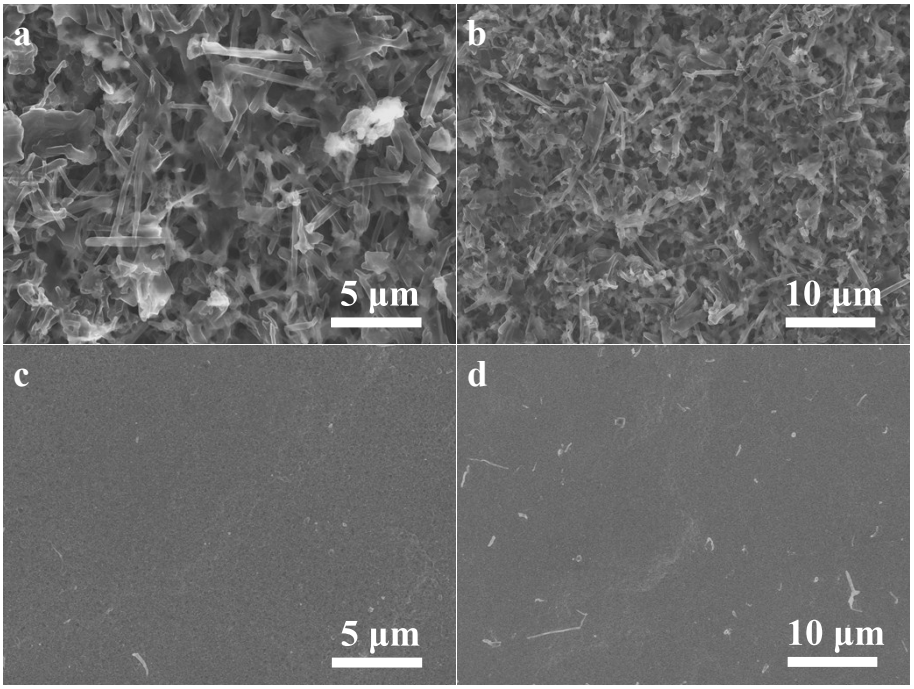

Fig. S11 SEM images of Cu surface (a, b) without SO_2Cl_2 and with 2% SO_2Cl_2 additive (c, d) after 50 cycles.

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