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$_6$S$_8$ Electrodes**: A slurry preparation of Mo$_6$S$_8$, 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 Kα radiation at a scan rate of 3° min$^{-1}$ (2θ). Thermogravimetric analysis and differential scanning calorimetry were performed on SDT-Q600 to evaluate the thermal properties of PCE under air and N$_2$ atmosphere, respectively (heating rate of 10 °C min$^{-1}$). Fourier transform infrared spectrum was measured using a Nicolet iS10 between the ranges of 4000 to 400 cm$^{-1}$. 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$^{-1}$.Constant current cyclic measurements were evaluated under a current density of 0.01 mA cm$^{-2}$ (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.$^1$ 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.$^2$ 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:

\[ E_{\text{bind}} = E_{\text{Mg}^{2+}/\text{SN}} - \left( E_{\text{Mg}^{2+}} + E_{\text{SN}} \right) \]

where \( E_{\text{Mg}^{2+}/\text{SN}} \), \( E_{\text{Mg}^{2+}} \) and \( E_{\text{SN}} \) 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.


All molecular modelling procedures, including geometric optimisation, were implemented using PACKMOL.\(^1\) 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.\(^2\) The polymer consistent force field\(^3\) 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:

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

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 \( \sigma = \frac{N e^2 D}{k_b T} \), 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.


**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 °C min⁻¹. SN is thermally stable above 100 °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 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\(^{2+}\) electrolyte

<table>
<thead>
<tr>
<th>Type</th>
<th>Material</th>
<th>(\sigma) (S/cm)</th>
<th>(E_a) (eV)</th>
<th>CV (vs Mg)</th>
<th>Etc.</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>SN-Mg(TFSI)(_2)</td>
<td>2.808 X 10(^{-5}) (RT)</td>
<td>0.674</td>
<td>~ 6V</td>
<td>-</td>
<td>This work</td>
</tr>
<tr>
<td>IC</td>
<td>Mg(BH(_4))(NH(_2))</td>
<td>10(^{-6}) (150(^\circ)C)</td>
<td>1.31</td>
<td>~ 3V /</td>
<td>-</td>
<td>S1</td>
</tr>
<tr>
<td>IC</td>
<td>Mg(en)(_3)(BH(_4))(_2)</td>
<td>5 X 10(^{-8}) (30(^\circ)C) 6 X 10(^{-5}) (70(^\circ)C)</td>
<td>1.6</td>
<td>1.2V</td>
<td>Thermal stability (75(^\circ)C)</td>
<td>S2</td>
</tr>
<tr>
<td>LC</td>
<td>C16O5-Mg(ClO(_4))(_2)</td>
<td>~ 10(^{-7.5}) (30(^\circ)C)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>S3</td>
</tr>
<tr>
<td>LC</td>
<td>2Mg(^{2+})/[CH(_2)CH(_2)O]</td>
<td>~ 10(^{-6.5}) (50(^\circ)C)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>S4</td>
</tr>
<tr>
<td>IC</td>
<td>Mg(_{0.5})Zr(_3)(PO(_4))(_3)</td>
<td>1.0 X 10(^{-6}) (RT) 7.1 X 10(^{-5}) (500(^\circ)C)</td>
<td>0.0977</td>
<td>~ 2.5V</td>
<td>Sintering 750(^\circ)C</td>
<td>S5</td>
</tr>
<tr>
<td>IC</td>
<td>Mg(_{0.5})Si(_2)(PO(_4))(_3)</td>
<td>1.83 X 10(^{-6}) (RT)</td>
<td>-</td>
<td>~ 3.21V</td>
<td>Sintering 800(^\circ)C</td>
<td>S6</td>
</tr>
<tr>
<td>IC</td>
<td>Mg(<em>{0.625})Si(</em>{1.75})Al(_{0.25})(PO(_4))(_3)</td>
<td>1.54 X 10(^{-4}) (RT)</td>
<td>-</td>
<td>~ 2.51V</td>
<td>Sintering 800(^\circ)C</td>
<td>S7</td>
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</tbody>
</table>

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 conformations, 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 conformations, 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 Mo$_6$S$_8$ electrode wetted with 1 mol% SN electrolyte.

<table>
<thead>
<tr>
<th>Element</th>
<th>At%</th>
</tr>
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<tbody>
<tr>
<td>N</td>
<td>11.53</td>
</tr>
<tr>
<td>F</td>
<td>5.75</td>
</tr>
<tr>
<td>Mo</td>
<td>2.11</td>
</tr>
<tr>
<td>S</td>
<td>43.74</td>
</tr>
<tr>
<td>Mo</td>
<td>36.87</td>
</tr>
</tbody>
</table>

Figure S6. EDS spectrum of the Mo$_6$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


S5 Anuar, N. K., Adnan, S. B. R. S. & Mohamed, N. S. Characterization of Mg$_{0.5}$Zr$_2$(PO$_4$)$_3$ for potential use as electrolyte in solid state magnesium batteries. Ceram. Int. 40, 13719-13727 (2014).


S7 Halim, Z. A., Adnan, S. B. R. S., Salleh, F. M. & Mohamed, N. S. Effects of Mg$^{2+}$ interstitial ion on the properties of Mg$_{0.5+x/2}$Si$_{2-x}$Al$_x$(PO$_4$)$_3$ ceramic electrolytes. J. Magnes. Alloy. 5, 439-447 (2017).