Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information for

A Robust Ionic Liquid Magnesium Electrolyte Enabling Mg/S Batteries

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Experiment Procedures

Materials

Sulfur (S_8, sublimated), magnesium chloride ($MgCl_2$, 99.99%), aluminum chloride ($AlCl_3$, 99.999%), N-and methyl pyrrolidone (NMP, 99.5%) were purchased from Sigma-Aldrich. Magnesium powder (325 mesh, 99.8%) and molybdenum foil (99.95%) were purchased from Alfa-Aesar. 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Pyr14TFSI, 98%) was purchased from TCI America, carbon black, and polyvinylidene fluoride (PVdF) were ordered from MTI. Carbon fiber paper (CFP, Sigracet 28 BC) was purchased from Fuel Cell Store. All materials were used as received.

Preparation of $Mg/MgCl_2/AlCl_3$- Pyr14TFSI (MMAC-IL) Electrolytes

$Mg/MgCl_2/AlCl_3$ (1:1 ratio) in DME (MMAC) was prepared as we reported.[1] 1,2-dimethoxyethane (DME, 99%) was purchased from TCI America, it was purified by distillation with sodium metal and stored with dried 3 Å molecular sieve before used to prepare electrolyte. The purchased Pyr14TFSIT was packaged by Nitrogen filled warp. It was directly transferred to glove box and used for electrolyte preparation without purification. To prepare the electrolyte with the ionic liquid additive, 95.2 mg of $MgCl_2$ was dissolved in 1.0 mL Pyr14TFSI and 1.0 mL DME mixed solvent. 133.3 mg of $AlCl_3$ was slowly added into the solution, and then 20 mg Mg powder was added. The prepared electrolytes (0.5 M) were stirred and heated at 50 ^oC for 6 hours. After cooling down to the room temperature, the electrolyte was filtered and used for other tests. All operations were conducted in an Argon filled glovebox where both O_2 and H_2O were below 0.1 ppm.

Preparation of CMK/S Cathodes

Cathode material, ordered mesoporous carbon (CMK, ACS Material LLC) was oxidized in nitric acid at 80 ^oC for 2 hours (0.1mg CMK in 100 mL nitric acid), then rinsed with deionized H_2O, and dried in vacuum oven at 80 ^oC overnight. Thermal diffusion method was used to prepare carbon and sulfur composite cathode material. Oxidized CMK and sulfur was grinded at 1:1 mass ratio and sealed into a hydrothermal autoclave in an Ar filled glovebox. After heating at 155 ^oC for 12 hours, the autoclave was transferred to the Ar filled glovebox directly to avoid moisture absorption.

SEM, XRD, XPS, and TGA Characterization

Scanning electron microscopy (SEM) measurement was conducted on a FEI Quanta 650 (FEI, USA) with EDS at the Microscopy Core Facility of Utah State University (WD 10mm, voltage 10-20 kV). X-ray diffraction (XRD) patterns were collected on a Rigaku Minifexll Desktop X-ray diffractometer.

Thermogravimetry (TG) was tested from room temperature to 700 ^oC at 10 ^oC/min rate under N_2 atmosphere.

Electrochemical tests

Cyclic voltammetry (CV), Linear sweep voltammetry (LSV), and chronoamperometry (CA) tests were conducted on Gamry 1000E or 5000. Conductivity of electrolytes (2 mL in a 5 mL vial) was measured using a Mettler Toledo conductivity meter. Galvanostatic charge and discharge was operated on a Landt battery tester. Mg-S coin cells were rested for 12 hours, and then activated at 50 mA/g current density 3-5 cycles before long cycling tests.

CMK/S, PVdF, and carbon black were used to prepare the sulfur electrode at the ratio of 8:1:1 in NMP solvent. After stirring for 6 hours, the slurry was casted on a piece of carbon fiber paper (CFP), and then dried at 60 °C for 12 hours. The coated carbon fiber paper was pouched to φ3/8inch discs as cathodes in magnesium sulfur batteries (sulfur loading is ~0.5 mg/cm^2). Then the punched discs were heated 80 °C under vacuum for 2 hours to remove absorbed moisture and then transferred to an Ar glovebox quickly. 60 μL electrolyte was used for coin cell assembling. In order to avoid the corrosion of the SS current collector, a piece of Mo foil was placed at the bottom of the cathode shell. Mg foil (GalliumSource, 99.9%) was polished by sandpaper and used as anode. Glass fiber (GF/A, whatman) was used as a separator.

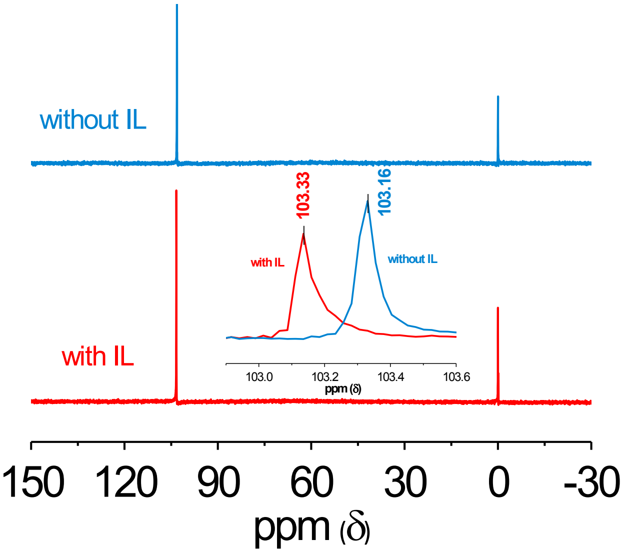

Figure S1. Comparison of ^{27}Al NMR spectra of **MMAC-IL** (red) and MMAC (blue).

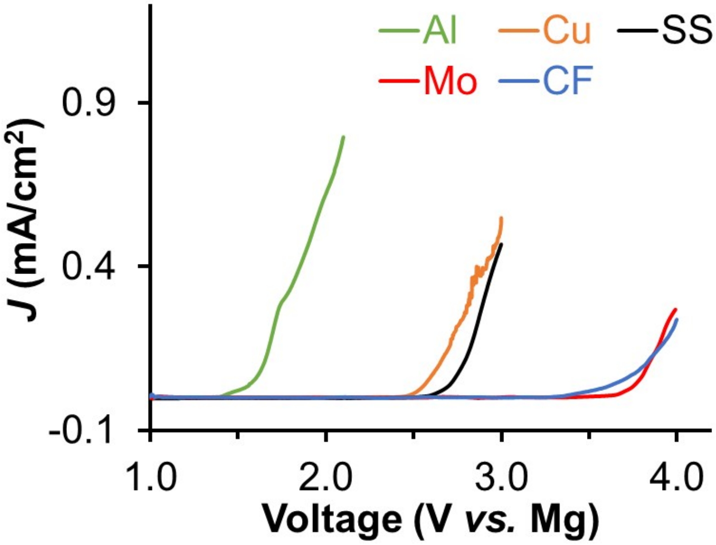

Figure S2. Linear sweep voltammograms of **MMAC-IL** using a coin cell setup (only adding 30 μL electrolyte). Anode is an Mg metal disc. Al, Cu, and Mo foil was put at the cathode side. SS was used cathode shell directly. During CF test, and a piece of Mo foil was put at the bottom. Scan rate, 1.0 mV/s.

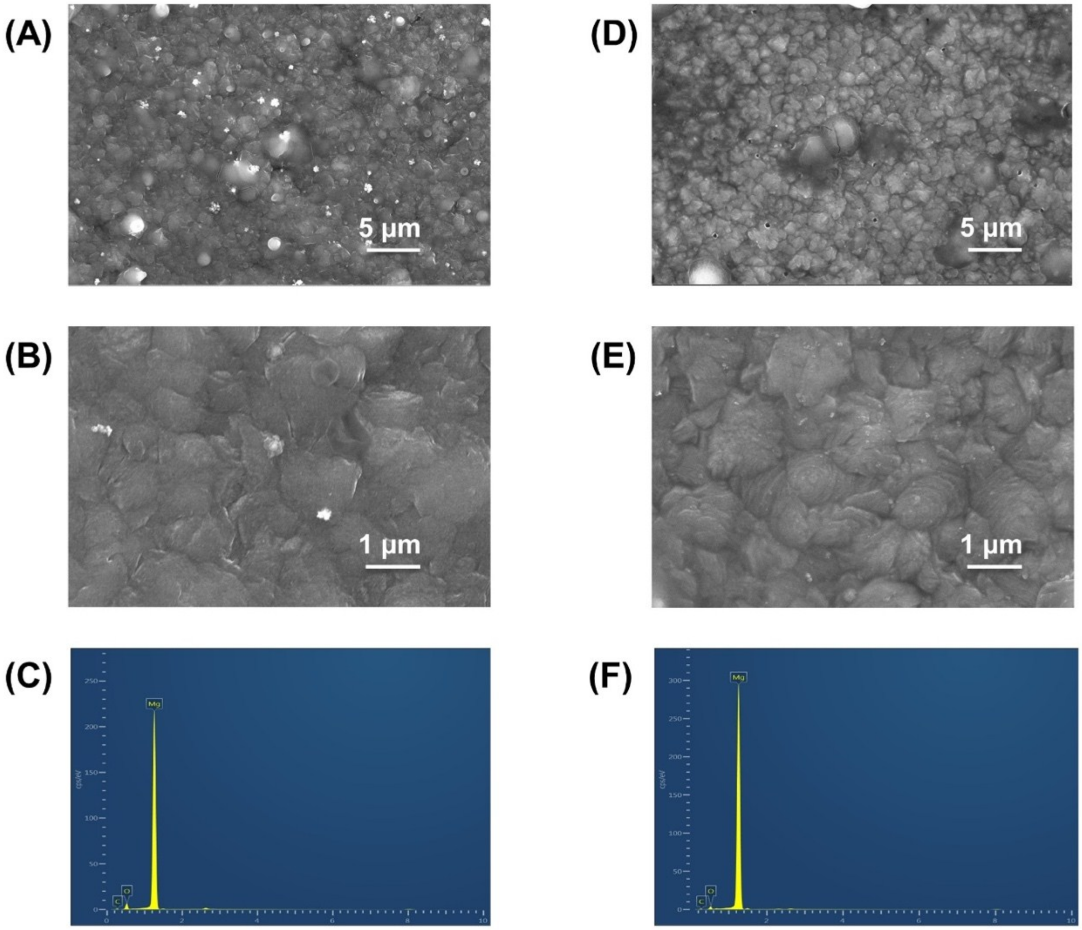

Figure S3. Electrochemical deposited Mg. (A), (B) SEM image and (C) EDS spectrum of deposited Mg using the MMAC DME electrolyte. (D), (E) SEM image and (F) EDS spectrum of deposited Mg using the **MMAC-IL** DME electrolyte.

Mg was deposited on glass carbon via chronoamperometry at 1.0 mA/cm^2 current density for 1 h. No matter with or without Pyr14TFIS ionic liquid in electrolyte, no Mg dendrite was observed in the deposited Mg as shown in the Fig S3. When Pyr14TFSI was used in electrolyte, the deposited Mg was denser and the primary Mg particle is smaller than the sample prepared in electrolyte without IL. Considering the cation concentration of **MMAC-IL** is higher than the electrolyte without IL, as well as the reduction stability of Pyr14$^+$ cation, it could help to stabilize and reduce the size of Mg particles. Little carbon and oxygen should be aroused by the short time exposure when transferring the tested samples from the glove box to the SEM chamber.

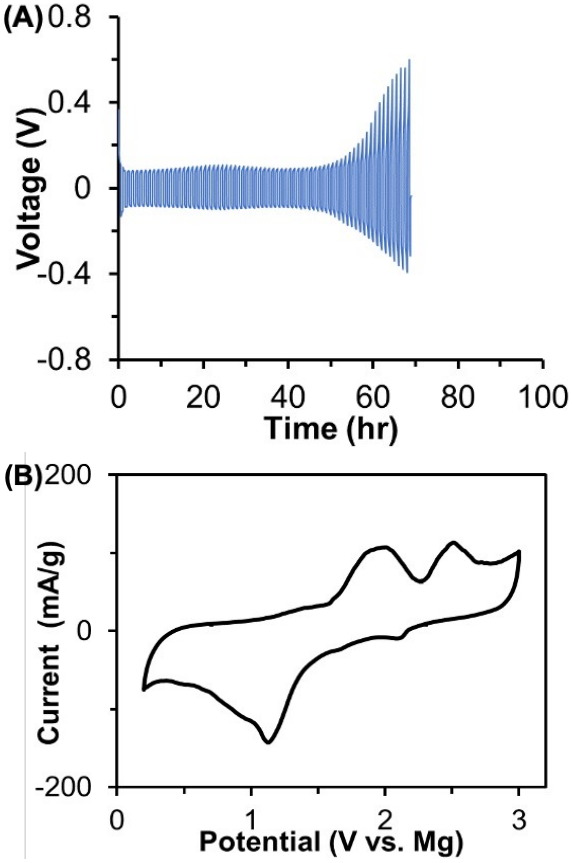

Figure S4. (A) Polarization of Mg platting/stripping in Mg|Mg symmetric cell using the MMAC electrolyte without Pyr14TFSI ionic liquid at 0.1 mA/cm^2. (B) Cyclic voltammogram of the CMK/S cathode in the Mg-S battery using the MMAC electrolyte without Pyr14TFSI ionic liquid at a scan rate of 50 uV/s.

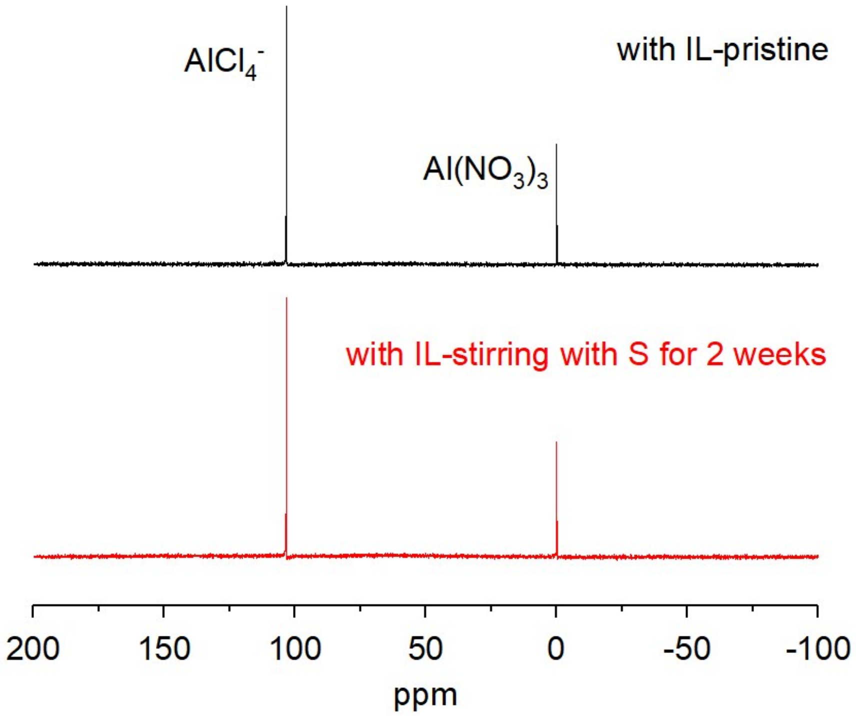

Figure S5. ^{27}Al NMR spectra of 0.5 M **MMAC-IL** before (black) and after (red) stirring with sulfur for 2 weeks.

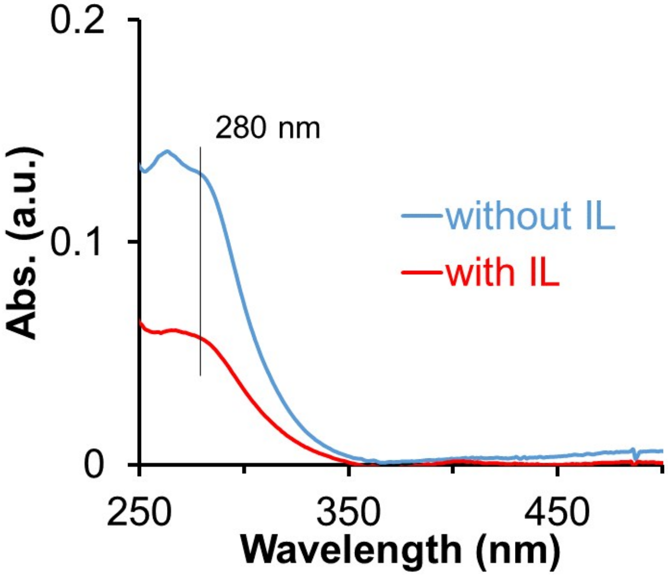

Figure S6. UV-vis spectra of sulfur saturated Mg electrolytes. The prepared Mg electrolytes with and without Pyr14TFSI were stirred with 0.2g/mL sulfur at room temperature for 2 weeks. After filtration, the obtained solutions were diluted to 50 mM using dried DME solvent for UV-vis tests. During tests, diluted pristine MMAC was used as background. Sulfur solubility in ionic liquid electrolyte is much lower than the electrolyte just using DME as solvent.

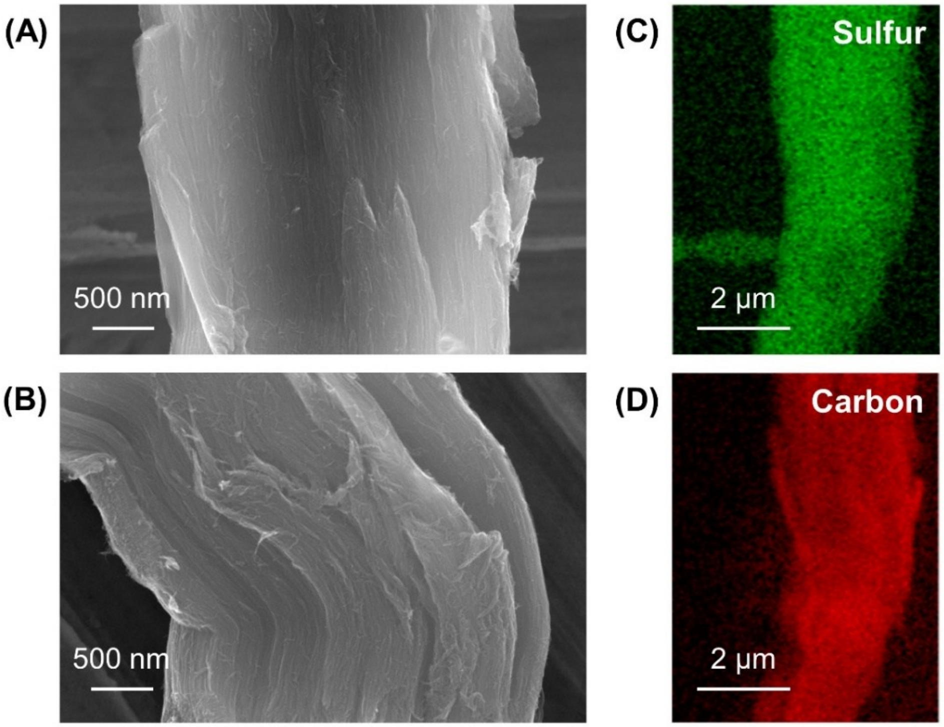

Figure S7. (A) SEM image of pristine CMK material. (B) SEM image of CMK/S composite cathode material. (C), (D) Sulfur and carbon mapping results of CMK/S cathode material by EDS.

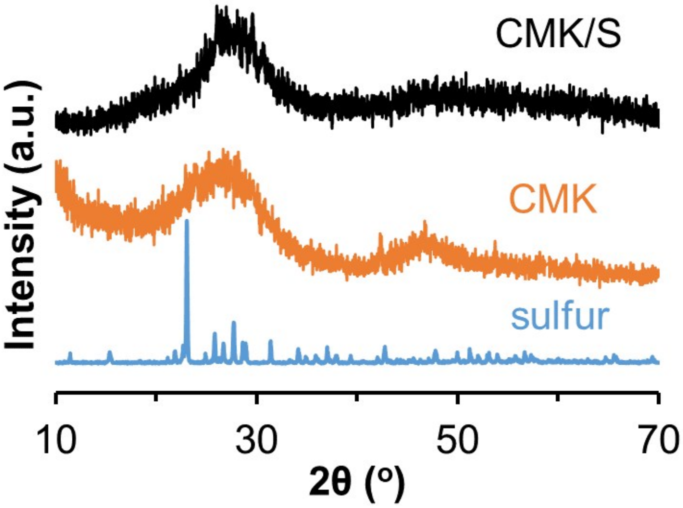

Figure S8. X-ray diffraction patterns of CMK/S composite compared with sulfur and CMK material.

The powder X-ray diffraction of the CMK/S composite has broad diffraction peak which is similar with pristine CMK. At same time, it indicates that sulfur is uniformly distributed in mesoporous of CMK.

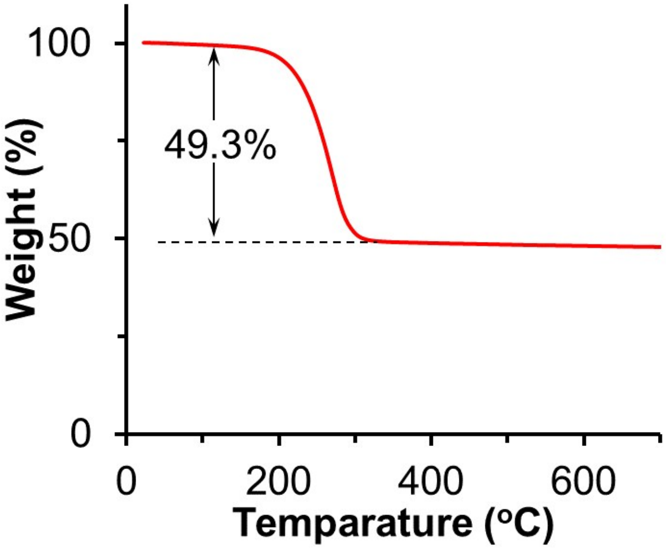

Figure S9. TGA curves of the CMK/S composite recorded in N_2 with a heating rate of 10 °C/min. From the TGA result, the sulfur loading is 49.3% after heat diffusion treatment.

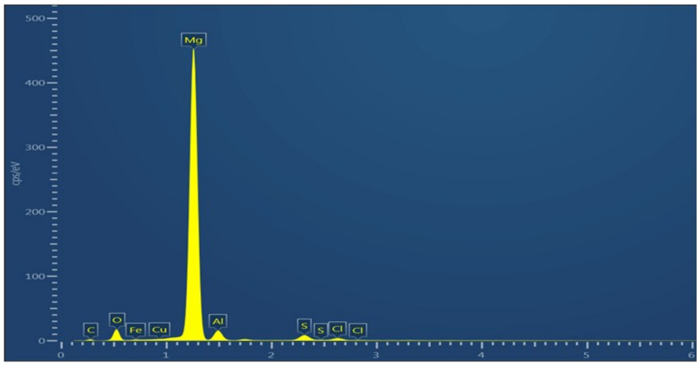

Figure S10. Post EDX-analysis of Mg anode after cycling tests using the MMAC electrolyte without ionic liquid.

Table S1. A general comparison of Mg-Cl complex electrolytes

	traditional Mg-Cl electrolytes[2]	1st-Gen $MgCl_2/AlCl_3$ (**MAC**)[3]	2nd-Gen $MgCl_2/AlCl_3$ (**MMAC**)[1, 4]	3rd-Gen $MgCl_2/AlCl_3$ (**MMAC-IL**)this work
Mg sources:	reactive nucleophilic RMgX or MgR2 (R =aryl or alkyl)	$MgCl_2$	$MgCl_2$	$MgCl_2$
Lewis acids	AlR_XCl_{3-x} and AlR_XCl_{3-x}; note: when R is present, Lewis acids are highly reactive and even pyrophoric.	$AlCl_3$: Low cost, non-pyrophoric	$AlCl_3$: Low cost, non-pyrophoric	$AlCl_3$: Low cost, non-pyrophoric

Synthesis	Require carefully control reaction conditions (free of O_2 and water); Require recrystallization to remove impurities	Require carefully control reaction conditions (free of O_2 and water); No need of recrystallization	Less than sensitive to water and O_2 with conditioning treatment; No need of recrystallization;	Less than sensitive to water and O_2 with conditioning treatment; No need of recrystallization
Anodic stability	ca. 2.5 V	3.4 V	3.6 V	3.6 V
Cathodic Stability	Not fully proved	Not fully proved	Not stable	Stable
Reversibility (Columbic efficiency)	Up to 100%	94%	Up to 100%	Up to 100%
Conductivity	7.0 mS/cm	0.26 mS/cm	5.9 mS/cm	15.5 mS/cm
Sulfur compatibility	No	Yes	Yes	Yes
Suppress sulfur shuttle	No	No	No	Yes

[1] J. Luo, S. He, T. L. Liu, *ACS Energy Lett.* **2017**, *2*, 1197-1202.

[2] S. He, K. V. Nielson, J. Luo, T. L. Liu, *Energy Storage Materials* **2017**, *8*, 184-188.

[3] T. Liu, Y. Shao, G. Li, M. Gu, J. Hu, S. Xu, Z. Nie, X. Chen, C. Wang, J. Liu, *J. Mater. Chem. A* **2014**, *2*, 3430-3438.

[4] C. J. Barile, E. C. Barile, K. R. Zavadil, R. G. Nuzzo, A. A. Gewirth, *J. Phys. Chem. C* **2014**, *18*, 27623–27630.