

## Supplementary Information

### A magnesium–sodium hybrid battery with high operating voltage

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#### Experimental Section

**Synthesis of FeFe(CN)<sub>6</sub> nanoparticles.** We used co-precipitation method to synthesize the Berlin green following reference.<sup>1</sup> Briefly, 50 mL of the 0.01 M FeCl<sub>3</sub> (Sigma-Aldrich, 97%) solution was added dropwise into 100 mL of the 0.005 M K<sub>3</sub>Fe(CN)<sub>6</sub> (Alfa Aesar, 98+%) under stirring in 2 hours. After the addition step was complete, the mixed solution was aged for another 6 hours at 60°C. The mixed solution was cooled down naturally and then filtered. The obtained dark green precipitate was washed with distilled water several times and dried in vacuum at 120°C overnight.

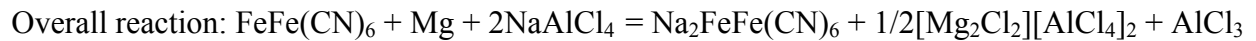
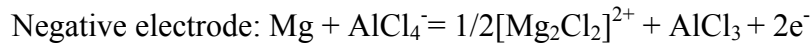
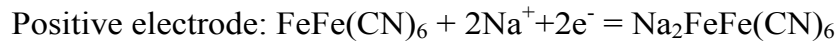
**Preparation of Electrolyte.** The electrolyte synthesis was carried out inside an Ar filled glove box. In a typical synthesis of 20 ml 0.2M  $[\text{Mg}_2\text{Cl}_2][\text{AlCl}_4]_2/\text{DME}$  electrolyte, 1.07 g  $\text{AlCl}_3$  powder (Sigma Aldrich, 99.99%) was added slowly (exothermic reaction) to a suspension of  $\text{MgCl}_2$  (Alfa Aesar, 99.999%, 0.76 g in 20 ml DME) in a 25 ml glass vial. The mixture was stirred at 60°C using a sand bath for 6 hours and was cooled to room temperature. A clear solution was obtained with no precipitants. The hybrid-ion electrolyte was prepared by dissolving appropriate amount of  $\text{NaAlCl}_4$  (Alfa Aesar) into the above electrolyte. 1M  $\text{NaPF}_6$  in ethylene carbonate/diethyl carbonate (EC/DEC, 50:50% vol) was used as the electrolyte in Na-ion battery.

**Electrochemical and Material Characterizations.** Tubular sealed three-electrode cells or two-electrode Swagelok cells were fabricated inside an Ar-filled glovebox (M-Braun Co.) for electrochemical characterizations. The slurry of active material (75 wt %), Super-P carbon (15 wt %), and polytetrafluoroethylene (10 wt %) was spread on a piece of Mo foil (0.8  $\text{cm}^2$ ) and dried as the working electrode. The active material mass loading was 4  $\text{mg cm}^{-2}$ . Freshly polished magnesium foils (0.2 mm thick, 99.95%, GalliumSource, LLC, Scotts Valley, CA) were used as both the counter and reference electrodes. For Swagelok cells, a glass fiber separator (0.68 mm thick, GF/D grade) was placed between a cathode and a Mg anode. 0.4 ml of hybrid  $\text{Mg}^{2+}/\text{Na}^+$  electrolyte was added in the glass fiber. Electrochemical characterizations were conducted using a potentiostat (VMP-3, Bio-Logic Co., Claix, France). The X-ray diffraction (XRD) spectra of the pristine BG nanoparticles were measured using a Rigaku diffractometer with  $\text{Cu K}\alpha$  radiation (1.5405 Å). Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy measurements were conducted using a JEOL JSM 6400 SEM and an EDAX with Octane Silicon Drift Detector (SDD). For the scanning electron microscopy (SEM)

and energy-dispersive X-ray (EDX) spectroscopy characterizations, the Mg anode and BG cathode were taken out from the cell in the Ar-filled glove box. Afterwards, the electrodes were dipped in fresh anhydrous DME for 10 mins, and this procedure was repeated for three times. The washed electrodes were then dried in evacuated antechamber of Ar-filled glove box for 2 hours before further characterizations. Thermogravimetric analysis (TGA) test was performed using thermogravimetric analyzer of TA Instruments Q50.

X-ray absorption near edge structure (XANES) of the Fe K-edge (7112 eV) was measured in the transmission mode on the bending-magnet beamline of the Advanced Photon Source (APS, 20-BM-B). The incident beam was monochromatized using a Si(111) fixed-exit, double-crystal monochromator. Ex-situ samples at different states of charge were sealed in a Kapton tube. XANES data were processed following standard methods using the ATHENA software package. The HEXRD measurements were carried out at Beamline 11-ID-C at APS. The X-ray wavelength was 0.1174 Å (105.1 keV). The XRD patterns were collected using a Perkin-Elmer 2D X-ray detector. 2D images were converted into a 1D plot of 2θ versus intensity using the FIT2D program calibrated against a CeO<sub>2</sub> standard.

### **Calculation of energy density and power density for the Mg-Na hybrid battery:**



Specific capacity =  $2 * 26800 / (\text{Na}_2\text{FeFe}(\text{CN})_6 + \text{Mg}^{2+} + \text{Cl}^- + \text{AlCl}_4^- + \text{AlCl}_3)$

$$= 2 * 26800 / (314 + 24.31 + 35.45 + 168.79 + 133.35) = 79.30 \text{ mAh/g}$$

Theoretical specific energy density for Mg-Na/BG =  $2.2 \text{ V} * 79.30 \text{ mAh/g} = 174.46 \text{ Wh/kg}$

where 2.2 V is the average discharge voltage.

Experimental demonstrated energy density:  $[1.52 \times 26800 / (302.96 + 24.31 + 35.45 + 168.79 + 133.35)]$

$\times 2.2 = 134.79 \text{ Wh/kg}$ .

where  $1.52 \text{ Na}^+$  is reversibly (de)inserted into BG framework instead of  $2 \text{ Na}^+$  in theoretical calculation.

Experimental power density: (Experimental capacity at x-C-rate \* average discharge voltage at x-C-rate) / Practical discharging time at x-C-rate

$[47.35 \times 2] / [(110/140) \times 0.1] = 1.20 \text{ kW/kg}$  [10C:  $1.16 \text{ Na}^+$  de(insertion)] and

$[24.98 \times 2] / [(85/140) \times 0.05] = 1.67 \text{ kW/kg}$  [20C:  $0.6 \text{ Na}^+$  de(insertion)], where we calculated

power density at 10, 20C according to the rate performance shown in Fig. 4b.



Figure S1. A transparent solution for  $0.4 \text{ M NaAlCl}_4$  with  $0.2 \text{ M } [\text{Mg}_2(\mu\text{-Cl})_2][\text{AlCl}_4]_2$  in DME.

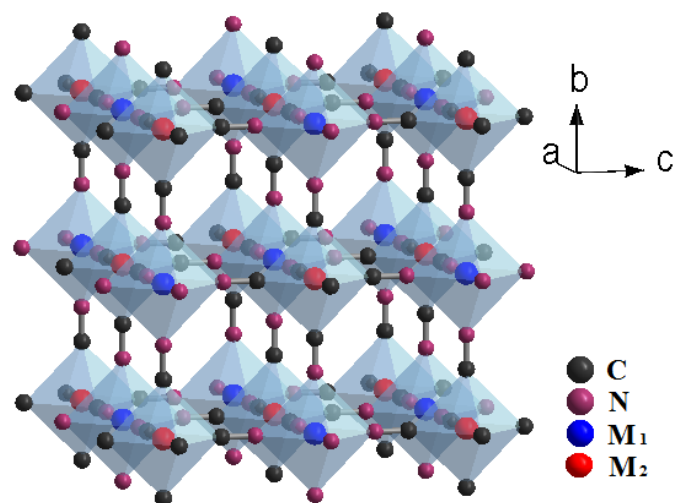


Figure S2. Framework of  $A_xM_1_nM_2_m(CN)_z$

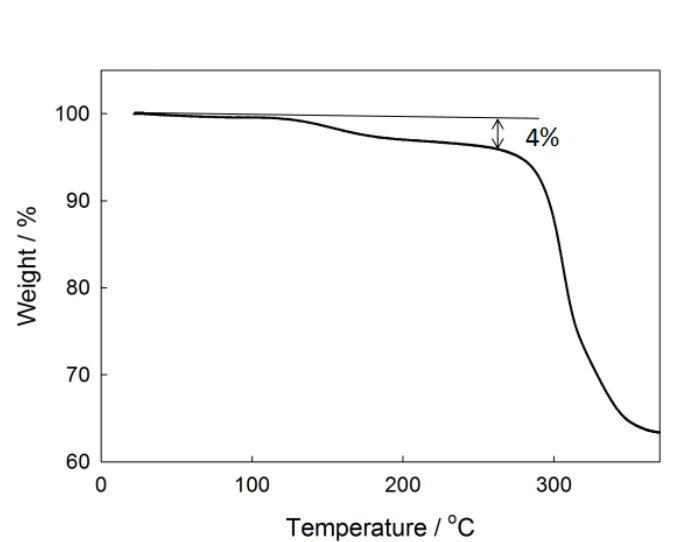


Figure S3. TGA profile of BG nanoparticles shows 4% weight loss due to crystalline  $H_2O$ , corresponding to the formula of  $K_{0.07}Fe[Fe(CN)_6]_{0.95} \cdot 0.61H_2O$ .

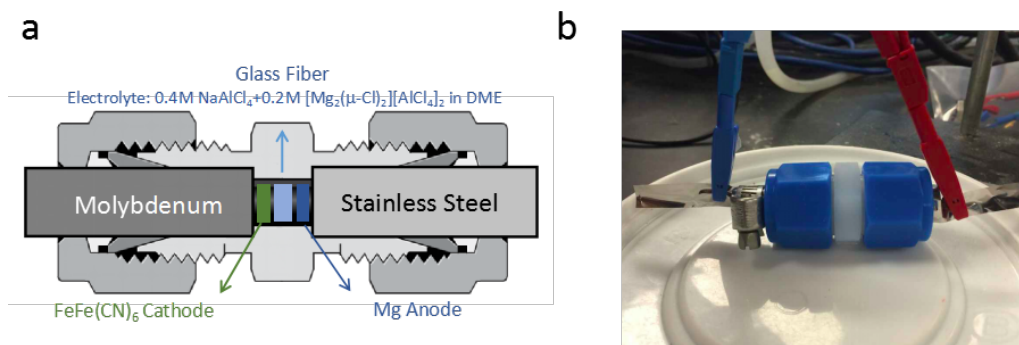


Figure S4. (a) Schematic and (b) picture of a Swagelok cell.

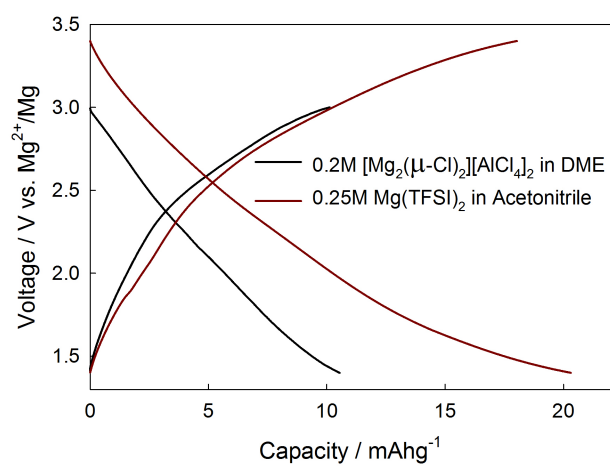


Figure S5. Discharge-charge profiles of  $\text{FeFe}(\text{CN})_6$  in the  $\text{FeFe}(\text{CN})_6|\text{Mg}^{2+}|\text{Mg}$  cell in 0.2M  $[\text{Mg}_2(\mu\text{-Cl})_2][\text{AlCl}_4]_2$  in dimethoxyethane) and 0.25 M  $\text{Mg}(\text{TFSI})_2$  in acetonitrile at the 2<sup>nd</sup> cycle at 28 mA/g, respectively.

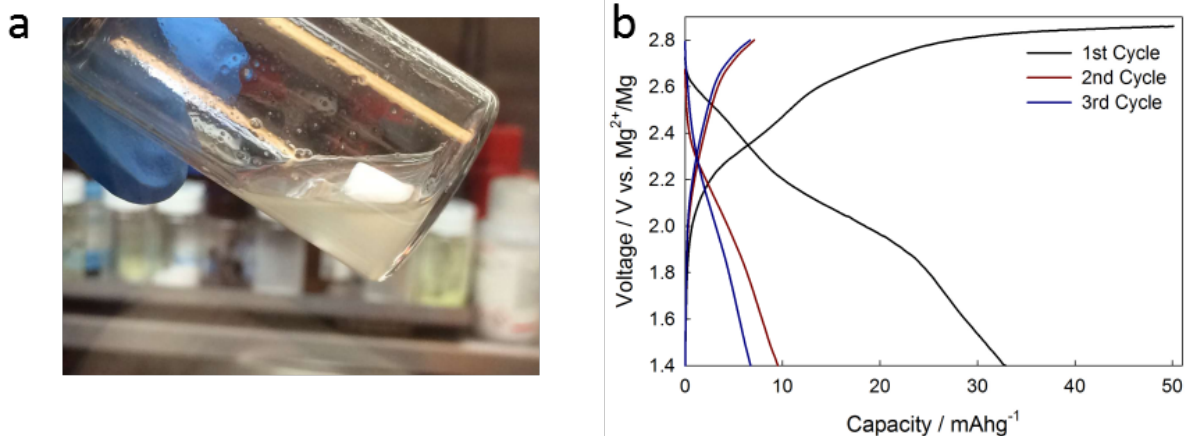


Figure S6. (a) Picture shows  $\text{NaAlCl}_4$  is insoluble in the all phenyl complex (APC) electrolyte at 0.2M concentration; (b) The first three galvanostatic profiles of a  $\text{FeFe}(\text{CN})_6$  cathode in the hybrid electrolyte.

1. Y. H. Lu, L. Wang, J. G. Cheng and J. B. Goodenough, *Chem. Commun.*, 2012, **48**, 6544-6546.