A magnesium–sodium hybrid battery with high operating voltage†

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We report a high performance magnesium–sodium hybrid battery utilizing a magnesium–sodium dual-salt electrolyte, a magnesium anode, and a Berlin green cathode. The cell delivers an average discharge voltage of 2.2 V and a reversible capacity of 143 mA h g\(^{-1}\). We also demonstrate the cell with an energy density of 135 W h kg\(^{-1}\) and a high power density of up to 1.67 kW kg\(^{-1}\).

The rapid growth of renewable energy from solar and wind power has created a strong demand for low-cost, safe, high-energy density energy storage systems to enable the integration of renewable energy into grid and peak shifting in energy demand. To meet the cost target of less than $100 per kW h, earth-abundant materials have been actively explored for beyond-lithium-ion batteries. For example, Prussian blue analogues (PBAs) have attracted significant attention due to their unique open framework structures for Na and K ion storage in aqueous\(^1\) and non-aqueous batteries.\(^2\)–\(^4\) Recently, Lu et al. developed long cycle life Na-ion batteries using PBAs as the cathode.\(^5\) The large interstitial space in the framework allows rapid Na-ion diffusion. However, the full cell rate performance is limited by the choices of anode. It is well known that metallic sodium could not function as a practical anode due to the dendritic growth behavior.\(^6\) Hard carbon is the most studied Na-ion anode.\(^7\) However, the voltage profile of hard carbon is too close to 0 V vs. Na/Na\(^+\), making Na deposition possible during fast charging and could lead to battery shorting.\(^8\)

Magnesium metal has recently attracted considerable attention as a safe anode due to the fact that Mg has a low standard potential (−2.37 V vs. SHE), fast deposition-stripping kinetics, and planar hexagonal crystal growth instead of dendritic growth.\(^9\) However, the challenge is the lack of stable high-voltage cathode material due to the slow solid-state diffusion of highly polarizing Mg\(^{2+}\) ions in host.\(^10\) The concept of a Mg–Li hybrid battery combining a Mg anode, a Li-insertion cathode, and a hybrid electrolyte is attractive since the hybrid cell combines the safety and low cost feature of Mg anode and the fast kinetics and high voltage feature of Li-insertion cathode.\(^11\)–\(^13\) However, there has been very limited study on a low-cost Mg–Na hybrid cell. Only one recent report from Kovalenko group used pyrite (FeS\(_2\)) as a cathode, Mg as an anode, and a hybrid electrolyte made of Mg[BH\(_4\)]\(_2\) and NaBH\(_4\) in diglyme.\(^14\)

The electrolyte has low anodic stability that limits the selection of high-voltage cathode. The cell showed a sloping voltage profile from 0.4 to 1.6 V vs. Mg with the average discharge potential of 1.1 V. It is therefore important to find a compatible cathode and hybrid electrolyte combination to demonstrate a stable high-voltage Mg–Na-ion battery.

In this work, we report such a hybrid battery combining a Berlin green (BG, FeFe(CN)\(_6\)) cathode, a Mg metal anode, and a hybrid Mg–Na-ion electrolyte. Inspired by the remarkable activity of the recently reported dimagnesiumdichloro dimer complex cation electrolyte,\(^15\) we prepared 0.2 M [Mg\(_2\)(μ-Cl)]\(_2\)[AlCl\(_4\)] in dimethoxythane (DME), and then dissolved 0.4 M NaAlCl\(_4\) in the electrolyte to form a clear and transparent solution (Fig. S1, ESI†). The hybrid electrolyte has high anodic stability (3.2 V vs. Mg\(^{2+}/\text{Mg}\)). The BG cathode shows reversible capacity of 143 mA h g\(^{-1}\) and stable cycling for 50 cycles.

Fig. 1 shows the working mechanism of the proposed hybrid magnesium–sodium-ion battery. The electrolyte has complicated equilibrium among four electroactive species: charged species of [Mg\(_2\)Cl\(_2\)]\(^{2+}\) and AlCl\(_4^-\), and less dominant neutral species of MgCl\(_2\) and AlCl\(_3\).\(^16\) The cell is assembled in the charged state. During the discharge, metallic Mg reacts with AlCl\(_4^-\) to form [Mg\(_2\)Cl\(_2\)]\(^{2+}\) dimer cations since AlCl\(_4^-\) is easier than MgCl\(_2\) to lose Cl\(^-\). Therefore no NaCl will form due to no free Cl\(^-\) available.
Electrons are transferred through the external circuit from the Mg anode to the BG cathode, where a reduction reaction results in Na-ion insertion into the BG framework. During the charge, Na-ions are deinserted from the Na$_2$FeFe(CN)$_6$ into electrolyte, and in the meantime $[\text{Mg}_2\text{Cl}_2]^{2+}$ dimer cations are reversibly reduced and deposited as Mg on the anode. Because the thermodynamic redox potential of Mg$^{2+}$/Mg is 0.36 V higher than that of Na$^+$/Na, reversible Mg deposition–dissolution should occur at the anode side before Na deposition–dissolution could take place. The following equations describe the reactions in the cell.

Positive electrode: FeFe(CN)$_6$$^+$ + 2Na$^+$ + 2e$^-$ ⇌ Na$_2$FeFe(CN)$_6$

Negative electrode: Mg + AlCl$_4$ ⇌ 1/2$[\text{Mg}_2\text{Cl}_2]^{2+}$ + AlCl$_3$ + 2e$^-$

Overall: FeFe(CN)$_6$ + Mg + 2NaAlCl$_4$ ⇌ Na$_2$FeFe(CN)$_6$ + 1/2$[\text{Mg}_2\text{Cl}_2]^{2+}$ + AlCl$_3$

PBAs are used as the cathode material, which have the general formula $A_{M1}M_{2n}A_{1n}$ and an open framework (Fig. S2, ESI†) that facilitates reversible intercalation processes for alkali and alkaline earth ions ($A_x$). The PBA capacity is determined by the available A-sites in the compounds into which the alkali and alkaline earth ions can be intercalated reversibly in a range of working voltages. From the electric neutrality perspective, the valences and vacancies of M1 and M2 mainly contribute to the amount of the available A-sites in the compounds into which the A-sites are inserted, and the thermodynamic redox potential of Mg$^{2+}$/Mg is 0.36 V higher than that of Na$^+$/Na, reversible Mg deposition–dissolution should occur at the anode side before Na deposition–dissolution could take place. The following equations describe the reactions in the cell.

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Fig. 2a shows its X-ray diffraction (XRD) pattern, which can be indexed to a face-centered cubic structure (FCC, space group Fm$\bar{3}$m). Scanning electron microscopy (SEM) shows the cubic nanoparticles with average size of 400 nm. Combining thermogravimetric analysis (TGA) (Fig. S3, ESI†) and Energy-dispersive X-ray (EDX) measurement, we obtained the chemical formula of our BG sample as $K_{0.25}Fe[Fe(CN)]_{0.61}H_2O$.

The hybrid electrolyte is the key to enable high capacity and stable cycling. As mentioned earlier, we used 0.2 M $[\text{Mg}_2(\mu-\text{Cl})_2][\text{AlCl}_4]$ and 0.4 M NaAlCl$_4$ in DME as the hybrid electrolyte due to the promise of high anodic stability. Fig. 2b shows the cyclic voltammetry (CV) from −0.5 V to 3.2 V vs. Mg/Mg$^{2+}$ using a three-electrode setup. Molybdobenzene (Mo) is used as the current collector in a Swagelok cell (Fig. S4, ESI†) due to its anti-corrosion property.¹⁷ Sun et al. recently reported a new cell design to prevent corrosion of current collectors.¹⁸ A halogen-free magnesium monocarborane based electrolyte would be ideal for coin cells.¹⁹ The overpotential for the magnesium deposition is 0.16 V and the Coulombic efficiency is ~87%. The electrolyte is stable up to 3.2 V, agreeing with the previous study.¹⁵ The Mg deposition and stripping behaviour was further assessed via chronopotentiometry in a coin cell containing a stainless steel positive electrode and a Mg negative electrode (Fig. 2c). The Coulombic efficiency is 70% in the first cycle and increases to over 87% in following cycles. The Mg electrode was investigated after 30 cycles using EDX spectroscopy and SEM (Fig. 2d). It is noteworthy that no Na deposition is observed, confirming the Mg-only deposition mechanism at the Mg electrode. The inset shows the SEM image of the electrode surface with an average Mg grain size of about 0.2 μm.

Fig. 3a shows the galvanostatic voltage profiles of BG cathodes in three cell configurations: (1) FeFe(CN)$_6$$^+$|Na$^+$|Na with 1 M NaPF$_6$/EC/DEC electrolyte; (2) FeFe(CN)$_6$$^+$|Mg$^+$|Mg with 0.2 M $[\text{Mg}_2(\mu-\text{Cl})_2][\text{AlCl}_4]$/DME electrolyte; and (3) FeFe(CN)$_6$$^+$|$\text{MgCl}_2$|$\text{NaCl}_2$ with 0.2 M $[\text{Mg}_2(\mu-\text{Cl})_2][\text{AlCl}_4]$|DME and 0.4 M NaAlCl$_4$ electrolyte. In cell configuration 1, the BG electrode exhibits two distinguishable plateaus during the discharge (2.9 and 3.5 V vs. Na/Na$^+$) and the charge (3.0 and 3.7 V vs. Na/Na$^+$), consistent with the results obtained by Lu et al.² According to previous study,⁵ the higher voltage plateau is attributed to the low-spin Fe$^{III}$/Fe$^{II}$ bonded to the C atom of C≡N and the lower voltage plateau to the high-spin Fe$^{III}$/Fe$^{II}$ bonded to the N atoms of C≡N. The specific capacity of BG cathode reaches 145 mAh g$^{-1}$, higher than the previous reported value of 120 mAh g$^{-1}$ obtained by Wu et al.$^4$
In cell configuration 2, BG delivers very low capacity around 10 mA h g\(^{-1}\). Test in another Mg electrolyte, 0.25 M Mg(TFSI)\(_2\) in acetonitrile (Fig. S5, ESI\(^\dagger\)), also shows very low capacity \(\sim 20\) mA h g\(^{-1}\).

For the cell configuration 3 (Fig. 3a), we observed similar voltage profile and comparable capacity as those seen in configuration 1. The voltage difference of 0.8 V between configuration 1 and 3 is attributed to thermodynamic potential difference between Mg/Mg\(^{2+}\) and Na/Na\(^+\) considering the electrolyte activity. This similarity in profile confirms the intercalation of Na\(^+\) into BG as the dominant cathode reaction. This conclusion is also supported by EDX shown in Fig. 3b. The intensity of Mg peak in the discharged sample is very small. This is not surprising given the observation of minimum Mg insertion in cell configuration 2. From the EDX spectra, we calculated the sodiated BG sample has 1.52 Na per formula of Fe[Fe(CN)]\(_{6}\), which agrees with the observed capacity of 143 mA h g\(^{-1}\).

Fig. 3c presents the galvanostatic voltage profiles of a FeFe(CN)\(_{6}\)[Na\(^+\)]Na cell (1), a FeFe(CN)\(_{6}\)[Mg\(^{2+}\)]Mg cell (2), and a FeFe(CN)\(_{6}\)[Na\(^+\)]Mg\(^{2+}\) cell (3), (b) EDX spectra of pristine and discharged BG electrodes in the range of 0.9–1.4 keV; (c) voltage profiles of the hybrid cell at the 1st, 2nd, 20th and 50th cycle at 1C; (d) capacity retention and Coulombic efficiency over 50 cycles at 1C; (e) Fe K-edge XANES and (f) HEXRD spectra of pristine, discharged, and recharged BG cathodes. *Indicates the diffraction peak from the PTFE binder.

Fig. 3a shows the discharge voltage profiles of the hybrid cell measured from 0.25C to 20C. The discharge capacity of the BG electrode decreases from 143 to 110 mA h g\(^{-1}\) when the current density increases from 0.25C (35 mA g\(^{-1}\)) to 10C (1400 mA g\(^{-1}\)). Even at 20C, more than 85 mA h g\(^{-1}\) can be retained. Note the capacity reported here is based on the mass of cathode active materials. Fig. 4b shows the rate capability plot in comparison with hybrid cells reported in literatures. Black symbols indicate the reported Na–Mg hybrid cell\(^{14}\) and blue symbols indicate reported Li–Mg hybrid cells.\(^{22–24}\) The excellent rate capability in this work compares favourably with previously reported hybrid cells. Such high power capability stems from the unique open
framework structure of BG and agrees with previous reports on their fast rate capability.\textsuperscript{1,2,4} Since the salt in electrolyte participates the overall reaction, we calculated the theoretical specific capacity for this battery reaction as 79 mA h g\textsuperscript{-1} and theoretical specific energy density as 174 W h kg\textsuperscript{-1} considering 2.2 V as the average discharge voltage. Experimentally, we demonstrated the energy density of 135 W h kg\textsuperscript{-1} and power density of 1.67 kW kg\textsuperscript{-1} at 20 C (see ESIT\textsuperscript{†} for the calculation details).

In summary, we have demonstrated a low-cost high-power Mg–Na hybrid battery enabled by high-voltage Mg–Na dual salt electrolyte (3.2 V vs. Mg/Mg\textsuperscript{2+}), open framework cathode, and the fast-kinetic Mg metal anode. The full cell delivers an average discharge voltage of 2.2 V and stable cycling for 50 cycles. We obtained the high power density of 1.67 kW kg\textsuperscript{-1} and obtain the high power density of 1.67 kW kg\textsuperscript{-1}. The unit cell of BG has only 5.3% volume increases than the pristine compound and slight non-uniform structural distortion when 1.52 Na inserts into the framework. XANES study shows a clear reversible shift of Fe K-edge to lower energy and a small hump around 7118 eV. At the anode side, EDX and SEM confirm fast and reversible Mg-only deposition mechanism. Therefore this work opens the door to many Na-ion cathode materials for high voltage Mg–Na hybrid batteries that could become a viable candidate for stationary energy storage.

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**Notes and references**