Supporting Information

1 Experimental

1.1 Electrolyte preparation

The 0.5 M Mg(TFSI)$_2$/DME electrolyte was synthesized by adding 0.585 g Mg(TFSI)$_2$ (Aladdin, 97.0%) to 2 ml 1,2-dimethoxyethane (DME, Aladdin, 99.5%) in an argon-filled glove box (<1 ppm of water and oxygen).

1.2 Preparation of KB/S composite

The Ketjenblack/sulfur (KB/S) composite was prepared by melting diffusion method following previous report [30]. The Ketjenblack (KB, Ketjenblack EC-600JD) and sublimed sulfur (Aladdin, 99.5%) were mixed in a molar ratio of 7:3 or 4:6 and then immersed in carbon disulfide (CS$_2$, Aladdin, 99.5%). The obtained slurry was stirred for 12 h to volatilize CS$_2$. The remained mixtures were milled and heated at 155℃ in Ar atmosphere for 20 h.

1.3 Electrochemical tests

The KB/S composite cathodes were fabricated by casting 8:1:1 wt.-ratio mixture of KB/S composite, super-P and binder in water solvent on carbon-coated aluminum collector. The above-mentioned binder was prepared by adding polyethylene oxide (PEO) and polyvinyl pyrrolidone (PVP) to water with 4:1 wt.-ratio. The cathodes were dried in vacuum at 50℃ for 12 h and tailored into disc with a diameter of 14 mm. The sulfur loading of cathode is about 0.18 mg cm^{-2}. The Mg foil and Mg-Li Alloy foil were tailored into disc with a diameter of 15 mm and polished by knife in argon-filled glove box before used as anode.

Galvanostatic discharge/charge tests were carried out in coin-cell with a battery test system (Neware, BST-5V 5mA). All coin-cells were assembled in argon-filled glovebox (<1 ppm of water and oxygen) at room temperature. The cathode was KB/S composite, the anode was Mg foil or Mg-Li alloy foil, the separator was glass fiber membrane (whatman GF/D), and the electrolyte was 80 μL 0.5 M Mg(TFSI)$_2$/DME solution. Electrochemical impedance spectroscopy (EIS) measurements were performed by PARSTAT-2273 electrochemical workstation. The frequency ranged from 100 mHz to 100 kHz and the amplitude was 10 mV.

1.4 Characterization

Scanning electron microscopy (SEM) and energy-dispersive spectrometry (EDS) were carried out with a Zeiss field-emission scanning electron microscopy (Merlin Compact). Transmission electron microscope (TEM) was conducted by a transmission electron microscope (FEI Tecnai T20). X-ray diffraction (XRD) measurements were performed by an Empyrean with Cu Ka radiation. Optical micrograph (OM) was carried out with an optical microscope (Olympus PMG3) under overpotential mode. Mg-Li alloy etching solution was prepared by mixing 0.5 g picric acid, 1 mL glacial acetic acid, 5 mL deionized water and 25 mL ethyl alcohol together. The Mg-Li alloy sample for OM was mechanically polished and etched in the obtained etching solution for 20 seconds. After that the Mg-Li alloy was immediately rinsed with alcohol and blown dry for OM test. X-ray nano-tomography measurements were carried out by the beamline BL13HB, SSRF at 20 keV, ~ 900 projections over an angular range of 180°. The field of view is 1000×1000 μm^2 with a 2k×2k CCD camera binning 2×2 camera pixels into one output pixel. The raw data is tomographically aligned and then reconstructed and analyzed by the software package Avizo (Thermo Fisher Scientific, Waltham, Massachusetts, USA). Inductively coupled plasma-optical emission spectrometer (ICP-OES) experiments were conducted with the Thermo iCAP 7400 instrument. X-ray photoelectron spectroscopy (XPS) measurements were performed with a thermo Fisher Scientific 4 ESCALAB 250XI spectrometer with Al Kα (1486.6 eV) as the X-ray source. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was conducted by the Thermo Scientific Nicolet iS10 instrument. All the electrode samples were rinsed thoroughly with DME solvent before characterization.

2 Calculation Processes

The amount of Li$^+$ in the KB/S cathode after the Mg-Li/S battery discharged.

The actual discharge specific capacity of the Mg-Li/S battery for ICP is 900 mAh g^{-1}. The actual mass of cathode active material is 0.778 mg. The number of charge transfers in the battery is

$$\frac{0.778}{32.06} \times 2 \times \frac{900}{1675} = 2.60 \times 10^{-2} \text{ mmol.}$$

According to the ICP results, the concentration of Mg^{2+} in the KB/S cathode sample is 0.355 mmol L^{-1} which can provide a charge of 0.355×2=0.710 mmol L^{-1}, and that of Li$^+$ is 0.010 mmol L^{-1}. The ratio of Mg^{2+} to Li$^+$ is constant, and the total number of

charge transfers in the battery is 2.60×10^{-2} mmol. Therefore, the amount of Li^+ in cathode is

$$\frac{0.026 \times 0.01}{0.71 + 0.01} = 3.60 \times 10^{-3} \text{ mmol.}$$

The amount of Li^+ in the electrolyte after the Mg-Li/S battery discharged.

According to the ICP results, the concentration of Mg^{2+} in the electrolyte sample is 2.023 mmol L^{-1}, and that of Li^+ is 0.008 mmol L^{-1}. The electrolyte originally contains 0.5 mol L^{-1} Mg^{2+}, and the dissolved Mg^{2+} are very small compared to it, so the concentration of Mg^{2+} in the electrolyte can be still counted as 0.5 mol L^{-1}. Therefore, the concentration of Li^+ in the electrolyte can be calculated as

$$\frac{0.5 \times 0.008}{2.023} = 1.977 \text{ mmol } L^{-1}.$$

Since the amount of electrolyte in the battery is 80 μL, the amount of Li^+ in the electrolyte is calculated to be

$$1.977 \times 80 \times 10^{-6} = 1.58 \times 10^{-4} \text{ mmol.}$$

In conclusion, the total amount of lithium in the KB/S cathode and in the electrolyte is 3.76×10^{-3} mmol.

Tab. S1 ICP result of the Mg-Li alloy.

	Mg	Li	Zn
Mass Percent (wt.%)	90.260	8.437	1.303

Tab. S2 Comparation of optical photograph of Mg, Mg-Li alloy and Li after exposed to air and water for 48 h.

Tab. S3 Fitting results of EIS of Mg-Li/S battery and Mg/S battery.

	R_Ω (ohm)	R_I (ohm)	R_{ct} (ohm)
Mg-Li/S	6.635	4.594	103.9
Mg/S	8.024	970400	2.929

Tab. S4 EIS fitting results of Mg-Li/S battery with different storage time.

Time (min)	R_Ω (ohm)	R_I (ohm)	R_{ct} (ohm)
0	6.635	4.594	103.9
900	3.910	34020	134.8
1500	3.551	53750	152.4
2400	3.709	78970	142.5
2940	3.945	101900	142.3
4500	4.113	127500	134
11400	4.616	160900	125

Tab. S5 EIS fitting results of Mg/S battery with different storage time.

Time (min)	R_Ω (ohm)	R_I (ohm)	R_{ct} (ohm)
0	8.024	970400	2.929
900	1.069	1855000	2.325
1500	2.602	1693000	2.699
2400	1.065	2526000	2.605
2940	9.953	2357000	3.193
4500	1.061	2281000	2.792
11400	9.669	2245000	3.813

Fig. S1 Optical photograph of Mg-Li alloy after exposure to air for 10 days and to water for 48 h.
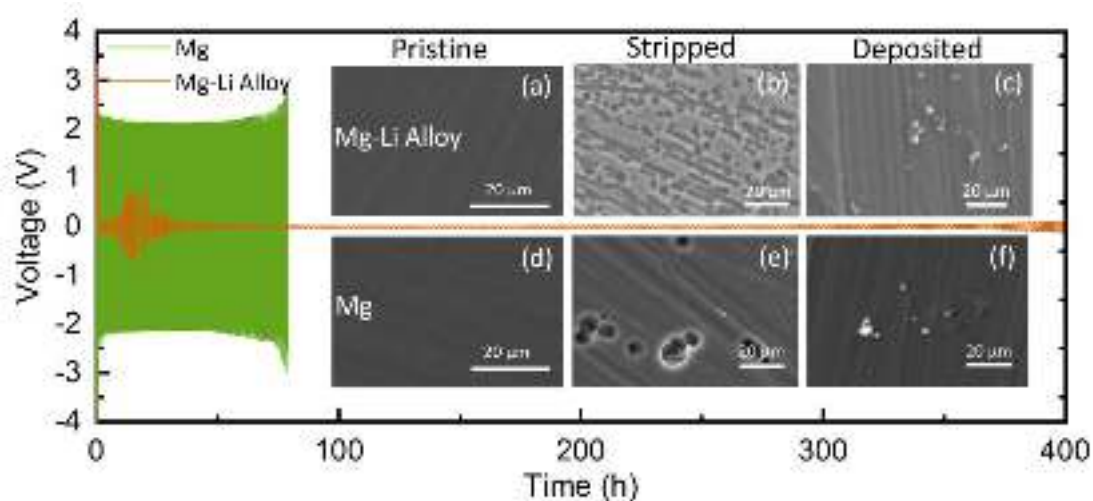
Fig. S2 Voltage profiles of symmetric Mg-Li battery and symmetric Mg battery. The current density is 0.1 mA cm^{-1}, and each charge/discharge process lasts for 1 h. Inset: (a-c) morphology of pristine, stripped and deposited Mg-Li alloy electrode, (d-f) morphology of pristine, stripped and deposited Mg electrode.
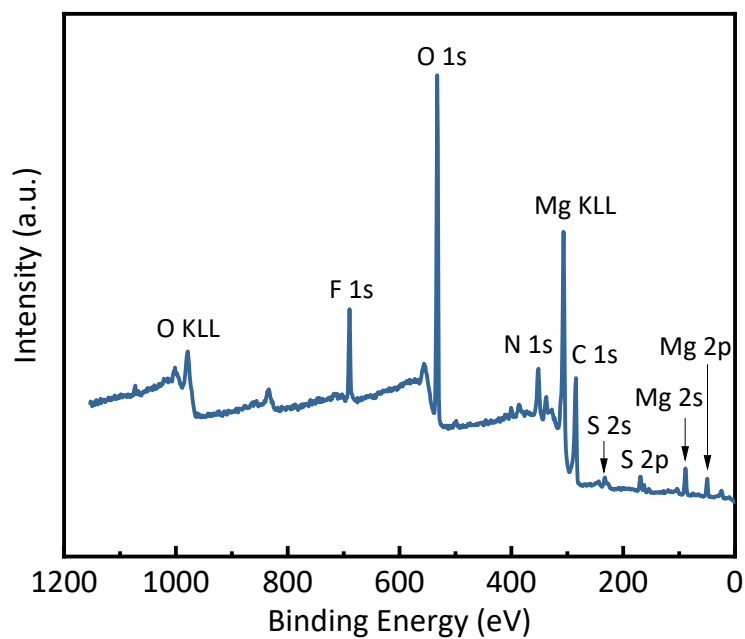
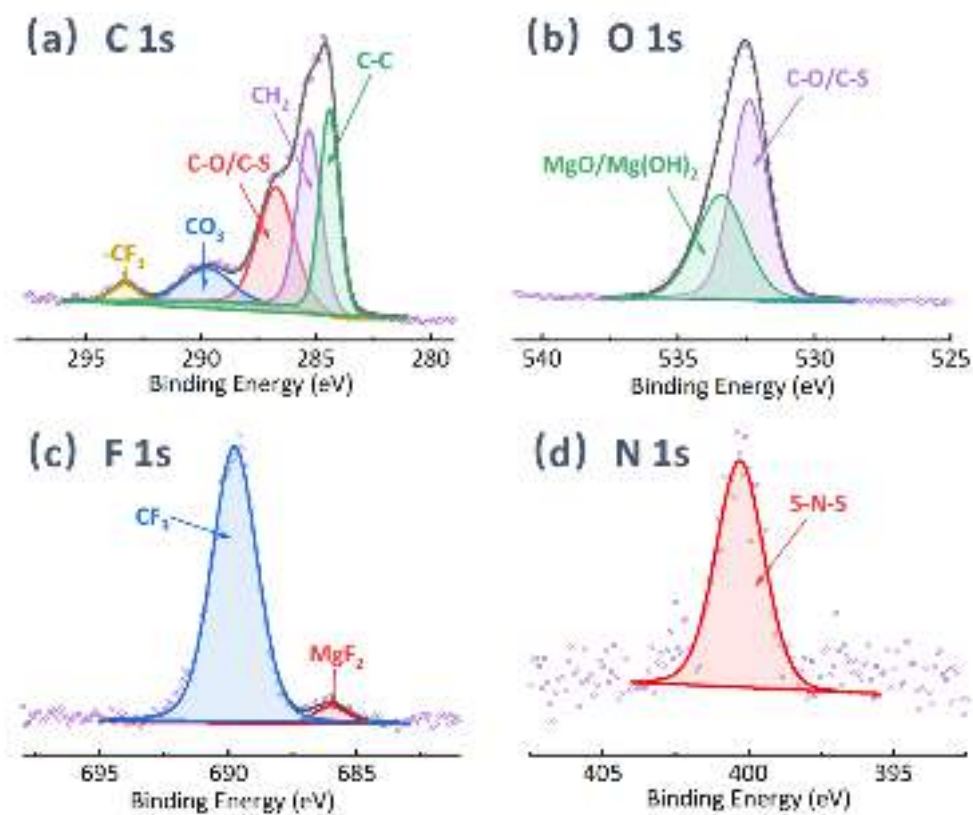Fig. S3 Full XPS spectrum of KB/S cathode of Mg-Li/S battery after first discharge.

Fig. S4 (a) C 1s, (b) O 1s, (c) F 1s and (d) N 1s high-resolution XPS spectrum of KB/S cathode of Mg-Li/S battery after first discharge.
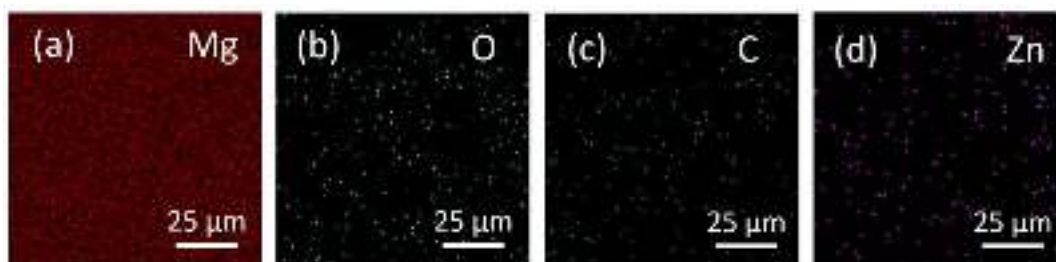
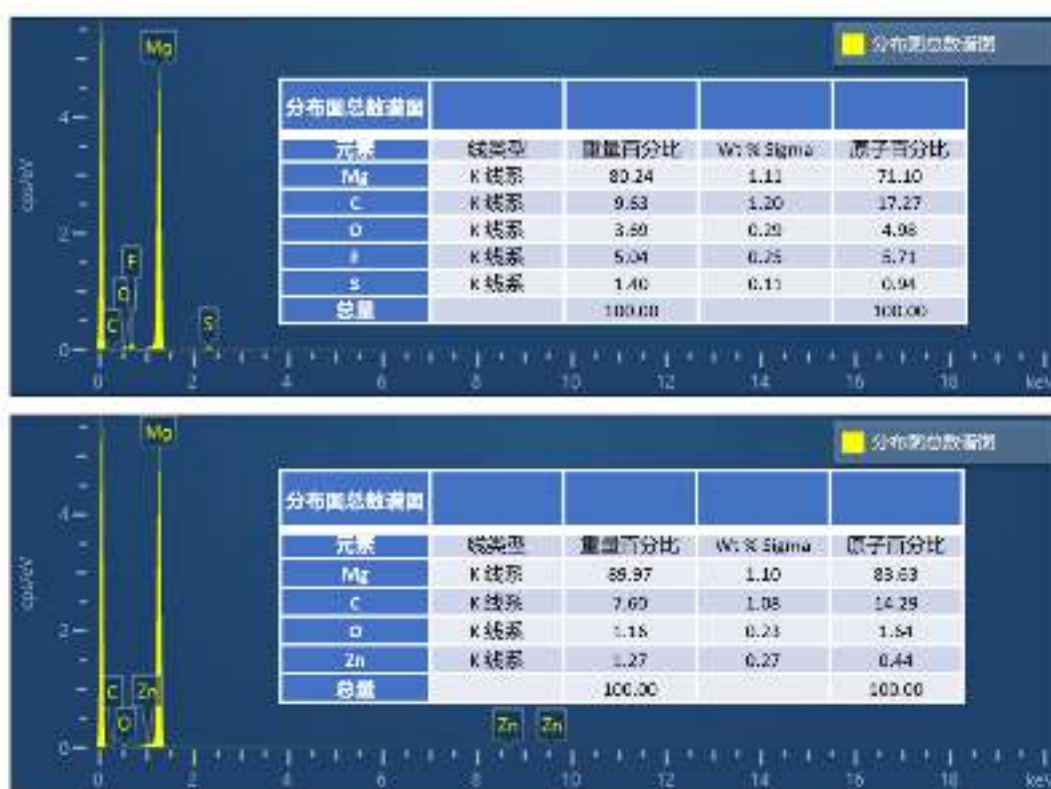Fig. S5 Mapping results of Mg-Li alloy foil after soaked in electrolyte for 30 s.

Fig. S6 EDS results of (a) Mg foil and (b) Mg-Li alloy foil after soaked in the electrolyte for 30 s.