# Supporting information for:

# An efficient organic magnesium borate based electrolyte with non-nucleophilic characteristic for magnesium sulfur battery

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### The preparation of cathodes:

 $Mo_6S_8$  cathode: Chevrel Phase Mo\_6S\_8 was synthesized following previously published work. <sup>1</sup> Mo\_6S\_8-carbon composite electrode slurry was prepared by mixing 80 wt% Mo\_6S\_8 powders, 10 wt% Super P and 10 wt% poly(vinylidene fluoride) (PVDF) in N-methylpyrrolidinone (NMP) to obtain a homogeneous solution. And then the slurry was pasted onto a stainless steel foil and dried at 393 K in a vacuum oven. The electrode foil was tailored into proper disc with a diameter of 10mm and the mass loading of the active Mo\_6S\_8 was estimated to be about 1.1 mg<sup>-cm<sup>-2</sup></sup> via weighting the mass changes of the loaded electrode and stainless steel foil.

*Sulfur-carbon composite cathodes*: S-AMC, S-CNT and S-CMK composites all were prepared following a melt-diffusion strategy. <sup>2</sup> Carbon materials (2.0 g) and sulphur (8.0 g) were mixed and ground together in a mortar, and heated at 155 °C for 24h in a sealed stainless steel autoclave filled with Ar. After the calcination process, the sulfur loss is almost negligible. Therefore, the content of each S-C composites is around 80%. About the preparation of S-C composite cathodes, S-C composites (S-AMC, S-CNT and S-CMK), Super P and PVDF were mixed together at a weight ratio of 80:10:10 within NMP solvent to form the homogeneous slurry. The slurry was coated onto Cu foil and dried at 333 K to evaporate NMP solvent. And then the electrode foil was cut into proper disc with a diameter of 10mm. Among these three kinds of S-C composite cathodes, their mass loading of the active sulfur all were estimated to be approximate 1.5 mg<sup>-cm<sup>-2</sup></sup>.

#### The details of cell assembly:

*Cyclic Voltammetry*: In our study, the cyclic voltammetry was performed on the two-electrode 2032-type coin cell comprising the Cu disc as working electrode, the glass microfiber filter as separator, the polished Mg foil as reference electrode. The electrolyte was determined according to different test requirements.

*Linear Sweep Voltammetry*: The cell for testing linear sweep voltammetry was a three-electrode cell comprising Cu foil or SS foil or Al foil or graphite film or Pt wire as the working electrode, polished Mg needle as counter electrode and reference electrode. The electrolyte was the 0.5 M

# OMBB electrolyte.

*The test of polarization properties*: Symmetric Mg/Mg cells were assembled in the 2032-type coin cell for evaluating the polarization properties of the 0.5 M OMBB electrolyte. The cathode and the anode were polished Mg discs, the separator was glass microfiber filter, and the electrolyte was the 0.5 M OMBB electrolyte.

*The measurement of ionic conductivity:* The ionic conductivity of 0.5 M OMBB electrolyte was studied by EIS measurements. The microporous membrane (Celgard 2400) were soaked in 0.5 M OMBB electrolyte and then sandwiched between a pair of stainless steel electrodes within 2032-type coin cell. The electrochemical impedance spectroscopy was recorded at room temperature over the frequency range from 1 MHz to 1 Hz by applying a sine wave with the amplitude of 10.0 mV. The ionic conductivity were calculated from the equation of  $\sigma = l/SR$ , where  $\sigma$  represents the ionic conductivity, the *l* is the thickness of Celgard 2400 membrane (25 µm), *S* is the area of the discal stainless steel electrode (2.01 cm<sup>2</sup>), and *R* represents the resistance determined by the Nyquist plot.

*The electrochemical deposition of magnesium*: Asymmetric Cu/Mg cells were assembled in the 2032-type coin cell for verifying the non-dendritic characteristic of Mg deposits in the 0.5 M OMBB electrolyte. The cathode was Cu disc and the anode was polished Mg disc, the separator was glass microfiber filter, and the electrolyte was the 0.5 M OMBB electrolyte. The cells were discharged for 12h at a constant current of densities of 0.5 mA·cm<sup>-2</sup>.

*Evaluation of Mg/Mo*<sub>6</sub> $S_8$  *and Mg/S batteries*: The polished Mg disc was served as anode. The pretailored glass microfiber filter was employed as separator and the as-prepared 0.5 M OMBB electrolyte was used as electrolyte. The Mo<sub>6</sub> $S_8$  cathode and each S-C composite cathode were used as cathode, respectively. These batteries were assembled in 2032-type coin battery.

### The details of single-crystal XRD:

The crystals with X-ray quality were in situ generated from the clear electrolytes by slow diffusion of hexane. A single crystal was selected for collecting crystal diffraction data. The slightly wet crystal was rapidly transferred to the cold N<sub>2</sub> stream on the instrument. The measurements were conducted on a Bruker Smart Apex II diffractometer using Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) with a graphite monochromator at 173K. Integration and scaling of intensity data was accomplished using the SAINT program. <sup>3</sup> The structure was solved by using intrinsic SHELXT2014 and the refinement was carried out by the full-matrix least-squares technique of SHELXT2014. <sup>4</sup> The hydrogen atoms were refined isotropically, and the heavy atoms were refined anisotropically. Hydrogens were placed in calculated positions and refind with a riding model. Data were corrected for the effects of absorption using SADABS. <sup>5</sup> The crystallographic data and the details

of data collection and structure refinement are presented in Table S1-S4.

Empirical formula	$C_{48}H_{68}B_2Cl_6F_{48}Mg_4O_{20}\\$
Formula weight	2208.58
Temperature/K	173
Crystal system	monoclinic
Space group	C2/c
a/Å	36.905(5)
b/Å	13.215(2)
c/Å	20.962(3)
a\^o	90
β/°	121.440(3)
γ/°	90
Volume/Å <sup>3</sup>	8722(2)
Z	4
$ ho_{calc}g/cm^3$	1.682
$\mu/mm^{-1}$	0.388
F(000)	4432
Crystal size/mm <sup>3</sup>	$0.2\times0.14\times0.12$
Radiation	MoKα ( $\lambda$ = 0.71073)
2θ range for data collection/°	3.342 to 55.09
Index ranges	$-44 \le h \le 47, -17 \le k \le 17, -27 \le l \le 27$
Reflections collected	37221
Independent reflections	9995 [ $R_{int} = 0.0498$ , $R_{sigma} = 0.0530$ ]
Data/restraints/parameters	9995/12/583
Goodness-of-fit on F <sup>2</sup>	1.025
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0538, wR_2 = 0.1426$
Final R indexes [all data]	$R_1 = 0.0895, wR_2 = 0.1683$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.63/-0.55

Table S1. Crystal data and structure refinement for [Mg<sub>4</sub>Cl<sub>6</sub>(DME)<sub>6</sub>][B(HFP)<sub>4</sub>]<sub>2</sub>

# Table S2. Crystal data and structure refinement for [Mg<sub>2</sub>Cl<sub>3</sub>(THF)<sub>6</sub>][B(HFP)<sub>4</sub>]

Empirical formula	$C_{36}H_{52}BCl_{3}F_{24}Mg_{2}O_{10}\\$
Formula weight	1266.55
Temperature/K	296.15
Crystal system	triclinic

Space group	P-1
a/Å	13.389(5)
b/Å	14.252(5)
c/Å	16.825(6)
α/°	108.785(10)
β/°	90.513(10)
$\gamma/^{\circ}$	114.274(9)
Volume/Å <sup>3</sup>	2733.5(17)
Ζ	2
$\rho_{calc}g/cm^3$	1.539
$\mu/mm^{-1}$	0.320
F(000)	1288.0
Crystal size/mm <sup>3</sup>	$0.12\times0.08\times0.05$
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
$2\theta$ range for data collection/°	3.356 to 50.05
Index ranges	$-15 \le h \le 15, -16 \le k \le 15, -20 \le l \le 20$
Reflections collected	20665
Independent reflections	9516 [ $R_{int} = 0.1029$ , $R_{sigma} = 0.1841$ ]
Data/restraints/parameters	9516/1534/721
Goodness-of-fit on F <sup>2</sup>	0.937
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.1167, wR_2 = 0.2898$
Final R indexes [all data]	$R_1 = 0.2889, wR_2 = 0.3644$
Largest diff. peak/hole / e Å-3	1.22/-0.50

# Table S3. Crystal data and structure refinement for [Mg<sub>2</sub>Cl<sub>2</sub>(DME)<sub>4</sub>][AlCl<sub>4</sub>]<sub>2</sub>

Empirical formula	$C_{16}H_{39}Al_2Cl_{10}Mg_2O_8\\$
Formula weight	816.55
Temperature/K	175.01
Crystal system	orthorhombic
Space group	Pca2 <sub>1</sub>
a/Å	26.533(5)
b/Å	7.3366(14)
c/Å	19.239(4)
α/°	90
β/°	90

$\gamma/^{\circ}$	90
Volume/Å <sup>3</sup>	3745.1(13)
Ζ	4
$\rho_{calc}g/cm^3$	1.448
µ/mm <sup>-1</sup>	0.858
F(000)	1676.0
Crystal size/mm <sup>3</sup>	$0.28\times0.15\times0.11$
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
$2\theta$ range for data collection/°	5.23 to 50.014
Index ranges	$-31 \le h \le 31, -8 \le k \le 8, -22 \le l \le 22$
Reflections collected	36723
Independent reflections	$6514 [R_{int} = 0.1050, R_{sigma} = 0.0741]$
Data/restraints/parameters	6514/367/353
Goodness-of-fit on F <sup>2</sup>	1.038
Final R indexes $[I \ge 2\sigma (I)]$	$R_1 = 0.1035, wR_2 = 0.2926$
Final R indexes [all data]	$R_1 = 0.1220, wR_2 = 0.3032$
Largest diff. peak/hole / e Å-3	0.99/-0.71

# Table S4. Crystal data and structure refinement for [Mg<sub>2</sub>Cl<sub>3</sub>(THF)<sub>6</sub>][HMDS<sub>2</sub>AlCl<sub>2</sub>]·THF

Empirical formula	$C_{34}H_{73}AlCl_6Mg_2NO_7Si_2$
Formula weight	952.41
Temperature/K	150.0
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	11.5604(9)
b/Å	13.8050(11)
c/Å	31.203(3)
$\alpha/^{\circ}$	90
β/°	93.357(2)
γ/°	90
Volume/Å <sup>3</sup>	4971.1(7)
Ζ	4
$\rho_{calc}g/cm^3$	1.273
$\mu/mm^{-1}$	0.477
F(000)	2028.0

Crystal size/mm <sup>3</sup>	$0.12\times0.08\times0.06$
Radiation	MoKa ( $\lambda = 0.71073$ )
$2\theta$ range for data collection/°	4.514 to 50.814
Index ranges	$-13 \le h \le 13, -16 \le k \le 16, -37 \le l \le 37$
Reflections collected	56085
Independent reflections	9138 [ $R_{int} = 0.1086$ , $R_{sigma} = 0.0968$ ]
Data/restraints/parameters	9138/483/484
Goodness-of-fit on F <sup>2</sup>	1.015
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0792, wR_2 = 0.1816$
Final R indexes [all data]	$R_1 = 0.1659, wR_2 = 0.2220$
Largest diff. peak/hole / e Å-3	0.40/-0.41



Fig. S1 The cyclic voltammogram of the Cu electrode in the OMBB electrolyte with different compositions of B(HFP)<sub>3</sub>:MgCl<sub>2</sub> 3:1 (a), 2:1 (b), 1:1 (c) and 0.5:1 (d), obtained at a scanning rate of 5 mV·s<sup>-1</sup> in a potential range of -0.8 V to 1.6 V vs. Mg/Mg<sup>2+</sup>.



Fig. S2 The comparison of coulombic efficiency for the OMBB electrolyte with different compositions of B(HFP)<sub>3</sub>:MgCl<sub>2</sub> 3:1, 2:1, 1:1 and 0.5:1.

Table S5 The systematic comparison of magnesium plating and stripping behaviors for theOMBB electrolyte with different compositions of B(HFP)3:MgCl2.

	The initial cycle			The 50th cycle		
The ratio of B(HFP) <sub>3</sub> :MgCl <sub>2</sub>	Plating overpotential (V vs. Mg/Mg <sup>2+</sup> )	Oxidative peak current (mA/cm <sup>-</sup> <sup>2</sup> )	Coulombic efficiency (%)	Plating overpotential (V vs. Mg/Mg <sup>2+</sup> )	Oxidative peak current (mA/cm <sup>-2</sup> )	Coulombic efficiency (%)
3:1	-0.72	0.17	24.32	-0.09	11.5	60.30
2:1	-0.48	11.4	91.37	-0.11	25.3	98.67
1:1	-0.75	0.088	30.51	-0.08	11.5	62.83
0.5:1	No obvious plating	No oxidation	Unavailable	-0.2	0.73	85.96



Fig. S3 ESI-MS spectrum in the negative sweep mode of the 0.5 M OMBB electrolyte.



Fig. S4 <sup>13</sup>B NMR spectra measured with the following solutions: (a) 0.5 M B(HFP)<sub>3</sub> in DME,
(b) the 0.5 M OMBB electrolyte, (c) 0.5 M solution of the crystals
[Mg<sub>4</sub>Cl<sub>6</sub>(DME)<sub>6</sub>][B(HFP)<sub>4</sub>]<sub>2</sub> in DME solvent.



Fig. S5 ORTEP plot (50% thermal probability ellipsoids) of the molecular structure of crystallized [Mg<sub>2</sub>Cl<sub>3</sub>(THF)<sub>6</sub>][HMDS<sub>2</sub>AlCl<sub>2</sub>]<sup>.</sup>THF. Hydrogen atoms are omitted for clarity.

According to the reported literatures, <sup>6, 7</sup> the crystal [Mg<sub>2</sub>Cl<sub>3</sub>(THF)<sub>6</sub>][HMDS<sub>2</sub>AlCl<sub>2</sub>] has been obtained from the Mg-HMDS based electrolyte and identified by same single-crystal XRD technique in our group as shown in Fig S5 and Table S4, which verify the accuracy of our analysis.



Fig. S6 ORTEP plot (50% thermal probability ellipsoids) of the molecular structure of crystallized [Mg<sub>2</sub>Cl<sub>3</sub>(THF)<sub>6</sub>][B(HFP)<sub>4</sub>]. Hydrogen atoms are omitted for clarity.

In order to explore the solvent influence on the active Mg cation species, solid crystals from the 0.5M OMBB/THF electrolyte have been prepared using similar method. Single-crystal XRD results (Figure S6 and Table S2) clearly show that the solid crystals compose of the common monovalent  $[Mg_2Cl_3(THF)_6]^+$  cation and the  $[B(HFP)_4]^-$  anion when THF serves as solvents. The  $[Mg_2Cl_3(THF)_6]^+$  cation is consistent with previous literatures reported by Muldoon et. al and Zhao-Karger et al. <sup>6,7</sup>



Fig. S7 ORTEP plot (50% thermal probability ellipsoids) of the molecular structure of crystallized [Mg<sub>2</sub>Cl<sub>2</sub>(DME)<sub>4</sub>][AlCl<sub>4</sub>]<sub>2</sub>. Hydrogen atoms are omitted for clarity.

The effect of counter anion on the formation of active Mg cation is also investigated via analysizing the solid crystals from 0.7 M MgCl<sub>2</sub>+AlCl<sub>3</sub>/DME electrolyte. As shown in Figure S7 and Table S3, the solid crystals contain divalent  $[Mg_2Cl_2(DME)_4]^{2+}$  cations and  $[AlCl_4]^-$  anions, which is consistent with the reported literatures. <sup>5</sup>



Fig. S8 The cyclic voltammogram of the Cu electrode in the 0.5 M OMBB/diglyme electrolyte (a) and 0.5 M OMBB/tetraglyme electrolyte (b), obtained at a scanning rate of 5 mV·s<sup>-1</sup> in a potential range of -0.8 V to 1.6 V vs. Mg/Mg<sup>2+</sup>.

The Mg plating/stripping performances of OMBB electrolytes have been examined in nonvolatile diglyme or tetraglyme (Fig. S8). The synthetic procedures of 0.5 M OMBB/diglyme electrolytes and 0.5 M OMBB/tetraglyme electrolytes are similar to the aforementioned 0.5 M OMBB electrolytes. For the 0.5 M OMBB/diglyme system, the first CV displays the reductive current associated with Mg plating starting at -0.22 V and two oxidative current peaks (1.21 mA·cm<sup>-2</sup> at 0.2 V and 1.75 mA·cm<sup>-2</sup> at 0.42 V). The overpotential for the Mg plating decreases to -0.12 V in the 10<sup>th</sup> cycle and the oxidative current density increases successively (6.67 mA·cm<sup>-2</sup> at 0.16 V and 9.2 mA·cm<sup>-2</sup> at 0.46 V). In the 0.5M OMBB/tetraglyme system, the first CV displays the overpotential for the Mg plating of -0.57 V and the oxidative peak current densities of 2.69 mA·cm<sup>-2</sup>. Similarly, the overpotential for the Mg plating decreases to -0.16 V in the 10<sup>th</sup> cycle and the oxidative current density increases to 5.48 mA·cm<sup>-2</sup> successively. The above results indicate that the OMBB electrolyte system has a wide universality toward ether solvents.







Fig. S9 Sulfur compatibility of the [Mg<sub>4</sub>Cl<sub>6</sub>(DME)<sub>6</sub>][B(HFP)<sub>4</sub>]<sub>2</sub> investigated by <sup>1</sup>H (a), <sup>13</sup>C (b) and <sup>11</sup>B (c) NMR in deuterated DMSO. <sup>1</sup>H and <sup>13</sup>C NMR were referenced to internal DMSO,









Fig. S10 shows the unchanged <sup>13</sup>C and <sup>11</sup>B NMR spectra of  $[Mg_4Cl_6(DME)_6][B(HFP)_4]_2$ after exposure to air for one week and after adding 1500 ppm water. The <sup>11</sup>H NMR spectra of the 1500 ppm water containing sample displays a weak signal of water appearing at 3.52 ppm. In view of good moisture absorption capacity from DMSO, the <sup>11</sup>H NMR spectra after exposure to air for one week also has a weak signal of water appearing at 3.52 ppm. These information demonstrate that  $[Mg_4Cl_6(DME)_6][B(HFP)_4]_2$  is air and water insensitive and the OMBB electrolyte is chemically inert to air and water.



Fig. S11 TGA-DSC profile of [Mg<sub>4</sub>Cl<sub>6</sub>(DME)<sub>6</sub>][B(HFP)<sub>4</sub>]<sub>2</sub>

The thermal stability of  $[Mg_4Cl_6(DME)_6][B(HFP)_4]_2$  crystal has been investigated by means of simultaneous TGA-DSC measurement with a N<sub>2</sub> flow at a heating rate of 10 °C·min<sup>-1</sup>. As seen in Fig. S11, the TGA-DSC profiles reveal that the compounds are stable to 90 °C. The Mg salts are decomposed at 140 °C and those decomposition products are released at 195 °C. The favourable thermal stability of this Mg salt should be attributed to the strong C–F bonds of anions.



Fig. S12 Electrochemical characterization of the Mg/S-AMC batteries: (a) the specific capacity at different charge–discharge current density; (b) galvanostatic charge–discharge profiles at different charge–discharge current density.



Fig. S13 Electrochemical characterization of the Mg/S-CMK3 batteries: (a) the specific capacity at different charge–discharge current density; (b) galvanostatic charge–discharge profiles at different charge–discharge current density.

Table S6 The fitting values of electronic elements in the equivalent circuit after different

charge-discharge cycles				
Cycle number	R <sub>0</sub>	R <sub>ct</sub>	CPE <sub>ct</sub>	CPE <sub>diff</sub>
Fresh	7.056	71.54	3.263E-5	0.02264
1	6.697	23.25	0.0002146	0.0003203
5	7.03	13.23	0.0001013	0.0003762
10	6.354	12.24	9.979E-5	0.000372
20	6.326	10.65	8.036E-5	0.0004967



Fig. S14 The cyclic voltammogram of the Cu electrode in the 0.2 M [Mg<sub>4</sub>Cl<sub>6</sub>(DME)<sub>6</sub>][B(HFP)<sub>4</sub>]<sub>2</sub>/DME electrolyte, obtained at a scanning rate of 5 mV·s<sup>-1</sup> in a potential range of -0.8 V to 1.6 V vs. Mg/Mg<sup>2+</sup>.

The Mg plating/stripping reversibility of the above obtained  $[Mg_4Cl_6(DME) _6][B(HFP)_4]_2$  crystals redissolved in DME solvent has been examined by CV measurement. As seen in Fig. S14, the obvious Mg plating/stripping behaviors occur from 1<sup>st</sup> cycle to 10<sup>th</sup> cycle, which testify the feasibility of  $[Mg_4Cl_6(DME)_6][B(HFP)_4]_2$  as the active salt of Mg electrolytes.



Fig. S15 Electrochemical characterization of the Mg/S-CNT batteries in the 0.2 M
 [Mg<sub>4</sub>Cl<sub>6</sub>(DME)<sub>6</sub>][B(HFP)<sub>4</sub>]<sub>2</sub>/DME electrolyte: (a) Galvanostatic charge–discharge profiles of different cycles at a current density of 160 mA·g<sup>-1</sup>; (b) Charge-discharge capacities and Coulombic efficiencies as a function of cycle number at a current density of 160 mA·g<sup>-1</sup>.

To further verify the performance improvement of Mg/S battery is benefited from the intrinsic active components of the OMBB electrolytes, the charge-discharge property of Mg/S-CNT battery with 0.2 M  $[Mg_4Cl_6(DME)_6][B(HFP)_4]_2/DME$  electrolyte has been examined. As shown in Fig. S15, this Mg/S-CNT battery delivers an initial discharge capacity of 892 mAh·g<sup>-1</sup> at the current density of 160 mA·g<sup>-1</sup> and remains a discharge capacity of 1032 mAh·g<sup>-1</sup> after 35 charge-discharge cycles. The excellent performances of this Mg/S-CNT battery compellingly

demonstrate the critical role of the proposed effective anion and cation species in the OMBB electrolytes on the enhancement of Mg/S batteries performance.



Fig. S16 Electrochemical characterization of the Mg/S-CNT batteries in the 0.9 M Mg-HMDS based electrolyte: (a) Galvanostatic charge–discharge profiles of different cycles at a current density of 160 mA·g<sup>-1</sup>; (b) Charge-discharge capacities and Coulombic efficiencies as a function of cycle number at a current density of 160 mA·g<sup>-1</sup>.



Fig. S17 Electrochemical characterization of the Mg/S-CNT batteries in the 0.7 M
MgCl<sub>2</sub>+AlCl<sub>3</sub> based electrolyte: (a) Galvanostatic charge–discharge profiles of different
cycles at a current density of 160 mA·g<sup>-1</sup>; (b) Charge-discharge capacities and Coulombic efficiencies as a function of cycle number at a current density of 160 mA·g<sup>-1</sup>.



Fig. S18 Electrochemical characterization of the Mg/S-CNT batteries in the 0.5 M Mg[B(HFP)<sub>4</sub>]<sub>2</sub> based electrolyte: (a) Galvanostatic charge–discharge profiles of different cycles at a current density of 160 mA·g<sup>-1</sup>; (b) Charge-discharge capacities and Coulombic

efficiencies as a function of cycle number at a current density of 160 mA·g<sup>-1</sup>.



Fig. S19 Electrochemical characterization of the Mg/S-CNT batteries in the BCM based electrolyte: (a) Galvanostatic charge–discharge profiles of different cycles at a current density of 160 mA·g<sup>-1</sup>; (b) Charge-discharge capacities and Coulombic efficiencies as a function of cycle number at a current density of 160 mA·g<sup>-1</sup>.

To confirm that the improved performance of Mg/S batteries are authentically due to the superiority of the OMBB electrolyte, we have also estimated the previously reported nucleophilic Mg electrolytes in the same battery setup, including 0.9 M Mg-HMDS based electrolyte, 0.7 M MgCl<sub>2</sub>+AlCl<sub>3</sub> based electrolyte, 0.5 M Mg[B(HFP)<sub>4</sub>]<sub>2</sub> based electrolyte and BCM based electrolyte of our group. 7-10 Expect for the electrolyte species, the S-CNT cathode with Cu current collector, Mg anode, battery structure, the amount of electrolyte and the charge-discharge current density (160 mA·g<sup>-1</sup>) are consistent. As seen in Fig. S16, the Mg/S batteries with 0.9 M Mg-HMDS based electrolyte deliver a capacity of 464 mAh·g<sup>-1</sup> for the first discharge. In the subsequent cycles, the discharge capacity badly decreased to 120 mAh·g<sup>-1</sup> and the overpotential of charge-discharge process remains at  $\sim 0.9$  V. As shown in Fig. S17, the discharge capacity of the Mg/S batteries using 0.7 M MgCl<sub>2</sub>+AlCl<sub>3</sub> based electrolyte can deliver 675 mAh·g<sup>-1</sup> in the first cycle. In the subsequent cycles, the discharge capacity gradually reduced to 138 mAh·g<sup>-1</sup>. The overcharging behavior arising from the corrosion of Cu current collector results in poor coulombic efficiency. As seen in Fig. S18 and Fig. S19, the Mg/S batteries with 0.5 M Mg[B(HFP)<sub>4</sub>]<sub>2</sub> based electrolyte and the Mg/S batteries with BCM based electrolyte also perform the inferior cycling stability and relatively larger overpotential. The above comparison data sufficiently demonstrate that the OMBB electrolyte is superior in improving the performance of Mg/S batteries.



Fig. S20 The battery performances of S-CNT cathode with Al current collector in 0.5 M OMBB electrolyte: (a) Galvanostatic charge–discharge profiles of different cycles at a current density of 160 mA·g<sup>-1</sup>; (b) Charge-discharge capacities and Coulombic efficiencies as



Fig. S21 Sulfur range XPS spectra of the fresh S-CNT cathode (a), the cycled S-CNT cathode (b) and the cycled Mg anode (c).



Fig. S22 Copper range XPS spectra of the cycled S-CNT cathode: (a) CuLM2 spectra; (b)

#### Cu2p spectra.

What's puzzling is that the aforementioned sulfur/carbon composite cathodes can perform reversible charge-discharge only on Cu current collector. As seen in Fig.S20, the S-CNT cathode with Al current collector delivers a capacity of 612 mAh·g<sup>-1</sup> for the first discharge at a current density of 160 mA·g<sup>-1</sup>, but there is barely capacity at the subsequent charge and discharge process. Our preliminary results indicate that copper current collectors play an intermediate role in activating the sluggish reaction between sulfur cathode and Mg anode. After the cycled Mg/S-CNT battery was dismantled, the cycled S-CNT cathode was analyzed by XPS measurement. The S2p spectra obtained from the cycled S-CNT cathode is compared with that of the fresh S-CNT cathode in Fig. S21. The fresh S-CNT cathode is composed of elemental sulphur and is evidenced by the S2p<sub>3/2</sub> peak located at 164.5 eV. <sup>6</sup> After the cycles, the sulphur has been reduced to lower oxidation state indicated by the lower binding energies of  $S2p_{3/2}$  peak, which proves the redox reaction between magnesium and sulfur during charge-discharge process. It is worth noting that the oxidation state of Cu element in the cycled S-CNT cathode has changed dramatically. As illustrated in Fig. S22, the Cu2p peaks have manifested the appearance of Cu on the surface of active S-CNT materials, and these Cu elements exhibit different oxidation states indicated by various CuLM2 Auger peaks. According to the previous work of Mg/Se battery in our group, <sup>9</sup> we speculate that Cu current collectors have a huge role on the performance improvement of Mg/S battery by forming certain  $Cu_x S_y$  intermediates. The detailed reasons are being investigated further.

### **Reference:**

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