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A high-voltage concept with sodium-ion conducting β -alumina for magnesium-sodium dual-ion batteries

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Rechargeable magnesium-sodium dual-ion batteries that use dendrite-free magnesium metal as an anode, magnesium-sodium dual-ion electrolyte and sodium-ion cathode are appealing as safe, low-cost systems for large-scale stationary electricity storage. Although substantial advances have been made on magnesium-sodium dual-ion batteries with various sodium-ion cathodes, further development of such batteries is inherently limited by the low electrochemical oxidative stability of known dual-ion electrolytes (2–2.6 V vs. Mg^{2+}/Mg). Here, we examine a magnesium-sodium dual-ion concept, which allows for higher operating voltages of magnesium-sodium dual-ion batteries by using oxidatively stable sodium-ion electrolytes along with a sodium-ion conducting β -alumina membrane on the cathode side. The proposed concept is assessed using a high-voltage $\text{Na}_{1.5}\text{VPO}_{4.8}\text{F}_{0.7}$ cathode demonstrating a high average discharge voltage of 3.0 V, a cathodic capacity of 110 mAh g^{-1} and an energy efficiency of 90%.

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The urgent need to shift from fossil fuels to renewable energy sources — and thus CO₂ emission-free energy production — is considerably impeded by the lack of efficient, low-cost solutions for large-scale storage of electricity. Whereas lithium-ion batteries (LIBs) dominate the market of portable electronics due to their high energy density, whether they are an economically viable option for large-scale stationary storage due to the limited and uneven global distribution of known natural reserves of lithium and the high cost of manufacturing is questionable^{1,2}. In this regard, magnesium-ion batteries (MIBs) might evolve as an inexpensive alternative because of the much higher natural abundance of magnesium (2.3 wt% in the Earth's crust, ~1100 times higher than that of Li)³ and hence significantly lower cost (4 USD kg⁻¹, 15 times lower in comparison with that of Li for pure metals). Notably, both the gravimetric charge storage capacity of metallic magnesium (3833 mAh cm⁻³, 2205 mAh g⁻¹) and its standard electrode potential (−2.35 V vs. SHE) compare favorably with those of lithium (2062 mAh cm⁻³, 3861 mAh g⁻¹, and −3.04 V vs. SHE, respectively) and sodium (1128 mAh cm⁻³, 1166 mAh g⁻¹, and −2.7 V vs. SHE, respectively)^{4–9}. Importantly, in contrast to lithium^{10,11} and sodium¹², metallic magnesium can be safely employed as an anode in MIBs due to dendrite-free electrodeposition^{4,5,13–16}. The development of practical MIBs is, however, hampered by several factors. First, contrary to the facile intercalation of monovalent Li⁺ and Na⁺ ions, the intercalation of Mg²⁺ ions, which are as small as Li⁺ ions but have a higher charge density, is found to be sluggish due to strong coulombic interactions with negatively charged anionic lattices in cathodic materials¹⁷. The second problem relates to the desolvation of Mg²⁺ ions at the electrolyte–cathode interface, where the strong coordination of Mg²⁺ ions with solvent hampers their insertion into a cathode^{18–22}. Consequently, most of the reported magnesium cathode materials are characterized by poor rate capability and cycling performance and high overpotentials between charge and discharge, reducing the energy efficiency^{4,6,23–25}. Chevrel-phase Mo₆S₈ developed by Aurbach et al.¹⁴ in the early 2000s remains the benchmark cathode material with an average discharge voltage of ~1.1 V (vs. Mg²⁺/Mg) and practical room temperature capacities of 80–100 mAh g⁻¹ (the theoretical capacity is 128 mAh g⁻¹).

To circumvent the issues associated with Mg-ion cathode materials, novel Mg/Na or Mg/Li dual-ion (hybrid) battery concepts have been recently proposed^{26–33}. Mg/Na(Li) dual-ion batteries consist of a dendrite-free magnesium metal as an anode, a Na-ion^{32,34–36} or Li-ion^{27,28,30,33,37–45} cathode and Mg/Na or Li/Mg dual-ion electrolytes that support reversible plating of Mg on the anode and provide a suitable voltage range for the concomitant insertion/removal of Na⁺(Li⁺) ions at the cathode. While recent research efforts on Mg/Na dual-ion batteries have been mainly focused on testing various Na-ion cathodes, the further development of such batteries is inherently limited by the low oxidative stability of dual-ion electrolytes. Specifically, typical Mg/Na dual-ion electrolytes are based on highly reductive Grignard reagents or borohydrides, needed for Mg-electroplating, which thus have a limited operational voltage range of 2–2.6 V. This choice of electrolytes imposes severe restrictions on the selection of cathode materials. We note that Mg electrolytes composed of more oxidatively stable magnesium salts (e.g., perchlorates) and solvents (e.g., carbonates) do not support reversible electroplating of Mg due to the formation of an ionically insulating layer of MgO⁴⁶.

To produce Mg/Na dual-ion batteries with higher working voltages, here we show an alternative cell employing oxidatively stable Na-ion electrolytes and Na-ion conductive membranes (β-alumina) on the cathode side of the battery (Fig. 1). This approach is tested with a high-voltage Na_{1.5}VPO_{4.8}F_{0.7} cathode

Fig. 1 Working principle of a high-voltage Mg/Na dual-ion battery.

a Schematic of the charge/discharge processes and **b** cell configuration of a high-voltage Mg/Na dual-ion battery (see Supplementary Fig. 1 for details)

and 1 M NaClO₄ in propylene carbonate (PC) as a Na-ion electrolyte. The resulting Mg/Na_{1.5}VPO_{4.8}F_{0.7} cells exhibited a high average discharge voltage of 3.0 V, cathodic capacity of 110 mAh g⁻¹, and energy efficiency of 90%.

Results

Synthesis and electrochemical performance of Na_{1.5}VPO_{4.8}F_{0.7} cathode. Na_{1.5}VPO_{4.8}F_{0.7} was synthesized according to the reported procedure of Park et al.⁴⁷ by a solid-state reaction of VPO₄, VOPO₄, NaF, and Na₂CO₃. Prior to electrode preparation, Na_{1.5}VPO_{4.8}F_{0.7} powder was mixed with carbon black (20 wt%) by ball-milling and annealed at *T* = 450 °C for 12 h to enhance its electrical conductivity and crystallinity (see Supplementary Fig. 2)⁴⁸. As illustrated in Fig. 2a, the X-ray diffraction (XRD) pattern of the resulting material points to a pure Na_{1.5}VPO_{4.8}F_{0.7} phase with particle sizes <5 μm (see inset, Fig. 2a). For the electrochemical measurements, electrodes were prepared by mixing a powder of Na_{1.5}VPO_{4.8}F_{0.7}/carbon with poly(vinylidene fluoride) binder in N-methyl-pyrrolidone as a solvent, and the resulting slurries were

Fig. 2 Characterization and electrochemical performance of $\text{Na}_{1.5}\text{VPO}_{4.8}\text{F}_{0.7}$. **a** Comparison of the experimental (black line) and calculated (rose dots) powder diffraction patterns of $\text{Na}_{1.5}\text{VPO}_{4.8}\text{F}_{0.7}$ together with the difference (dark green line) and the reflection positions (black bars) obtained from the Rietveld refinement (space group $P4_2/mnm$, $a = b = 9.044 \text{ Å}$, $c = 10.627 \text{ Å}$, see Supplementary Table 1). The inset shows a scanning electron microscopy (SEM) image of $\text{Na}_{1.5}\text{VPO}_{4.8}\text{F}_{0.7}$ after ball-milling and annealing with carbon black (scale bar: $5 \mu\text{m}$; see Supplementary Fig. 3 for additional SEM images). **b** Galvanostatic charge/discharge curve (5th cycle) and **c** capacity retention for $\text{Na}_{1.5}\text{VPO}_{4.8}\text{F}_{0.7}$ tested as cathode material in Na-ion half-cells. Cells were cycled at room temperature with a current density of 64.9 mA g^{-1} (0.5 C) in the potential range of 2.5–4.3 V vs. Na^+/Na using 1 M NaBF_4 in EC:PC (1:1 by vol.) as the electrolyte

cast onto tungsten foil as a current collector (for details see Methods section). Prior to carrying out Mg/ $\text{Na}_{1.5}\text{VPO}_{4.8}\text{F}_{0.7}$ dual-ion battery tests, the electrochemical performance of the $\text{Na}_{1.5}\text{VPO}_{4.8}\text{F}_{0.7}$ cathode was individually assessed using elemental sodium as both the counter and reference electrode and 1 M NaBF_4 in a mixture of ethylene carbonate (EC) and PC (1:1 by vol.) as the electrolyte. As shown in Fig. 2b, the $\text{Na}_{1.5}\text{VPO}_{4.8}\text{F}_{0.7}$ cathode exhibited a high capacity of 112 mAh g^{-1} , close to the theoretical value of 129.7 mAh g^{-1} . Two reversible redox processes— $\text{V}^{3.8+}/\text{V}^{4.3+}$ and $\text{V}^{4.3+}/\text{V}^{4.8+}$ —occur at ca. 3.55 V and 4.0 V vs. Na^+/Na , respectively⁴⁷. We note that low initial coulombic efficiency of $\text{Na}_{1.5}\text{VPO}_{4.8}\text{F}_{0.7}$ cathode (Fig. 2c, Supplementary Fig. 4) could be related to the formation of the solid electrolyte interface formed on sodium metallic anode during first charge.

Electrochemical performance of Mg/ $\text{Na}_{1.5}\text{VPO}_{4.8}\text{F}_{0.7}$ dual-ion batteries. Next, we assembled Mg/ $\text{Na}_{1.5}\text{VPO}_{4.8}\text{F}_{0.7}$ dual-ion cells using a $\text{Na}_{1.5}\text{VPO}_{4.8}\text{F}_{0.7}$ cathode and magnesium metal as the anode. On the anode and cathode side of the battery, Mg/Na dual-ion (2 M NaBH_4 + 0.2 M $\text{Mg}(\text{BH}_4)_2$ in tetraglyme) and Na-ion (1 M NaClO_4 in PC) electrolytes were used, respectively. The β -alumina membrane was placed between the two electrolytes,

providing charge transfer between the anode and cathode of the battery through Na-ion transport^{49–52}. We note that the Mg/Na dual-ion borohydride electrolyte was chosen based on our previous study of Mg/Na dual-ion batteries with FeS_2 nanocrystals as a cathode material³². One important advantage of borohydride electrolytes compared to frequently used Grignard-based electrolytes is the absence of Cl^- ions, which would otherwise significantly limit the concentration of Na^+ ions in solution due to the limited solubility of NaCl in the used solvents. The electrochemical properties of the Mg/Na dual-ion battery are summarized in Fig. 3. Similar to Na-ion half-cell tests, $\text{Na}_{1.5}\text{VPO}_{4.8}\text{F}_{0.7}$ measured in the Mg/ $\text{Na}_{1.5}\text{VPO}_{4.8}\text{F}_{0.7}$ configuration delivers a stable discharge capacity of 98 mAh g^{-1} on average with a coulombic efficiency of $\sim 99.0\%$ at a rate of 1C in the potential range of 2.4–3.8 V vs. Mg^{2+}/Mg (see Supplementary Fig. 5 for details). Figure 3c shows the rate capability of $\text{Na}_{1.5}\text{VPO}_{4.8}\text{F}_{0.7}$ at rates of 0.2C, 1C, and 2C, yielding capacities of 110–80 mAh g^{-1} . The galvanostatic charge/discharge curves for $\text{Na}_{1.5}\text{VPO}_{4.8}\text{F}_{0.7}$ in the Mg/Na dual-ion cell match those observed for the Na-ion half-cell tests (see Figs. 2b and 3a), indicating that the same electrochemical cathodic processes occur. It should be noted that the potentials shifted by $\sim 0.7 \text{ V}$, which is $\sim 0.35 \text{ V}$ higher than the value expected based on the difference in the standard potentials of Na^+/Na and Mg^{2+}/Mg . This mismatch and slight hysteresis

Fig. 3 Electrochemical performance. **a** Galvanostatic charge/discharge curves and **b** corresponding capacity retention and coulombic efficiency at a current density of 129.8 mA g⁻¹ (1C). **c** Rate capability tests at rates of 0.2C, 1C, and 2C. The performance is for Mg/Na dual-ion batteries composed of a Mg anode and a Na_{1.5}VPO_{4.8}F_{0.7} cathode

between charged and discharged galvanostatic curves are most likely caused by the overpotential for Mg plating/stripping on the anode, as previously reported in the literature³². The resulting average discharge voltage of Mg/Na_{1.5}VPO_{4.8}F_{0.7} with the β -alumina membrane is 3.0 V at a rate of 1C. To the best of our knowledge, this is the highest voltage demonstrated thus far for Mg/Na dual-ion batteries (see Supplementary Table 2 for a detailed comparison).

From the non-rocking-chair operation principle of the dual-ion concept, the large mass/volume of the electrolyte, which is a reservoir of all the ions needed for battery operation, must be

factored into energy density calculations. Specifically, in the case of Mg/Na dual-ion batteries utilizing Mg/Na dual-ion electrolytes, the anodic capacity associated with reversible magnesium electrodeposition/stripping depends on the concentration of Mg²⁺ ions in the electrolyte. Thus, the solubility of the respective Mg salt is a limiting factor. Considering the whole mass of the liquid electrolyte, the theoretical charge storage capacity of the Mg/Na dual-ion battery at the cell level can be determined from the standard relationship $C_{\text{total}} = \frac{C_A C_C}{C_A + C_C}$ ⁵³, as follows (see Supplementary Note 1 for details):

$$\text{Gravimetric } C_{\text{cell}} = \frac{F x (M_d - M_c) C_c}{F x (M_d - M_c) + C_c \rho \cdot 10^3} (\text{Ah kg}^{-1}) \quad (1)$$

where $F = 26.8 \times 10^3 \text{ mAh mol}^{-1}$ (Faraday constant), x is the charge of the electroactive species, (M_d) and (M_c) are molarities (mol L⁻¹) of Mg(BH₄)₂ in electrolyte in discharged and charged state of battery, respectively, C_c is the specific gravimetric capacity of the cathode in mAh g⁻¹, and ρ is the density of the electrolyte in g ml⁻¹. To estimate the energy density, the C_{cell} value must be multiplied by the average battery voltage, $E = C_{\text{cell}} \cdot V$.

According to Eq. (1), with an average discharge voltage of 3.0 V, the theoretical gravimetric energy density of the Mg/Na_{1.5}VPO_{4.8}F_{0.7} dual-ion battery can be estimated at 57 Wh kg⁻¹ with an overall energy efficiency of 90%.

Discussion

In summary, we have demonstrated a proof-of-concept for high-voltage Mg/Na_{1.5}VPO_{4.8}F_{0.7} dual-ion batteries utilizing oxidatively stable Na-ion electrolytes separated from Mg/Na dual-ion electrolytes by Na-ion conducting β -alumina membranes. The Mg/Na_{1.5}VPO_{4.8}F_{0.7} battery delivers a stable cathodic capacity of 98 mAh g⁻¹ at a current rate of 129.8 mA g⁻¹ (1C) with an average discharge voltage of 3.0 V. Its energy density of 57 Wh kg⁻¹ is comparable with that of state-of-the-art lead-acid and vanadium redox-flow batteries, illustrating great potential in large-scale energy storage applications. To further maximize its energy density, we suggest that future work in this field should focus on finding Mg/Na dual-ion electrolytes with higher Mg²⁺ molarity (solubility).

Methods

Chemicals and battery components. Carbon black (CB, Super C65, TIMCAL), poly(vinylidene fluoride) (PVdF, Sigma-Aldrich), N-methyl-2-pyrrolidone (NMP, 99%, Sigma-Aldrich), NaBF₄ (>98%, Sigma-Aldrich), NaClO₄ (98%, Alfa Aesar), NaBH₄ (98%, ABCR), Mg(BH₄)₂ (95%, Sigma-Aldrich), propylene carbonate (PC, BASF, battery grade), ethylene carbonate (EC, Novolyte, battery grade), tetraethylene glycol dimethyl ether (tetraglyme, ≥98%, Sigma-Aldrich, dried), sodium (Sigma-Aldrich), magnesium (99.95%, GalliumSource), glass microfiber separator (GF/D, Whatman), and β -alumina membrane (Ionotec).

Electrode fabrication and electrochemical measurements. Prior to electrode preparation, Na_{1.5}VPO_{4.8}F_{0.7} was carbon coated by ball-milling with CB (20 wt%) following annealing at 450 °C for 12 h⁴⁸. Electrodes were prepared by mixing the Na_{1.5}VPO_{4.8}F_{0.7}/CB powder with PVdF and NMP using a Fritsch pulverisette 7 classic planetary mill (500 rpm, 1 h). The resulting electrode composition was 72 wt % Na_{1.5}VPO_{4.8}F_{0.7}, 18 wt % CB and 10 wt % PVdF. Slurries were coated onto tungsten current collectors and dried at 80 °C for 12 h under vacuum. All electrochemical measurements were conducted on homemade, reusable, airtight two-electrode cells assembled in an Ar-filled glove box (O₂ < 0.1 ppm, H₂O < 0.1 ppm). Elemental sodium and magnesium were employed as both reference and counter electrodes in Na-ion half-cells and Mg/Na dual-ion cells, respectively. For Na-ion half-cell tests, 1 M NaBF₄ in EC:PC (1:1 by vol.) served as the electrolyte. For Mg/Na dual-ion batteries, 2 M NaBH₄ + 0.2 M Mg(BH₄)₂ in tetraglyme and 1 M NaClO₄ in PC were used as Mg/Na dual-ion and Na-ion electrolytes on the anode and cathode side of the battery, respectively. Absence of dendritic Mg plating/stripping on the anode upon cycling in 2 M NaBH₄ + 0.2 M Mg(BH₄)₂ in tetraglyme had been confirmed by SEM measurements (see Supplementary Fig. 6). We note that despite of relatively small difference between Na⁺/Na (~-2.7 V vs. SHE) and Mg²⁺/Mg (~-2.4 V vs. SHE) redox potentials, only Mg is plated in 2 M NaBH₄ + 0.2 M Mg(BH₄)₂ in tetraglyme (see Supplementary Fig. 7 for EDX data of plated electrode). A piece of glass fiber served as a separator for the Na-ion half-cell

tests, whereas an ion-selective β -alumina membrane (thickness: 0.5 mm; weight: 5 g) was used for the Mg/Na dual-ion batteries. Galvanostatic cycling tests were carried out at room temperature on an MPG2 multichannel workstation (BioLogic). Capacities were normalized by the mass of $\text{Na}_{1.5}\text{VPO}_{4.8}\text{F}_{0.7}$.

Materials characterization. Powder X-ray diffraction was conducted by STOE STADI P powder X-ray diffractometer (Cu-K α_1 irradiation, $\lambda = 1.540598 \text{ \AA}$). Scanning electron microscopy imaging was carried out using a NanoSEM 230 instrument.

Data availability

The data that support the plots within this paper and other finding of this study are available from the corresponding author upon reasonable request.

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Author contributions

K.V.K., M.W., and M.V.K. designed the experimental work. K.V.K., and M.W. conducted all experiments reported in the paper. K.V.K., M.W., and M.V.K. wrote the paper.

Additional information

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