

## **Realizing high-stability anode for rechargeable magnesium battery via in-situ-formed nanoporous Bi and nanosized Sn**

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### **1 Experimental methods**

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## 1.1 Material synthesis

The  $\text{Bi}_2\text{Sn}_2\text{O}_7$  (BSO) sample was prepared according to previous reports <sup>1</sup>. The obtained BSO particles were heated at 600 °C for 3 h under a mixed gas flow of 95% Ar and 5%  $\text{H}_2$  atmosphere to prepare Bi-Sn@ $\text{SnO}_2$ -600 (BSS-600) alloys. The Bi-Sn@ $\text{SnO}_2$ -400 (BSS-400) and Bi-Sn@ $\text{SnO}_2$ -500 (BSS-500) alloys were prepared under the heated temperature was 400 °C and 500 °C with the same process, respectively.

## 1.2 Alloy characterization

$\text{N}_2$  adsorption isotherms and pore size distributions were obtained at 77 K using a Micromeritics ASAP-2460 instrument. X-ray diffraction (XRD) measurements were carried out in a PANalytical X'Pert Powder instrument (Spectris Pte. Ltd, Netherlands) using  $\text{Cu K}\alpha$  radiation with a step size of  $0.026^\circ$  and a scanning speed of  $4^\circ$  per minute. X-ray photoelectron spectroscopy (XPS) was collected on an X-ray photoelectron spectrometer (Thermo Scientific K-Alpha, USA). All the high-resolution spectra were calibrated by referencing the binding energy of C 1s as 284.8 eV. The morphology and microstructure of the as-prepared samples were characterized by JEOL JSM-7800F scanning electron microscopy and transmission electron microscopy (TEM, FEI Talos F200S).

## 1.3 Electrochemical measurement

*Electrolyte preparation.* 0.4 M all phenyl complex (APC) in THF solution was prepared according to previous reports <sup>2</sup>. The obtained 0.4 M APC solution was used as the electrolyte for all half-cell experiments. For the preparation of 0.4 M  $\text{Mg}(\text{TFSI})_2/\text{G2}$  electrolyte, 0.935 g  $\text{Mg}(\text{TFSI})_2$  (99%, DoDoChem) was dispersed in 4 mL G2 (99.5%, water  $\leq 50$  ppm, MkSeal). The 4 Å molecular sieves (1-1.6 mm, Aladdin) were added to the  $\text{Mg}(\text{TFSI})_2/\text{G2}$  electrolyte overnight before use. All operations are carried out in the Ar-filled glove box with water and oxygen less than 0.01 ppm.

*Cell fabrication and measurements.* The electrodes were prepared by mixing active materials (70 wt %), acetylene black (20 wt %), and poly (vinylidene fluoride) (PVDF, 10 wt %) using N-methyl-2-pyrrolidone (NMP) solvent. The above slurry was coated onto the stainless steel (SS) foil. The film was dried at 80 °C for 12 h to evaporate NMP in a vacuum oven. Electrode disks (diameter: 10 mm) were then cut out and the active material mass per electrode was about 1-2 mg cm<sup>-2</sup>.

For half cells, Mg//Bi-Sn@SnO<sub>2</sub> CR2032 coins were assembled in an Ar-filled glove box to evaluate the electrochemical performance, using polished Mg foils as both the counter and reference electrodes and glass fiber (GF/A) as the separator. Galvanostatic discharge/charge tests were conducted using the Neware battery test systems at various current densities between 0.005 and 1 V (vs. Mg<sup>2+</sup>/Mg) at room temperature. Cyclic voltammogram (CV) studies were performed at a potential window of 0-1 V (vs. Mg<sup>2+</sup>/Mg) on a CHI660E electrochemical workstation (CH instrument, USA) with the desired scan rate. For *ex-situ* XRD and XPS characterization, the Mg//BSS-600 cells at different states during cycling were disassembled, and then the cycled BSS-600 electrodes were washed with THF before tests.

For full cells, Mo<sub>6</sub>S<sub>8</sub> cathode and V<sub>2</sub>O<sub>5</sub>-PAN were synthesized following previously published work<sup>3,4</sup>. Galvanostatic discharge/charge experiments of cathode were run using a pre-magnesiated BSS-600 anode in 0.4 M Mg(TFSI)<sub>2</sub>/G2 electrolytes at the current density of 50 mA g<sup>-1</sup> (calculated by Mo<sub>6</sub>S<sub>8</sub> or V<sub>2</sub>O<sub>5</sub>-PAN mass). The BSS-600 anodes were electrochemically pre-magnesiated by half-cell complete discharge. Magnesiated anodes were washed with THF prior to use and then dried in the glove box. The Mg//Mo<sub>6</sub>S<sub>8</sub> and Mg//V<sub>2</sub>O<sub>5</sub>-PAN full-cells were assembled using 0.4 M APC electrolytes as a control.

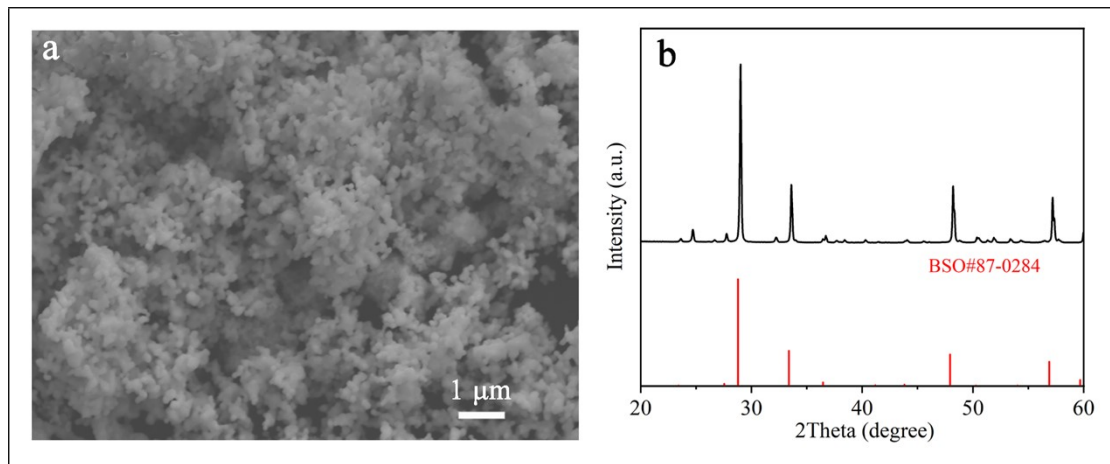


Fig. S1 (a) SEM image and (b) XRD pattern of the BSO annealed at 800 °C for 3 h in Ar atmosphere.

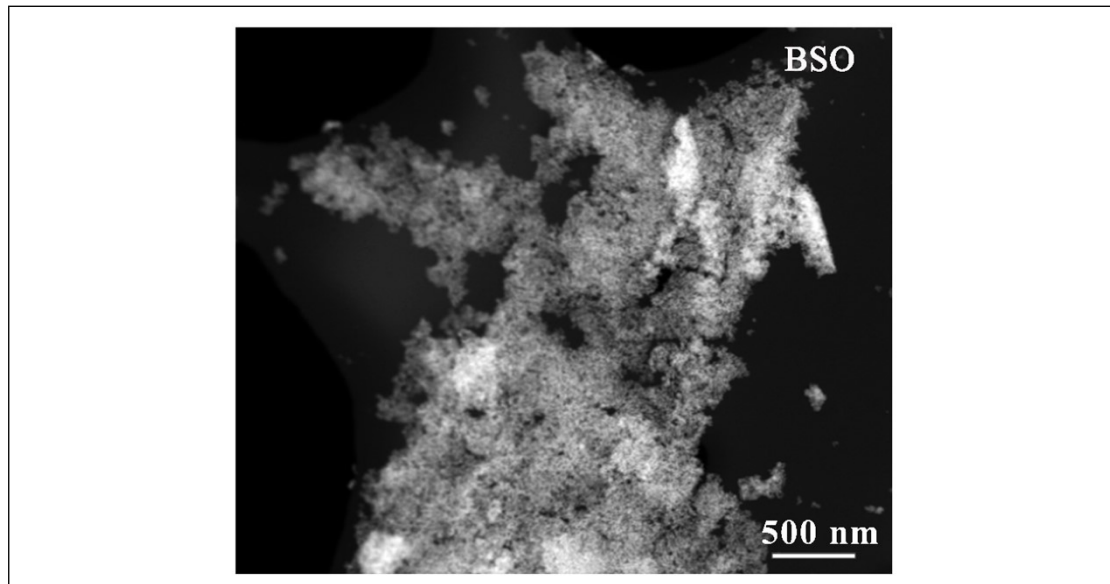


Fig. S2 High-angle annular dark-field scanning TEM (HAADF-STEM) of BSO.

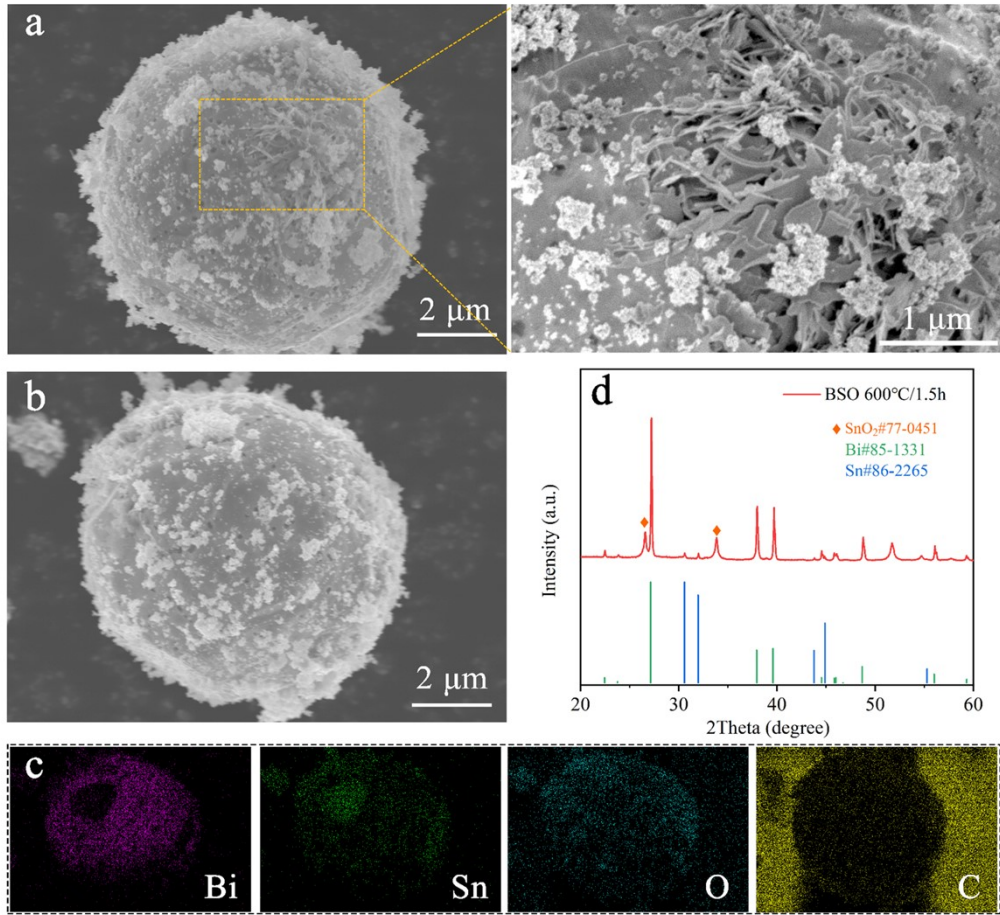


Fig. S3 (a-c) SEM image and elemental mappings of BSO particles annealed at 600 °C for 1.5 h in 95% Ar and 5% H<sub>2</sub> atmosphere; (d) corresponding to XRD pattern.

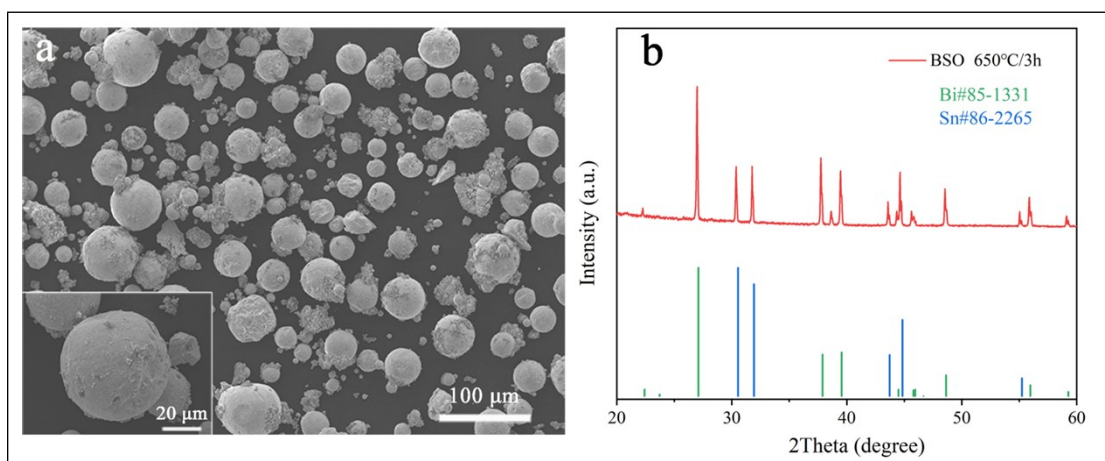


Fig. S4 (a) SEM images and (b) corresponding to XRD pattern of BSO particles annealed at 650 °C for 3h in 95% Ar and 5% H<sub>2</sub> atmosphere.

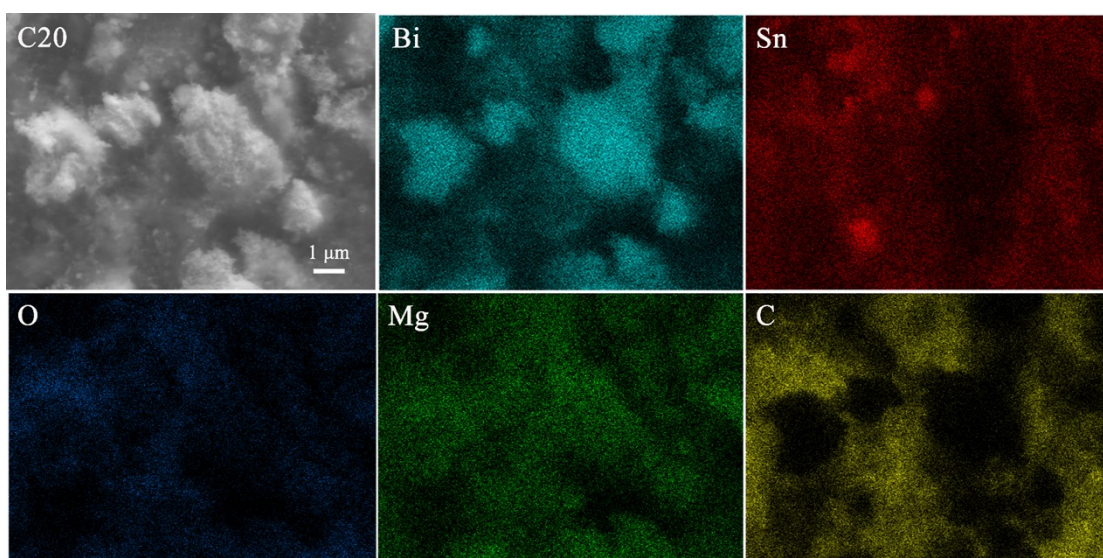


Fig. S5 SEM image and elemental mappings of BSS-600 electrode after 20<sup>th</sup> charge.

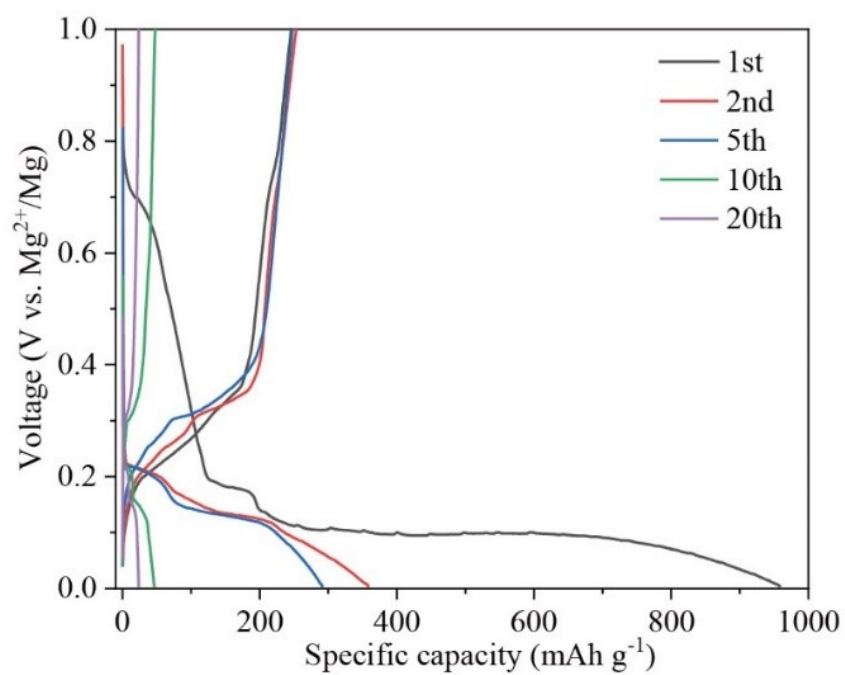


Fig. S6 Discharge/charge profiles of the BSO electrode after different cycles.

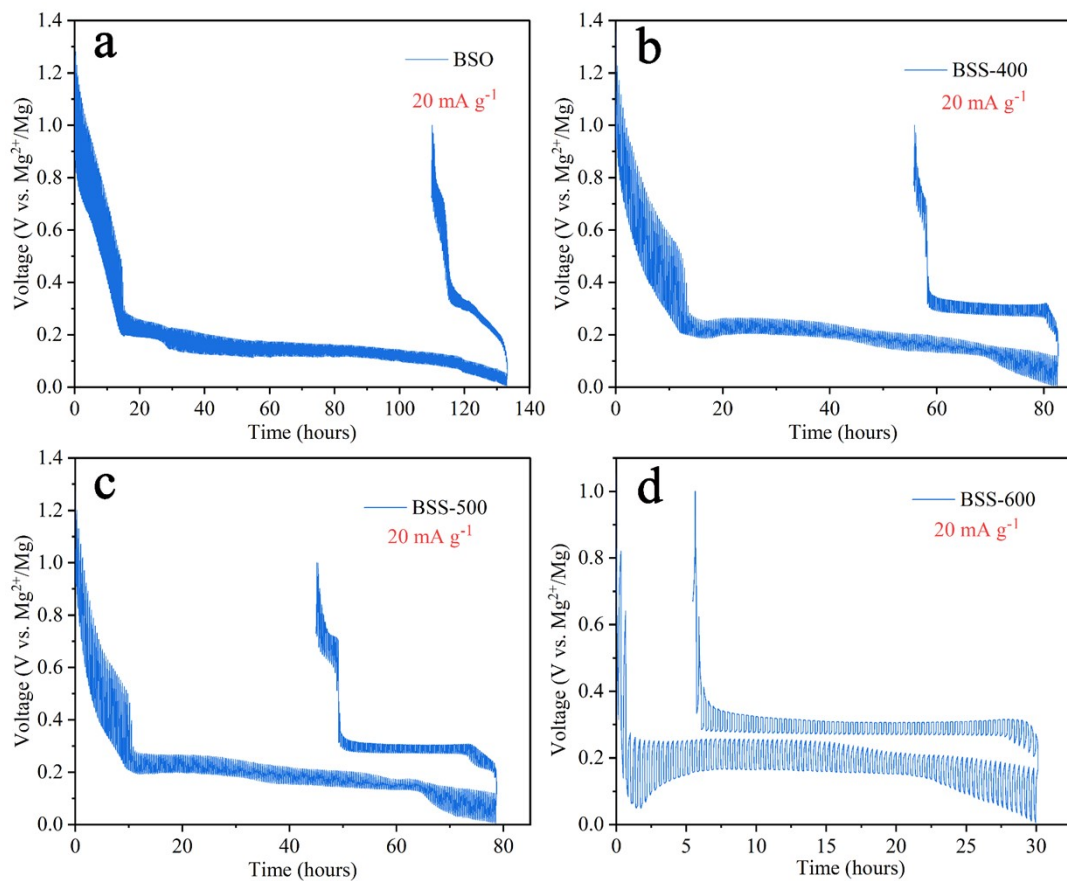


Fig. S7 GITT curves at the first cycle obtained from the BSO//Mg, BSS-400//Mg, BSS-500//Mg and BSS-600//Mg half cells (10 min of reduction/oxidation at  $20 \text{ mA g}^{-1}$  followed by 10 min of relaxation at OCV).

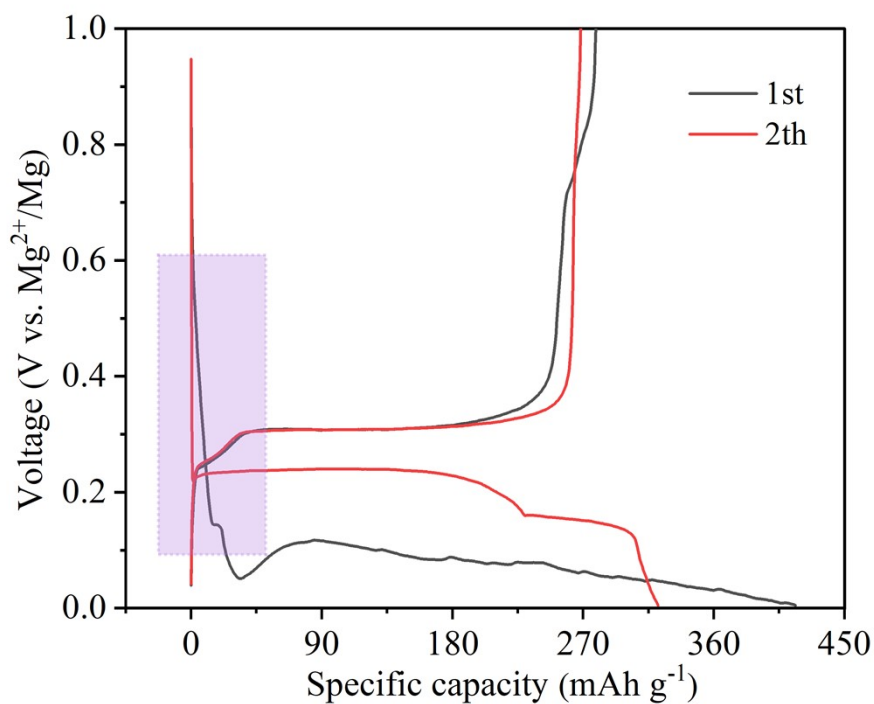


Fig. S8 First two discharge/charge curves of the BSS-600 electrode at 500 mA g<sup>-1</sup> test during the activation process.

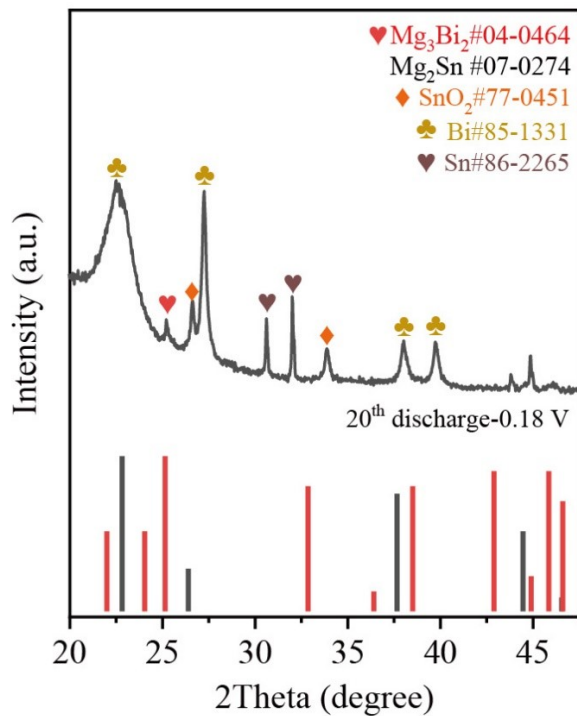


Fig. S9 The *ex-situ* XRD pattern of the BSS-600 electrode at the 20<sup>th</sup> discharge to 0.18 V.



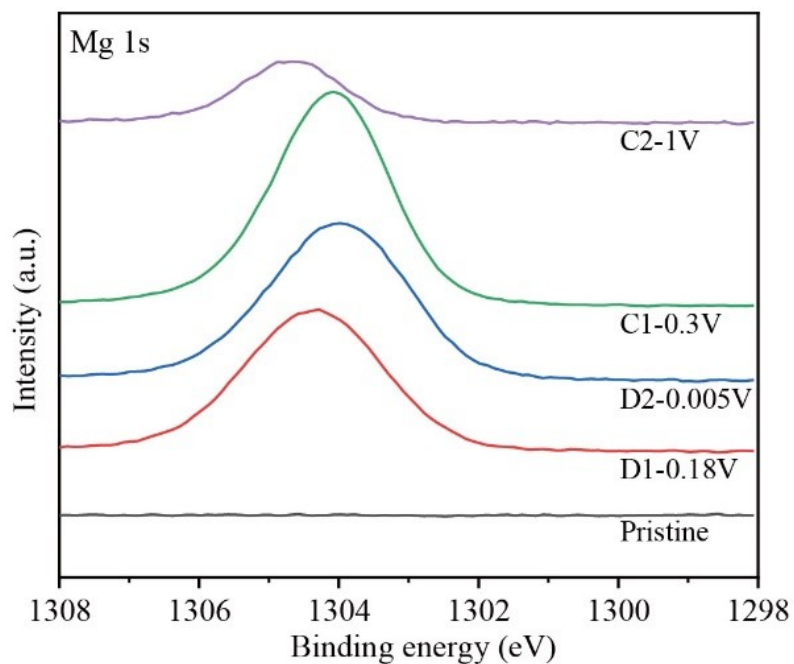


Fig. S10 *Ex-situ* XPS spectra of Mg 1s in the BSS-600 anodes at different discharge/charge status.

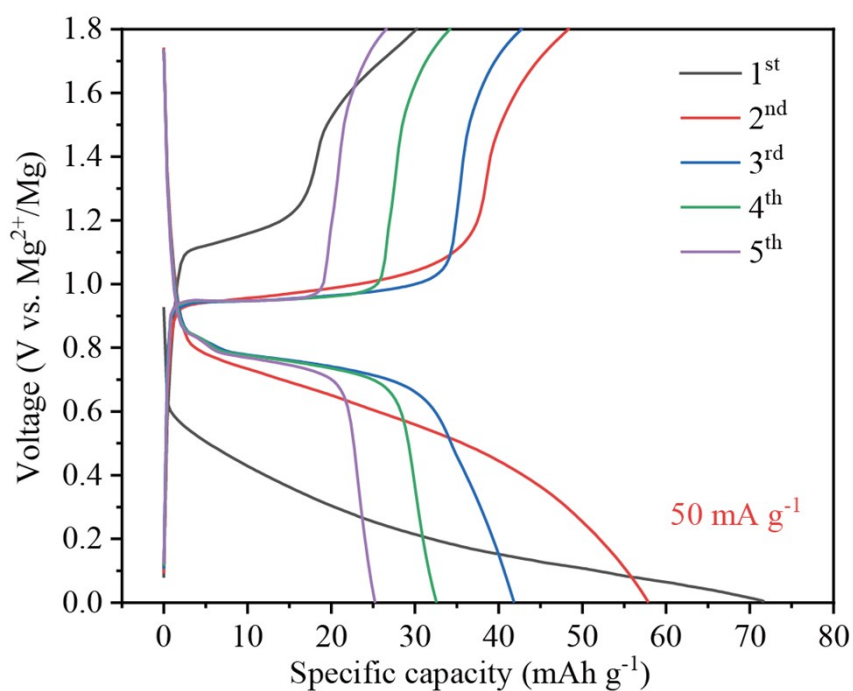


Fig. S11 The first five discharge/charge profiles of the pre-magnesiated BSS-600//Mg(TFSI)<sub>2</sub>//Mo<sub>6</sub>S<sub>8</sub> with a potential range of 0-1.8 V at the current density of 50 mA g<sup>-1</sup>.

Table S1 The physical properties of as-prepared samples.

Samples	$S_{BET}$ ( $m^2 g^{-1}$ )	Pore volume ( $cm^3 g^{-1}$ )	Average pore size (nm)
BSO	52.0	0.191	11.864
BSS-400	44.9	0.210	14.000
BSS-500	25.5	0.122	14.960
BSS-600	3.3	-	-

Table S2 The corresponding kinetic parameters calculated from Nyquist plots.

Electrode	$R_s$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )	CPE1 (F)	$D_{Mg^{2+}}$ ( $cm^2 s^{-1}$ )
Pristine BSS-600	12.96	5989.00	$9.95 \times 10^{-6}$	$5.88 \times 10^{-17}$
Activated BSS-600	6.54	22.15	$3.19 \times 10^{-6}$	$1.17 \times 10^{-15}$

#### Calculation of the $Mg^{2+}$ diffusion coefficient according to EIS:

$$D_{Mg^{2+}} = \frac{R^2 T^2}{2 A^2 n^4 C_{Mg^{2+}}^2 F^4 \sigma^2}$$

Here, A is the surface area of the electrode ( $0.785 \text{ cm}^2$ ), n is the number of electrons per molecule during a reaction, F is the Faraday constant ( $96485 \text{ C mol}^{-1}$ ),  $C_0$  is the bulk concentration of  $Mg^{2+}$ , R is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ), T was the room temperature ( $298.15 \text{ K}$ ), and  $\sigma$  is the Warburg factor.  $\sigma$  has a relationship with the real part of impedance  $Z'$ , which is expressed as follows:

$$Z' = R_s + R_{ct} + \sigma \omega^{-1/2}$$

$\omega$  is the angular frequency which is equal to  $2\pi f$  where f is the frequency in Hertz.

### Calculation of the Mg<sup>2+</sup> diffusion coefficient according to CV:

The Randles-Sevcik equation calculates the apparent Mg<sup>2+</sup> diffusion coefficient at room temperature as follows:

$$I_p = 269000n^{3/2}AD_{Mg^{2+}}^{1/2}C_{Mg^{2+}}v^{1/2}$$

Where  $v$  is the scanning rate ( $V s^{-1}$ ),  $C_{Mg^{2+}}$  is the molar concentration of  $Mg^{2+}$ ,  $D_{Mg^{2+}}$  is the chemical diffusion coefficient ( $cm^2 s^{-1}$ ),  $A$  is the surface area of the electrode and  $n$  is the number of electrons per molecule during the reaction.

## References

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