

## Supplementary data

### **A phase-convertible fast ionic conductor with a monolithic plastic crystalline host**

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## **Preparation of phase-convertible Mg-ion electrolytes**

*PCE preparation:* PCEs were prepared in an argon-filled glovebox (Braun, Inc. <0.1 ppm of water and oxygen). Magnesium(II) bis(trifluoromethane)sulfonamide salt (Solvionic, 99.5%) and succinonitrile (Sigma-Aldrich, 99%) were dried before use. PCE was prepared by adding the Mg salt into melted succinonitrile and stirred overnight at temperatures greater than 60°C. For the iodine additives (Sigma-Aldrich, ≥99.8%), 0.1 M of the molar concentration was used.

*Mo<sub>6</sub>S<sub>8</sub> Electrodes:* A slurry preparation of Mo<sub>6</sub>S<sub>8</sub>, carbon, and polyvinylidene fluoride in excess 1-methyl-2-pyrrolidinone (NMP) [80:10:10 (wt%)] was used to coat the molybdenum foils. Coatings were dried overnight and then placed in a vacuum oven at 80 °C. The electrodes were then punched into 12 mm disks to be assembled.

## **Characterisations**

Powder X-ray diffraction patterns were obtained by using Dmax2500/PC with Cu K $\alpha$  radiation at a scan rate of 3° min<sup>-1</sup> (2 $\theta$ ). Thermogravimetric analysis and differential scanning calorimetry were performed on SDT-Q600 to evaluate the thermal properties of PCE under air and N<sub>2</sub> atmosphere, respectively (heating rate of 10 °C min<sup>-1</sup>). Fourier transform infrared spectrum was measured using a Nicolet iS10 between the ranges of 4000 to 400 cm<sup>-1</sup>. Scanning electron microscopy images and energy-dispersive X-ray spectroscopy were obtained by using a Regulus 8230. X-ray photoelectron spectroscopy was carried using Nexsa. In using VMP3, electrochemical impedance spectroscopy analysis was conducted at a frequency range from 50 mHz to 1 MHz and an applied amplitude of 10 mV, cyclic voltammetry was measured under a sweep rate of 0.1 mV s<sup>-1</sup>. Constant current cyclic measurements were evaluated under a current density of 0.01 mA cm<sup>-2</sup> (1 h per cycle) using a WBCS 3000.

## **Density functional theory and molecular dynamic simulation**

The electronic structure and energetics of molecules were modelled with the DMol3 program using density functional theory.<sup>1</sup> The exchange and correlation energies were treated with the generalised gradient approximation and the Perdew–Burke–Ernzerhof functional was used to describe the exchange-correlation interaction between electrons.<sup>2</sup> A global orbital cut off 5.0 Å was chosen and employed for all calculations. The double-

numeric polarised basis set with fine quality was adopted. In our calculation, the binding energies were calculated by the following equation:

$$E_{bind} = E_{Mg^{2+}/SN} - (E_{Mg^{2+}} + E_{SN})$$

where  $E_{Mg^{2+}/SN}$ ,  $E_{Mg^{2+}}$  and  $E_{SN}$  are total electronic energies of the ground state of the  $Mg^{2+}$  interacting with SN, adsorbed species of  $Mg^{2+}$  and SN molecule(s), respectively.

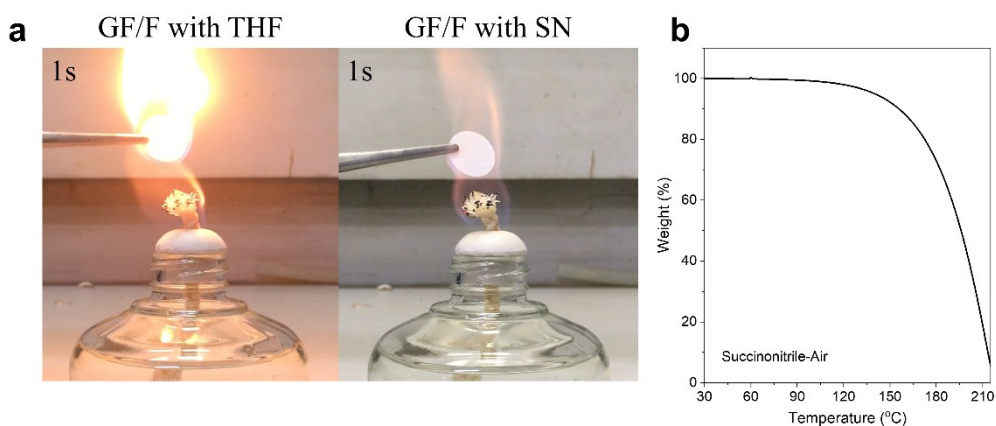
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All molecular modelling procedures, including geometric optimisation, were implemented using PACKMOL.<sup>1</sup> The production runs to predict the mobility of ions in SN were implemented using the Large-Scale Atomic/Molecular Massively Parallel Simulation program provided by Sandia National Research Laboratories.<sup>2</sup> The polymer consistent force field<sup>3</sup> parameterised from *ab-initio* calculations was used to describe all inter- and intra-molecular interactions. The PCFF force-field used to describe the interaction between  $Mg^{2+}$  and SNs does not distinguish the van der Waals potential and Coulombic interaction parameters of  $Mg^{2+}$  and N atoms in *gauche* and *trans* conformations. Nonetheless, the PCFF force-field can describe conformational changes of the *gauche-trans* transition. Therefore, the MD simulation part focuses on the conformation change of SN and  $Mg^{2+}$  ion mobility. During the NPT process, the MSD of  $Mg^{2+}$  ion at time t is given as follows:

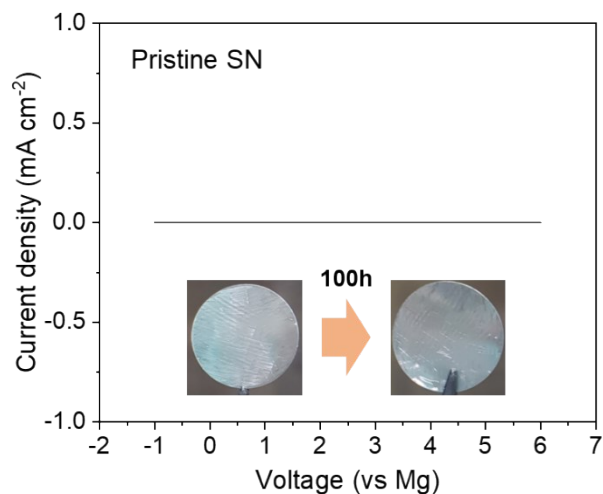
$$MSD = \frac{1}{6} \sum_{i=0}^{N-1} \langle |\vec{R}_i(t) - \vec{R}_i(0)|^2 \rangle$$

where  $\vec{R}_i(t)$  denotes the current position of the *i*th atom at time t. Through the variation of the MSD curve with temperature, the relative diffusivity of a molecular system undergoing a temperature change can be estimated. The ionic conductivity of Mg-ion was calculated via the Nernst-Einstein relations  $\sigma = Ne^2D/k_bT$ , where  $\sigma$  is the isotropic ionic conductivity, *N* is the number of cations per  $cm^3$ , *e* is the electronic charge,  $k_b$  is the Boltzmann constant, and *D* is the diffusion coefficient of the anion, respectively.

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**Figure S1.** **a**, Safety comparison: the combustion test of THF and SN. A GF/F separator was used as a mechanical supporter. **b**, TGA thermograms of SN under air at a rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ . SN is thermally stable above  $100\text{ }^{\circ}\text{C}$ . However, measurements for THF were not available due to its high volatility.

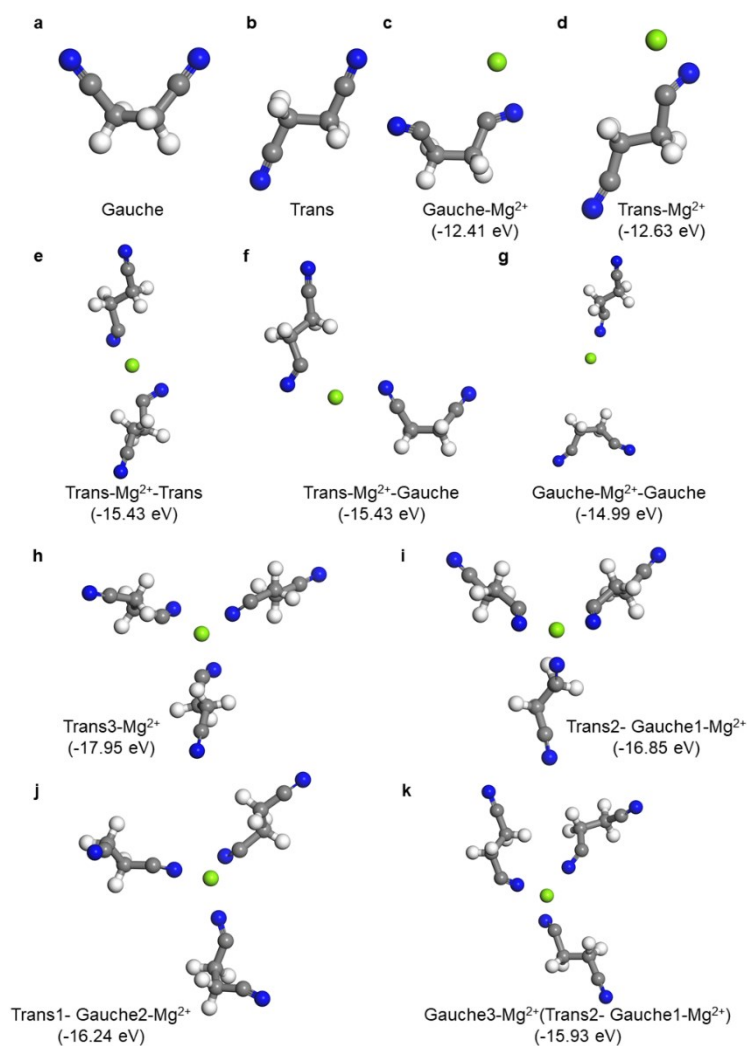


**Figure S2.** Cyclic voltammetry curve of pristine SN using a Mg/Mo asymmetric cell at a scan rate of  $10\text{ mV s}^{-1}$ . Inset shows Mg-metal surface after being held in succinonitrile for 100 h.

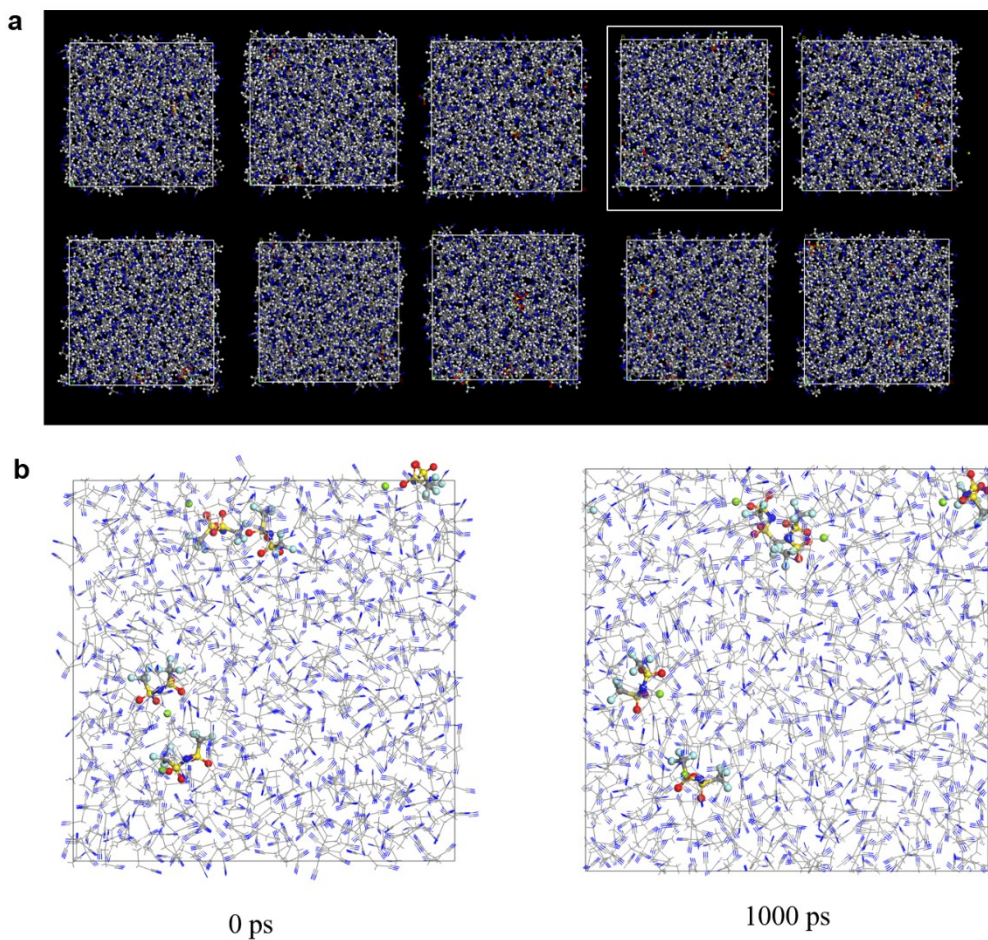
**Table S1.** Properties of the crystalline solid-state Mg<sup>2+</sup> electrolyte

Type	Material	$\sigma$ (S/cm)	$E_a$ (eV)	CV (vs Mg)	Etc.	Ref
PC	SN-Mg(TFSI) <sub>2</sub>	2.808 X 10 <sup>-5</sup> (RT)	0.674	~ 6V	-	This work
IC	Mg(BH <sub>4</sub> )(NH <sub>2</sub> )	10 <sup>-6</sup> (150°C)	1.31	~ 3V /	-	S1
IC	Mg(en) <sub>1</sub> (BH <sub>4</sub> ) <sub>2</sub>	5 X 10 <sup>-8</sup> (30°C) 6 X 10 <sup>-5</sup> (70°C)	1.6	1.2V	Thermal stability (75°C)	S2
LC	C16O5-Mg(ClO <sub>4</sub> ) <sub>2</sub>	~ 10 <sup>-7.5</sup> (30°C)	-	-	-	S3
LC	2Mg <sup>2+</sup> /[CH <sub>2</sub> CH <sub>2</sub> O]	~ 10 <sup>-6.5</sup> (50°C)	-	-	-	S4
IC	Mg <sub>0.5</sub> Zr <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	1.0 X 10 <sup>-6</sup> (RT) 7.1 X 10 <sup>-5</sup> (500°C)	0.0977	~ 2.5V	Sintering 750°C	S5
IC	Mg <sub>0.5</sub> Si <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	1.83 X 10 <sup>-5</sup> (RT)	-	~ 3.21V	Sintering 800°C	S6
IC	Mg <sub>0.625</sub> Si <sub>1.75</sub> Al <sub>0.25</sub> (PO <sub>4</sub> ) <sub>3</sub>	1.54 X 10 <sup>-4</sup> (RT)	-	~ 2.51V	Sintering 800°C	S7

PC: plastic crystal; IC: inorganic crystal; LC: liquid crystal; en: ethylenediamine

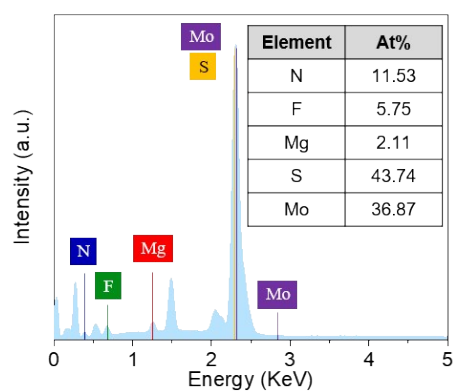


**Figure S3. Conformation of succinonitrile molecules.** **a**, *gauche* conformation and **b**, *trans* conformation. Simulation results of  $Mg^{2+}$  interacting with succinonitrile molecule(s): **c**,  $Mg^{2+}$  with *gauche* conformation, **d**,  $Mg^{2+}$  with *trans* conformation, **e**,  $Mg^{2+}$  with two *trans* conformation, **f**,  $Mg^{2+}$  with *trans* and *gauche* conformation, **g**,  $Mg^{2+}$  with two *gauche* conformations. The Mg-ion is positioned near the nitrogen atom of the single succinonitrile molecule and the center of the two succinonitrile molecules. The binding energies of conformations (**c-g**) are -12.41, -12.63, -15.43, -15.43, and -14.99 eV, respectively. Calculation results of  $Mg^{2+}$  interacting with three succinonitrile molecules: **h**,  $Mg^{2+}$  with three *trans* conformation **i**,  $Mg^{2+}$  with two *trans* conformations and one *gauche* conformation, **j**,  $Mg^{2+}$  with one *trans* conformation and two *gauche* conformations, **k**,  $Mg^{2+}$  with three *gauche* conformations. The binding energies of  $Mg^{2+}$  with three succinonitrile molecules (**h-i**) are -17.95, -16.85, -16.24, and -15.93 eV, respectively.

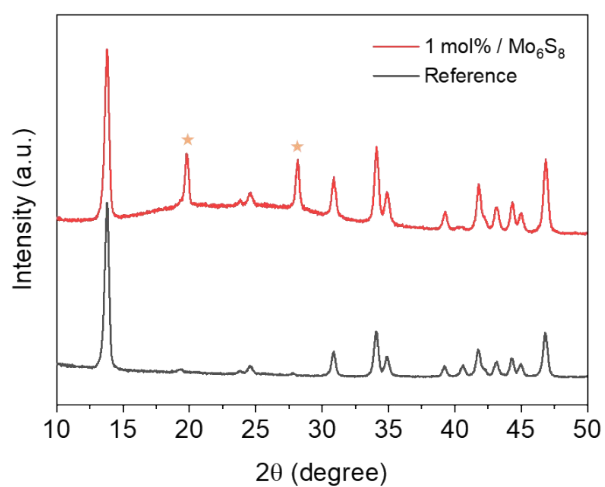


**Figure S4.** **a**, Equilibrium structure of blend system with 495 *gauche* succinonitrile conformations (99% mole) and 5 MgTFSI (1% mole). The lowest energy configuration (white box) was selected for molecular dynamics simulation analysis of MgTFSI. **b**, Molecular dynamic simulation results of NPT ensemble before and after MD simulation. Temperature was set at 300 K and the simulation time was 1000 ps with 1 fs time steps for fully relaxed structures without added pressure.

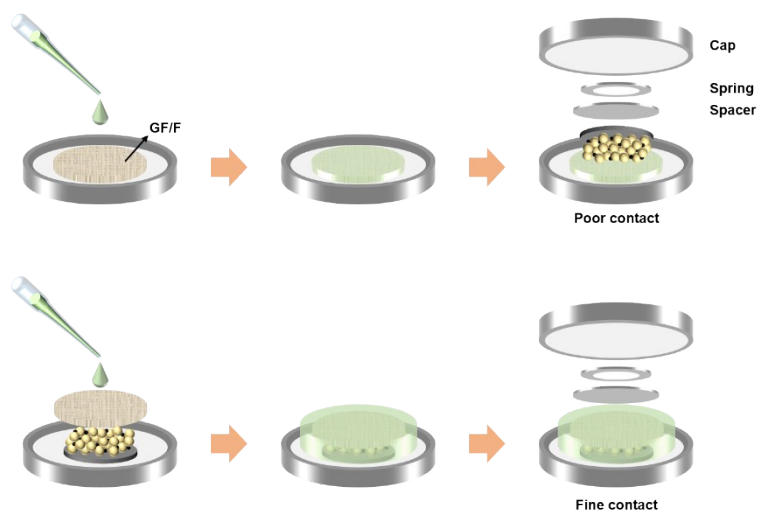




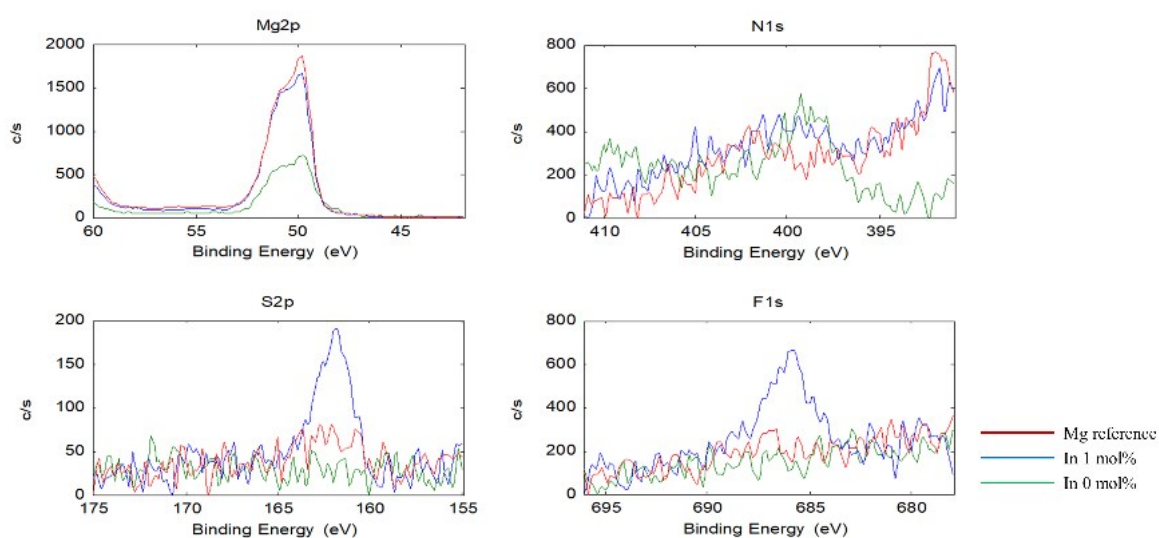
**Figure S5.** EDS spectrum of the  $\text{Mo}_6\text{S}_8$  electrode wetted with 1 mol% SN electrolyte.



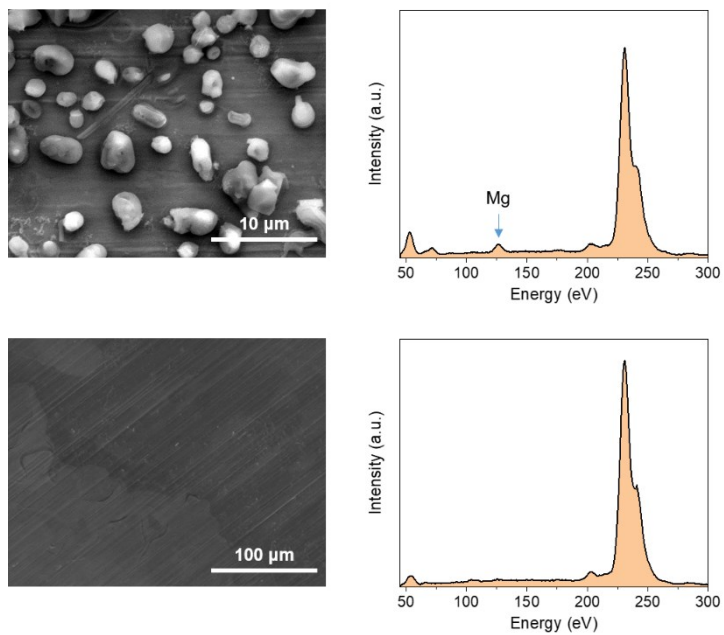
**Figure S6.** XRD pattern of the  $\text{Mo}_6\text{S}_8$  electrode wetted with 1 mol% SN electrolyte.



**Figure S7.** Schematic illustration comparing the processes for the poor contact and fine contact.



**Figure S8.** XPS spectra of the Mg-metal surfaces immersed in molten SN and 1 mol% SN electrolyte and stored at 50°C for 3 days in an Ar-filled glovebox. All Mg metals were washed with THF to eliminate soluble residue before measuring XPS. The surface Mg oxide was mechanically polished out before the experiment.



**Figure S9.** SEM images and corresponding EDS analysis of a magnesium deposit on a Mo substrate from a 1 mol% SN electrolyte containing iodine additives.

## Reference

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