Supporting Information

Zinc Blende Magnesium Sulfide in Rechargeable Magnesium-Sulfur Batteries

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SI. 1 Experimental Details

Materials used in this study are listed below. Cathodes and anodes for magnesium sulfur batteries used in this study are summarized in Table S1, whose cell performances are shown in Figure S3. Other experimental details are described in this section.

Materials

Sulfur (S): 99.999%, Wako
Sulfur isotope (^{33}S): 99.8%, ISOFLEX USA
Magnesium sulfide (MgS): 99.9%, Aldrich
Ketjen black (KB): Lion, EC600JD
Acetylene black (AB): Denka Co. Ltd.
polytetrafluoroethylene (PTFE): Fluon®PTFE CD1E, AGC Inc.
Styrene butadiene rubber (SBR): TRDA104, JSR
Carboxymethyl cellulose (CMC): BSH-6, DKS Co. Ltd.
Ni mesh: 100 mesh, Nilaco
Ni foil: 0.008mm thick, Aldrich
Magnesium (Mg 0.2mm): 0.2mm thick, RIKAZAI CO.,LTD.
Magnesium (Mg 0.05mm): 0.05mm thick, Goodfellow
Glass Fiber filter (Separator): GC-50, Advantec
Magnesium chloride (MgCl2): anhydrous, 99.99%, Aldrich
Ethyl n-propyl sulfone (EnPS): anhydrous, >99%, Tomiyama Pure Chemical Industries, Ltd.

Table S1 Cathodes and anodes used in this study

#	Fig.#	Cathode						Anode
		Active Material	Carbon	Binder	Current Collector	Form	S mg/cm^2	
1	1b, S2, S3a, S3c	S 10wt%	KB 84wt%	PTFE 6wt%	Ni mesh	Pellet	0.57	Mg 0.2mm
2	1b	MgS 10wt%	KB 84wt%	PTFE 6wt%	Ni mesh	Pellet	-	Mg 0.2mm
3	2, S3a,S3b	S 10wt%	AB 84wt%	PTFE 6wt%	Ni mesh	Pellet	0.57	Mg 0.2mm
4	3a	S 20wt%	AB 74wt%	PTFE 6wt%	Ni mesh	Pellet	0.58	Mg 0.2mm
5	4, S3b, S4a, S5	S 48.8wt%	AB 48.8wt%	SBR 2wt% CMC 0.4wt%	Ni foil	Sheet	0.57	Mg 0.05mm
6	3b, S3c,S4b	S 48.8wt%	KB 48.8wt%	SBR 2wt% CMC 0.4wt%	Ni foil	Sheet	0.69	Mg 0.2mm
7	5a, 5b, S6	S 24.4wt% ^{33}S 24.4wt%	KB 48.8wt%	SBR 2wt% CMC 0.4wt%	Ni foil	Sheet	0.69	Mg 0.2mm

Pellet cathode preparation

After 10 minutes mixing of active material and conductive carbon with mortar and pestle, PTFE was added to the mixture, and then everything was mixed with some acetone for 10 minutes. Obtained mixture was put between a pair of Capton polyimide films, and stretched to make a 150 μm-thick cathode sheet using a roll press, followed by a drying in vacuum at 70°C for 12 hours. Finally 15mm ϕ pellets were punched out from the sheet, and them pressed with Ni mesh (15 mm ϕ) using a hydraulic press under 30 kPa. All the procedures were performed in a dry room where the dew point was below -50°C.

Sheet cathode preparation

After mixing the active material and conductive carbon with mortar and pestle for 10 minutes, the mixture was transferred to a vial together with SBR, CMC, water, and ethanol, where the latter two were used to control the viscosity. The mixture was stirred for 5 minutes using a pencil mixer to form slurry. Then the slurry was coated on a Ni film with a bar coater whose gap was set to 150 μm. The coated cathode was dried in vacuum at 40°C for 12 hours, and then, dried again in a dry room at 70°C for 30 minutes. The obtained sheet was punched to form 15 mm ϕ, or cut as 80 × 80 mm^2 to be used for cathodes.

Electrolyte preparation

In an Ar filled glovebox, $MgCl_2$ and EnPS was sealed in a PFA jar (Savillex) with a molar ratio of $MgCl_2$/EnPS=1/8. Then, Mg electrolyte was obtained by stirring on a hotplate at 150°C for 12 hours.

Sample preparation for XPS, XAFS, and XRD measurements

Coin cells 2016 consisting of 15mm ϕ-cathode, 19 mm ϕ-separator, 15 mm ϕ-polished Mg metal, and 200 μL-electrolyte were crimped in a glovebox. Cathodes were obtained by disassembling the cells after discharging or charging with 0.1C (*I*=0.1 mA). Samples were prepared by washing cathodes with EnPS for 30 seconds, and subsequently with toluene for 30 seconds, and then dried in a glovebox.

In this study, “pristine” means the cathode without assembling that does not involve any Mg electrolytes, while “assembled” means the one being disassembled after cell-crimping without discharging, which means it contains some Mg electrolytes even after washing treatment.

Operando cell preparation for TXM measurements

Assembling 15mm ϕ-sheet cathode (#5 in Table S1), 19mm ϕ- separator, 15mm ϕ polished Mg anode together with Ni tabs as electrodes, polyester pouch cells were prepared. After introducing Mg electrolytes, cells were heat-sealed in a glovebox. In the operando measurement in Figure 4, discharging current was set to *I*=0.1 mA (0.1C), while charging one was *I*=0.2 mA (0.2C) due to the lack of experimental time.

Sample preparation for HE-XRD, and NMR measurements

Assembling sheet cathode (80x80 mm^2, #6 or #7 in Table S1), GC-50 separator (100x100 mm^2), polished Mg anode (90x90 mm^2) together with Ni tabs as electrodes, aluminum laminate pouch cells (120x120 mm^2) were prepared. Subsequently Mg electrolytes were injected, and then, cells were heat-sealed in a glovebox. After discharging or charging with 0.05C, cathodes were obtained by disassembling the cells in a glovebox. Samples were collected by scratching out from the current collectors, and then, dried in vacuum for 24 hours without any washing treatment. Obtained samples were sealed in 2mm ϕ glass capillaries for HE-XRD, or zirconia 4mm rotors for NMR.

SI. 2 Electrochemistry

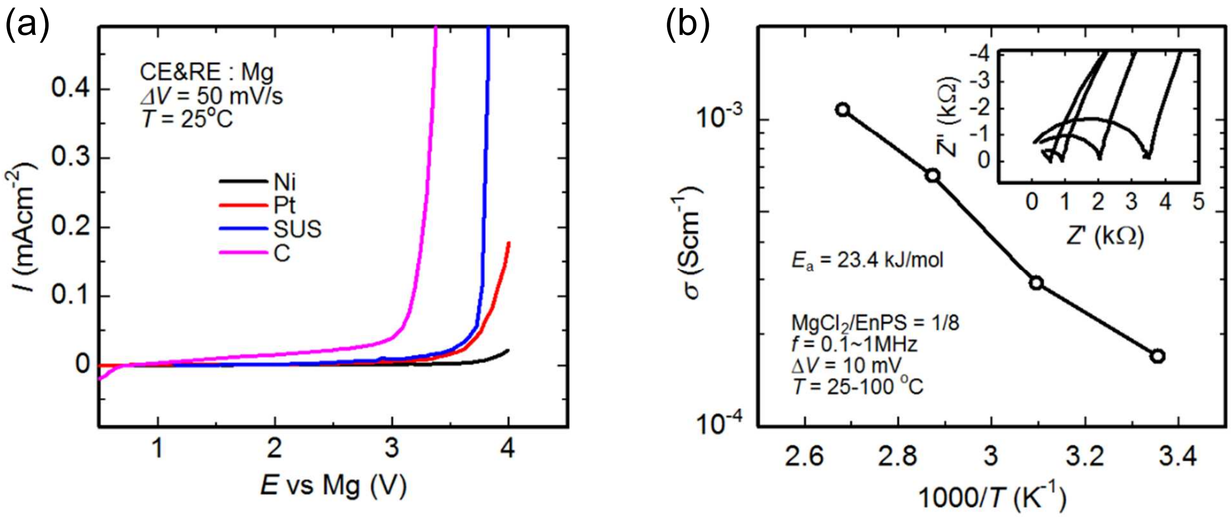

Figure S1. Electrochemical windows and ionic conductivities of MgCl2/EnPS=1/8(mol). a) Linear sweep voltammetry's for MgCl2/EnPS=1/8(mol) with various working electrodes, Ni, Pt, stainless (SUS), and carbon (C). b) Ionic conductivities of MgCl2/EnPS=1/8(mol) as a function of temperatures. Inset shows the cole-cole plots observed at various temperatures, T=25, 50, 75, and 100°C.

SI. 3 Discharge and charge profiles of Mg-S batteries

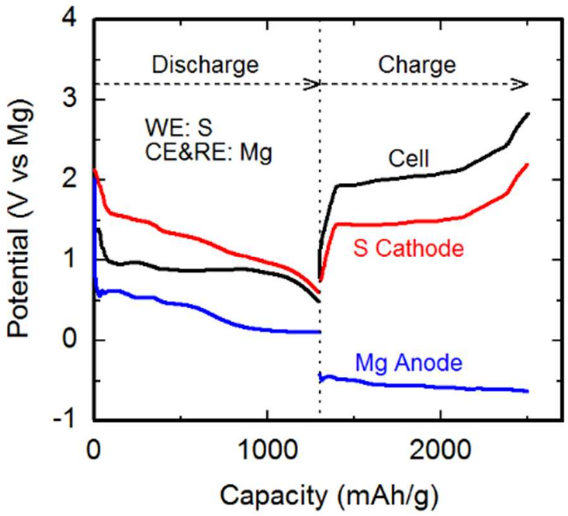

Figure S2 Discharge and charge profile of Mg-S battery observed by 3 electrode cell, where Mg is used as both reference and counter electrodes, while sulfur cathode is used as working electrode. Large over potential of this system is caused by that of Mg anode.

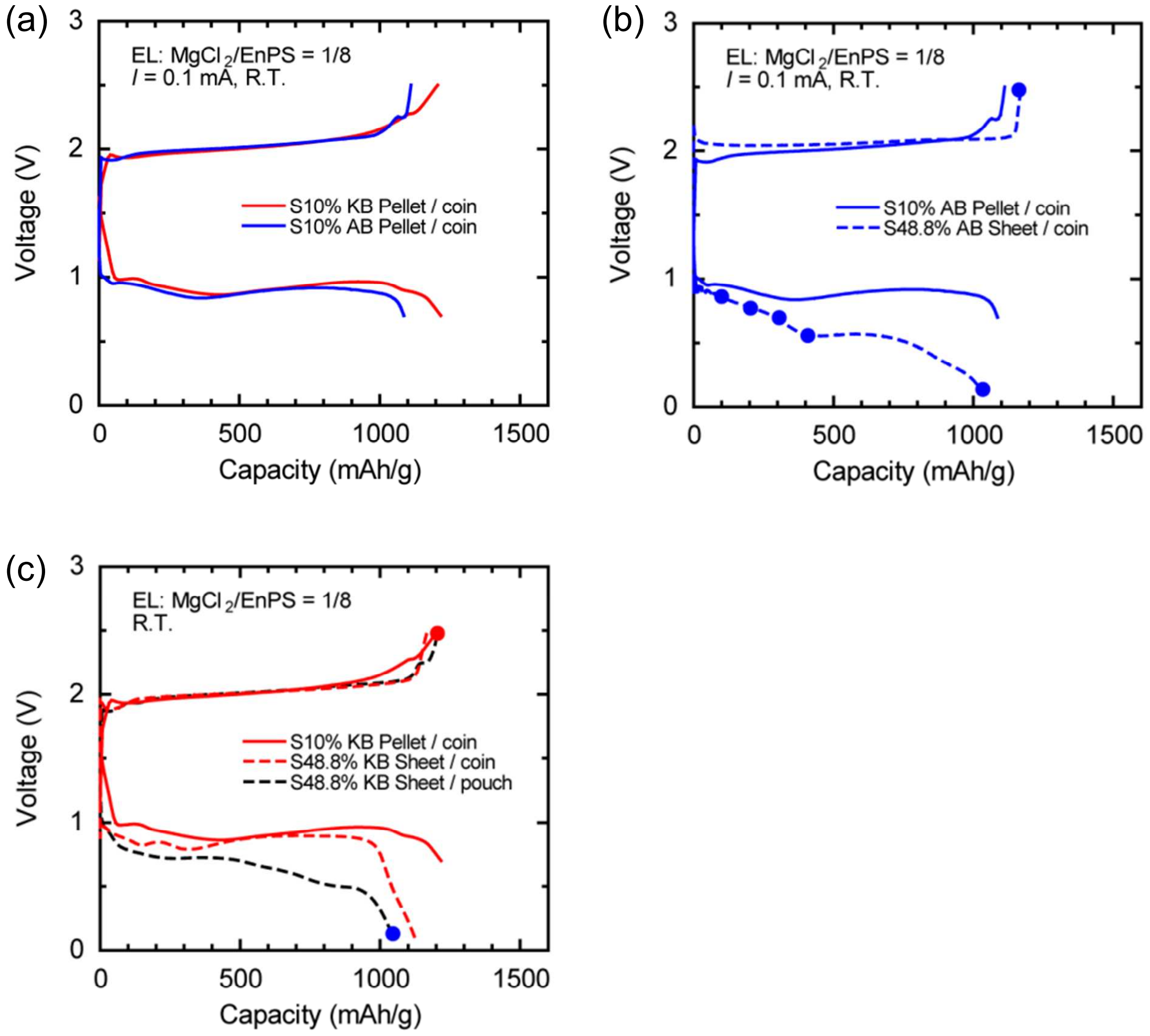

Figure S3 Discharge and charge profile of Mg-S batteries with various cathodes. a) Comparison of conductive carbons between KB and AB. b) Comparison between sulfur 10wt% pellet and 48.8wt% sheet cathodes with AB. Blue dots describe the points where XRD was measured in Figure S4a. c) Comparison between sulfur 10wt% pellet (red, solid line) and 48.8% sheet (red, broken line) cathodes with KB and coin cells. Black broken line shows the pouch cell with sulfur 48.8% KB cathodes. Note that pouch cells were tested with lower rates (0.05C) than that for coin cells (0.1C) to escape from their large impedance. Blue and red dots describe the point where HE-XRD was measured in Figure 3b and S4b.

SI. 4 XRD of sulfur cathodes

To investigate the peak disappearance in Figure 3a, ex-situ XRD measurements for sulfur cathodes (#5 in Table S1) with various depth of discharge were performed, whose results are shown in Figure S4a. Measured points on the discharge and charge curves are described in Figure S3b as blue dots. Incident X-ray power was 40 keV and 40 mA, and the acquisition time was 0.5 seconds for each 0.02^{o}/step between 2 θ = 15-45^{o}. Here we can see that Bragg diffraction peaks corresponding to sulfur crystal disappear above discharge capacity of 300 mAh/g. When the cell was kept at OCV without discharging even for longer time (4h OCV), the cathode still show the Bragg peaks, indicating that discharge accelerate the peak disappearance.

HE-XRD measurements were performed for sulfur cathodes (#6 in Table S1, blue and red dots in Figure S3c) with higher X-ray energy (61.4 keV) for longer acquisition time (90 seconds for each 0.1^{o}/step). Figure S4b shows the angle-dispersive data of HE-XRD, where we cannot see any Bragg peaks, suggesting that no ordered structure exists in these cathodes.

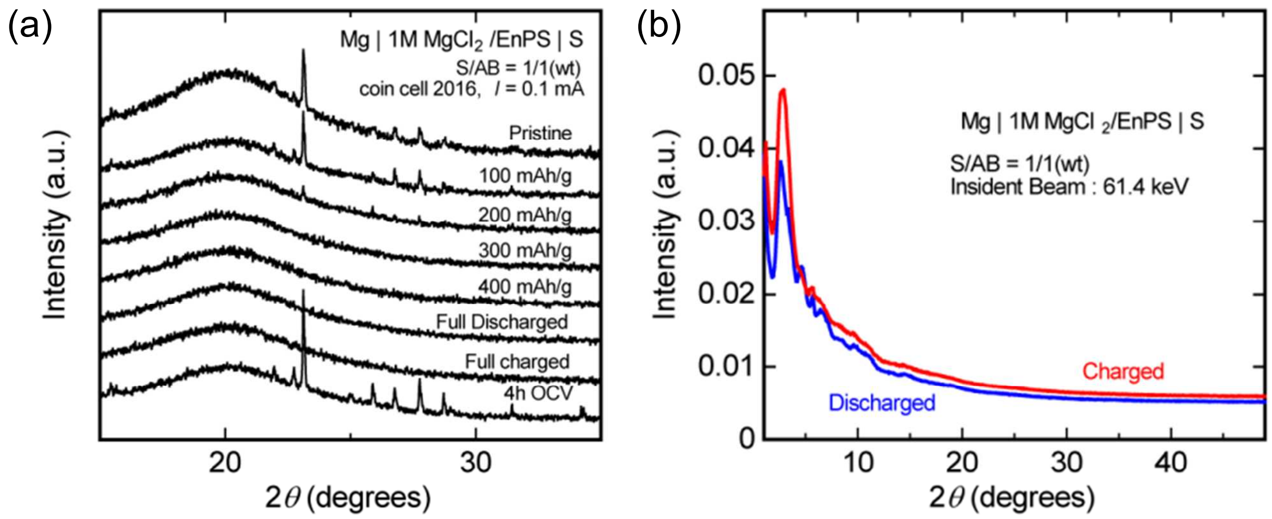

Figure S4 a) XRD patterns of sulfur cathodes with various depth of discharge. b) HE-XRD patterns for fully discharged (blue) and charged (red) sulfur cathodes.

SI. 5 TXM images

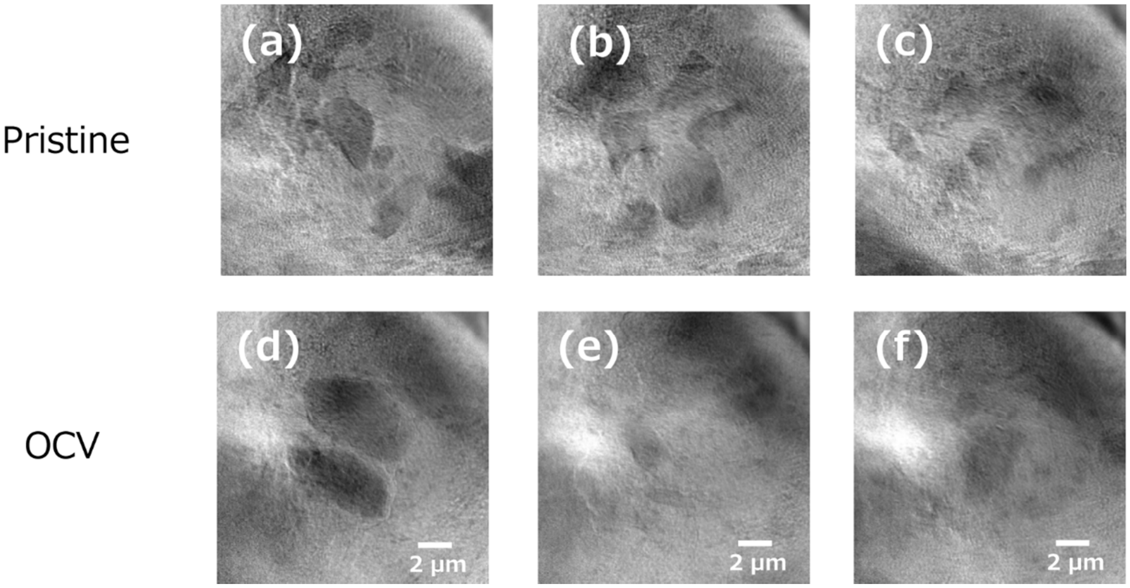

Figure S5. Ex-situ TXM images for pristine and OCV-stored sulfur composite cathodes of Mg-S batteries. a)-c) Three images for pristine sulfur composite cathodes. d)-f) Three images for sulfur composite cathodes that have been stored for 6 hours at open circuit voltages (OCV). Note that cathode discharged for 5.5 hours does not show any particles (Figure 4d, 550mAh/g). As several particles are still observed in OCV-stored cathodes, it is obvious that discharge process accelerates the particle dissolutions.

SI. 6 NMR spectra

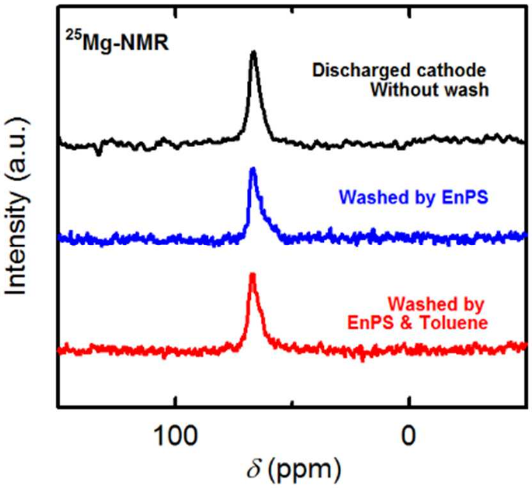

Figure S6. Ex-situ ^{25}Mg MAS-NMR spectra for discharged cathodes with various preparation process. Cathode without any wash (black) shows a peak corresponding to ZB-MgS, while those with washing treatments (blue, red) show the same peaks, indicating the chemical stability of discharge reaction product ZB-MgS.