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Layered electrode materials for non-aqueous multivalent metal batteries

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The global transition to clean energy production accelerates the necessity for efficient energy storage solutions. Lithium-ion batteries (LIBs), developed considerably over the past three decades, have been widely applied in portable electronics and electric vehicles. Nevertheless, the application of LIBs in large-scale energy storage applications is restricted by the Li resource scarcity, high-cost raw materials, and severe safety issues, which thus triggers the development of new battery chemistries beyond Li^+ . In this regard, multivalent metal batteries (MVMBs, e.g., Zn, Mg, and Al batteries) are promising alternatives owing to the advantages brought by the direct use of corresponding metals as anodes, such as high elemental abundance, low anode redox potential, multielectron redox capability, and facile metal stripping and plating chemistry. However, MVMBs suffer from the lack of available cathodes for efficiently accommodating multivalent metal ions (i.e., Zn^{2+} , Mg^{2+} , and Al^{3+}), which originates from the strong electrostatic interactions between charge carrier ions and cathodes. Promising cathode candidates for MVMBs to address this challenge are layered electrode materials, whose structures can be engineered with versatile approaches to regulate the charge-storage behaviour. Here, layered electrode materials used for non-aqueous MVMB cathodes are thoroughly reviewed. We first introduce the cell configurations and the thus-far developed anode–electrolyte–cathode chemistries for non-aqueous MVMBs. Recent progress in the exploration of layered materials for non-aqueous MVMBs is subsequently summarized. Emphasis is put on examining the employed structure engineering strategies and their effects on both the intrinsic properties and electrochemical behaviours of layered electrode materials. Finally, perspectives on the challenges and future directions in this research field are provided with aspects to the cathode structure engineering, performance assessment, and device demonstration.

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1. Introduction

Global warming is pushing towards the transition from traditional fossil fuels to clean energy resources like solar, wind, and tidal energies.^{1,2} However, the intermittent nature of these clean

and cheap energy resources restricts their direct utilization, which imposes a strong demand for high-performance energy storage technologies.^{3–5} Among existing electrochemical energy storage technologies, lithium-ion batteries (LIBs) represent the most commercially successful one, and they have been implemented in diverse applications, such as portable electronics and electric vehicles.^{6,7} However, the severe safety issues of LIBs, limited Li resource in the earth crust (20 ppm, 0.002%), and the increasing demand for cheap energy storage solutions motivate the development of new battery chemistries relying on cheap and abundant elements. In this context, multivalent metal batteries (MVMBs) are proposed as promising alternatives, which directly employ resource-abundant and low-cost multivalent metals (*e.g.*, Zn, Mg, and Al) as anodes.^{8–16} Typically, multivalent metal anodes present low stripping/plating potentials (−0.76, −2.37, and −1.66 V *vs.* standard hydrogen electrode (SHE) for Zn, Mg, and Al, respectively), which are beneficial for the construction of high-voltage and high-energy storage devices (Fig. 1). Importantly, Zn, Mg, and Al are the 24th, 8th, and 3rd most abundant elements in the Earth's crust, respectively. These metal anodes can deliver high specific capacities due to their multielectron redox capability (820, 2206, and 2981 mA h g^{−1} for Zn, Mg, and Al, respectively). Meanwhile, the high mass densities of multivalent metals empower the corresponding anodes with impressive volumetric capacities (5849, 3834, and 8047 Ah L^{−1} for Zn, Mg, and Al, respectively). Interestingly, the partial compatibility of multivalent metals (especially Zn) with water-based electrolytes inspired researchers to develop aqueous MVMBs. Aqueous electrolytes enable the fabrication of low-cost and safe MVMBs with fast cation-storage kinetics of the cathodes.^{17,18} However, aqueous MVMBs suffer from low voltage windows (normally less than 1.8 V) due to the narrow stable potential windows of water-based electrolytes. Moreover, water in electrolytes would lead to the formation of passivation layers on metal anodes, which can inhibit the stripping/plating of Mg and Al and accelerate the dendrite growth of Zn. By contrast, multivalent metals show negligible passivation or dendrite growth in non-

aqueous electrolytes, providing the metal stripping/plating process with high coulombic efficiency.^{19–24} Additionally, non-aqueous electrolyte displays substantially higher potential window than aqueous electrolytes, enabling the use of many cathode materials with high redox potentials. All these features allow non-aqueous MVMBs to be promising candidates to abreast with LIBs as leading energy storage technologies.

However, the construction of practical non-aqueous MVMBs is hindered by severe challenges induced by the multivalent metal ions as charge carriers for cathodes. Multivalent metal ions display large charge densities, resulting from the multivalent nature and the small ionic radii (0.74, 0.72, and 0.53 Å for Zn²⁺, Mg²⁺, and Al³⁺ compared with 0.76 Å for Li⁺). It further leads to the strong electrostatic interactions between charge carrier ions and cathodes during the charge/discharge of non-aqueous MVMBs. Consequently, most well-recognized metal oxide cathodes for LIBs stand inappropriate for non-aqueous MVMB cathodes.^{25–31} In this sense, cathode structures for non-aqueous MVMBs should be re-designed at the atomic level to enable facile Zn²⁺, Mg²⁺, and Al³⁺ storage.

As promising cathode candidates for non-aqueous MVMBs, natural layered materials are a class of materials with strong atom bonding in the basal plane and weak van der Waals (vdW) interaction between layers. These materials are equipped with versatile physical, chemical, electronic properties, as well as broad structural diversity.^{32–35} Particularly, layered materials are appealing for energy storage, as they exhibit some intrinsic advantages over non-layered materials. For example, compared with non-layered materials, layered materials depicted higher accessibility of exposed active sites, enabling higher specific capacities and better ion diffusion kinetics.^{36–38} However, some layered materials suffer from phase transition during electrochemical processes and poor stability in the ambient environment.³⁹ Thus far, a variety of layered materials have been explored as cathodes for MVMBs, including layered transition metal oxides (TMOs),^{32,40} transition metal dichalcogenides (TMDs),^{41–43} graphite,^{44,45} and two-dimensional (2D) covalent organic frameworks (COFs).⁴⁶ Pristine layered materials as non-aqueous MVMB cathodes generally exhibit limited electrochemical performance.⁴⁷ Importantly, the weak vdW interaction between the stacked layers enables layered materials with diverse possibilities for rational structure engineering, such as exfoliation into 2D nanoflakes, interlayer expansion with guest molecules, and hybrid structure construction (Fig. 2).⁴⁸ These structure engineering strategies are highly desired for layered materials to tailor their intrinsic properties (*e.g.*, electronic structure, conductivity, and redox capability) and electrochemical behaviours (*e.g.*, ion desolvation energy, solid-state ion diffusion kinetics, charge-storage mechanism) for multivalent metal ion storage.

In this review, the latest development of layered materials for non-aqueous MVMB cathodes is reviewed. We first summarize the typical configurations of non-aqueous MVMBs in terms of the developed electrolytes, typical anode–electrolyte–cathode chemistries, and possible charge carrier ions. Next, a comprehensive overview of state-of-the-art layered materials used for

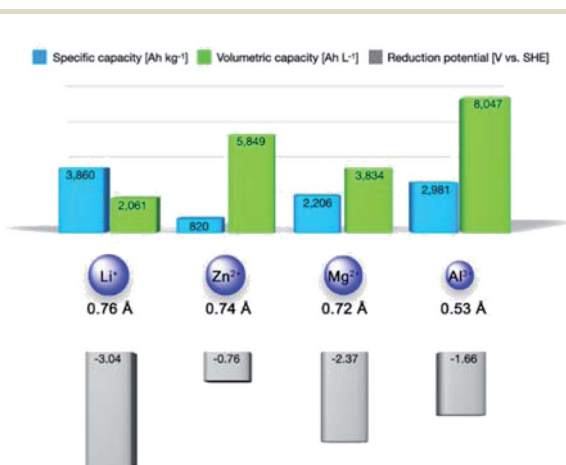


Fig. 1 Specific capacities, volumetric capacities, ionic radii, and stripping/plating potentials of various metal ions.

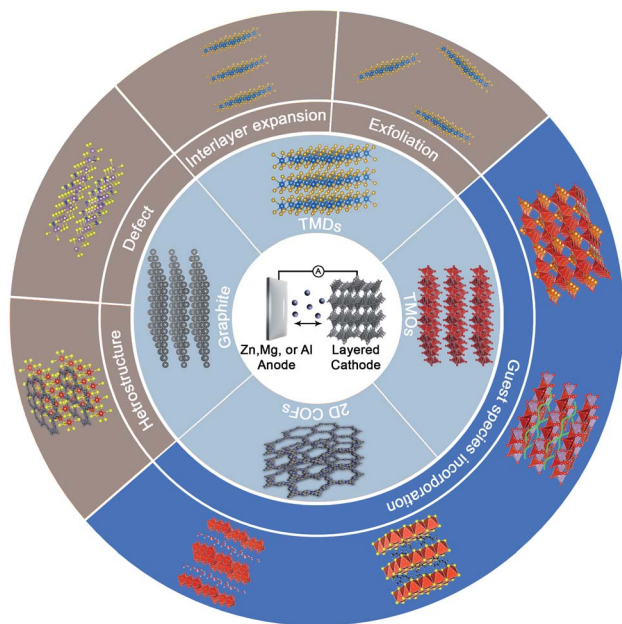


Fig. 2 Schematic illustration of the review content, including the cell configuration of non-aqueous MVMBs, layered cathode materials, and structure engineering methods.

non-aqueous MVMBs is carried out by emphasizing the strategies applied to tailor the structures of layered materials. Emphatic efforts are devoted to analysing the induced changes in the intrinsic properties and electrochemical behaviours of layered materials upon the structure regulation. Finally, perspectives on the current challenges and future directions of layered materials for non-aqueous MVMBs are presented.

2. Cell configurations of non-aqueous MVMBs

Contrasting to Li-metal anodes, Zn-, Mg-, and Al-metal anodes can be easily processed and show no aggressive dendrite growth in non-aqueous electrolytes during battery operation.⁴⁹ Although multivalent metals can be directly used as anodes, their stripping/plating reactions are not the simple $M^{x+} + xe^- \rightarrow M$ reaction. Exact reaction mechanisms on multivalent metal anodes are introduced in this section. Additionally, according to the different cathode chemistry, non-aqueous MVMBs can be briefly categorized into cation ‘rocking-chair’ cells and dual-ion cells. In ‘rocking-chair’ cells, cation released from cathodes and metal plating on anodes occur during the charge of cells, while cation storage in cathodes and metal stripping on anodes occur during the discharge of cells. The electrolyte concentration in the ‘rocking-chair’ cells keeps constant during the cell operation. In dual-ion cells, anions serve as charge carrier ions for cathodes, which are stored/released in/from cathodes during the charge/discharge process of cells. The charge process would consume ions in electrolytes, and high-concentration or large amounts of electrolytes are preferred for dual-ion cells.⁵⁰ In this section, we also

discuss the cathode chemistries of MVMBs with a particular focus on the different charge carrier species.

2.1 Zn-metal batteries

The Zn^{2+}/Zn couple has a sufficiently high redox potential of -0.76 V vs. SHE, which enables the Zn stripping/plating reaction to be feasible in either alkaline or close-to-neutral aqueous electrolytes. Moreover, the use of water-based electrolytes brings the advantages of low cost, high safety, high ionic conductivity, and easy-to-manufacture feature.⁵¹ Thereby, dominant researches of Zn-metal batteries (ZMBs) are focused on aqueous systems. Aqueous ZMBs are not covered in this review, and interested readers are directed to recent comprehensive reviews of this field.^{52–57} It is worth noting that aqueous ZMBs are restricted by several intrinsic drawbacks arising from the use of aqueous electrolytes. Cathode materials like MnO_2 and $VOPO_4$ suffer from dissolution in water, resulting in fast capacity degradation during cycling.^{58,59} Additionally, Zn-metal anodes in aqueous electrolytes exhibit severe side reactions (e.g., hydrogen evolution, ZnO formation) and Zn dendrite growth, which further lead to the electrolyte decomposition, irreversible Zn consumption, low stripping/plating coulombic efficiency, and safety issues.⁶⁰

Non-aqueous electrolytes based on ionic liquid, acetonitrile (AN) or carbonate solvents with Zn salts (e.g., zinc bis(trifluoromethylsulfonyl)imide ($Zn(TFSI)_2$), $Zn(CF_3SO_3)_2$ ($Zn(OTf)_2$), $Zn(ClO_4)_2$, $Zn(BF_4)_2$, and $Zn(PF_6)_2$) were demonstrated feasible for reversible Zn stripping and plating.^{24,61–66} These electrolytes offer much wider voltage windows than aqueous electrolytes. For example, Han *et al.*⁶⁴ showed that both AN and propylene carbonate (PC), dissolving different Zn salts (e.g., $Zn(TFSI)_2$, $Zn(OTf)_2$, $Zn(BF_4)_2$, and $Zn(PF_6)_2$), demonstrated high anodic stability of 3.8 V vs. Zn^{2+}/Zn . Wang *et al.*²⁴ developed a Li^+ -containing hybrid electrolyte, exhibiting high anodic stability of 4 V vs. Zn^{2+}/Zn . The high anodic stability was achieved by adding $LiPF_6$ to $Zn(TFSI)_2$ in ethyl methyl carbonate (EMC). The wide voltage windows of non-aqueous Zn electrolytes are crucial for the fabrication of high-voltage and high-energy ZMBs.

According to the cathode chemistries, two possible charge storage mechanisms for non-aqueous ZMBs are presented in Fig. 3. The first one relies on the Zn^{2+} ‘rocking-chair’ mechanism. The high energy barrier of Zn^{2+} desolvation on the cathode surface accounts for the large charge-transfer resistance of these ZMBs.^{61,66,67} The second mechanism is based on dual-ion cells, involving Zn plating/stripping on the anode and anion storage/release on the cathode. The charge-transfer resistance of anion storage is considerably lower than that of Zn^{2+} storage, enabling the excellent rate performance of ZMBs.^{24,68} So far, several cathode materials with the Zn^{2+} -storage mechanism were reported for non-aqueous ZMBs, including MnO_2 ,⁶⁶ vanadium oxide,^{61,65} and $VOPO_4$.⁶⁹ On the other hand, graphite-based cathodes, exhibiting anion intercalation/deintercalation, were used for constructing dual-ion ZMBs.^{23,24,68} Anions, such as PF_6^- , $TFSI^-$, and OTf^- can be used as charge carriers for cathodes, providing ZMBs with high operation

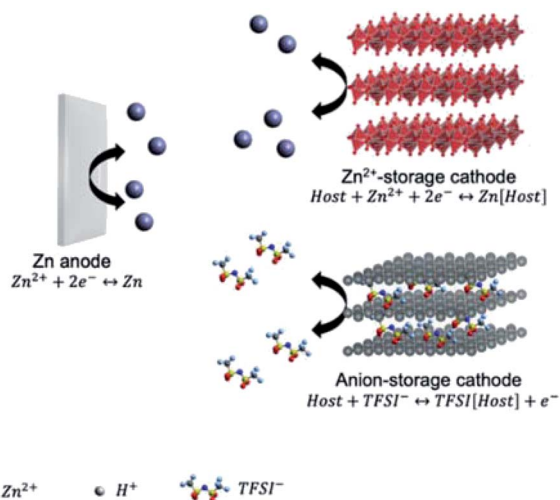


Fig. 3 Schematic illustration showing the charge storage mechanism of ZMBs.

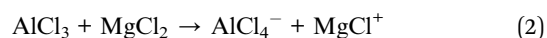
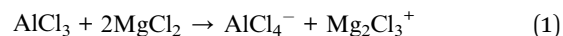
voltages and high energy densities. Overall, compared with aqueous ZMBs, non-aqueous ZMBs benefit from high anodic stability and dendrite-free Zn stripping and plating.

2.2 Mg-metal batteries

The Mg metal surface would be passivated in most solvents by an Mg^{2+} non-conducting layer, preventing the electrochemical Mg plating. In detail, electrolytes comprised of conventional solvents and Mg salts, such as $\text{Mg}(\text{TFSI})_2$ or $\text{Mg}(\text{ClO}_4)_2$ in AN or carbonate solvents, are not suitable for Mg-metal batteries (MMBs),⁷⁰ because these electrolytes tend to form ionic-insulating passivation layers (e.g., MgO , MgCl_2 , and Mg_xClO_y) on Mg metal. Grignard reagents (e.g., EtMgBr , and $\text{Mg}(\text{BR}_4)_2$, where R = butyl, phenyl) dissolved in ethers were presented as the first suitable electrolytes for the facile Mg stripping/plating.^{70–72} However, Grignard reagent-based electrolytes show low anodic stability (<1.5 V vs. Mg^{2+}/Mg).^{72,73} In 2000, Aurbach with his colleagues reported the MMB electrolyte, $\text{Mg}(\text{AlCl}_2\text{-BuEt})_2$, with high anodic stability.⁷⁴ The electrolyte was prepared by mixing MgR_2 (R is butyl or ethyl) and $\text{AlCl}_2\text{R}/\text{AlCl}_3$ in tetrahydrofuran (THF). The reaction between RMgCl and $\text{R}_x\text{AlCl}_{3-x}$ produced $\text{R}_x\text{AlCl}_{4-x}^-$ and active Mg-containing cations (e.g., MgCl^+ and Mg_2Cl_3^+).^{75–78} Importantly, the $\text{Mg}(\text{AlCl}_2\text{BuEt})_2$ electrolyte exhibited a large electrochemical window of 2.5 V vs. Mg^{2+}/Mg , superior to electrolytes without the addition of AlCl_3 (e.g., $\text{Mg}(\text{BPh}_2\text{Bu}_2)_2$ and BuMgCl). Moreover, all phenyl complex (APC) electrolytes, the most commonly used electrolytes for MMBs, can be obtained by substituting the alkyl group of RMgCl with the phenyl group. These APC electrolytes can demonstrate wide stable potential windows of more than 3 V vs. Mg^{2+}/Mg .⁷⁹ Recent studies revealed that reducing the $\text{R}_x\text{AlCl}_{3-x}^-$ concentration and increasing the AlCl_4^- concentration further improved the anodic stability of electrolytes. The low HOMO level of AlCl_4^- played an important role in improving the potential window. Zhao *et al.*⁸⁰ further improved the anodic stability of APC electrolytes by adding 1-butyl-1-

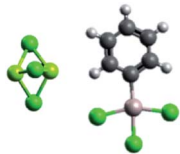
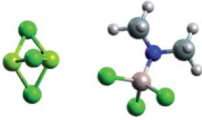
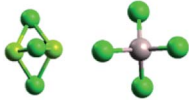
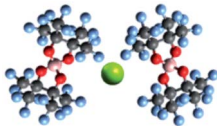
methylpiperidinium chloride (PP_{14}Cl). The Cl^- ions reacted with $\text{R}_x\text{AlCl}_{4-x}^-$ to produce AlCl_4^- , consequently increasing the anodic stability from 2.9 to 3.1 V vs. Mg^{2+}/Mg .

Magnesium aluminium chloride complex (MACC) dissolved in ether solvents (e.g., dimethoxyethane (DME)) represents an important type of MMB electrolytes with all-inorganic salts (e.g., AlCl_3 and MgCl_2).^{81–83} During the preparation of MACC electrolytes, different acid–base reactions occur depending on the ratio between AlCl_3 and MgCl_2 . For MgCl_2 : AlCl_3 ratio of 2 : 1 and 1 : 1, the dominating $\text{Mg}_x\text{Cl}_y^{2x-y}$ species in the electrolyte are Mg_2Cl_3^+ and MgCl^+ through eqn (1) and (2). In these cases, Mg undergoes facile electrochemical stripping and plating due to the presence of $\text{Mg}_x\text{Cl}_y^{2x-y}$ species. Increasing the MgCl_2 : AlCl_3 ratio to 1 : 2 inhibits Mg plating due to the low concentration of $\text{Mg}_x\text{Cl}_y^{2x-y}$ species.⁸² Moreover, when the AlCl_3 : MgCl_2 ratio is higher than 2 : 1, the formation of AlCl_2^+ would cause severe Mg metal corrosion.⁸⁴ Typical MACC electrolytes require the pre-cycling process to reduce the overpotential and improve the electrochemical stripping/plating coulombic efficiency.⁸⁵ The pre-cycling process is termed conditioning, and would complicate the production of MMBs. Conditioning-free MACC electrolytes can be obtained by adding additional salts like $\text{Mg}(\text{TFSI})_2$ and $\text{Mg}(\text{hexamethyldisilazide})_2$ ($\text{Mg}(\text{HMDS})_2$).^{84,86} Besides, these Mg-salt additives can improve the water-resistance of MACC electrolytes, allowing excellent Mg plating at a water content of 2000 ppm. Electrochemical Mg plating is also feasible by completely replacing AlCl_3 in MACC electrolytes with either $\text{Mg}(\text{TFSI})_2$ or $\text{Mg}(\text{HMDS})_2$.^{87,88} In the $\text{MgCl}_2/\text{Mg}(\text{TFSI})_2$ electrolyte, salts and solvents must have high purity by removing water residue to realize the facile Mg stripping and plating. By contrast, purification is not necessary for the $\text{Mg}(\text{HMDS})_2/\text{MgCl}_2$ electrolyte to achieve reversible Mg stripping and plating.



Chloride presence in MMB electrolytes accounts for the corrosive nature of electrolytes for common current collectors (e.g., Al and stainless steel), thus encouraging the development of chlorine-free Mg electrolytes. Mohtadi *et al.*⁹⁰ presented a chlorine-free electrolyte based on $\text{Mg}(\text{BH}_4)_2$ in DME. Nevertheless, the electrolyte displayed low coulombic efficiency (67%), and the decomposition of BH_4^- lead to the low anodic stability (2.3 V vs. Mg^{2+}/Mg) of the electrolyte. Inspired by Mohtadi's work, Tutusaus and co-workers⁹¹ reported a halogen-free electrolyte with dodecaborate dianions for successful Mg stripping and plating. Impressively, the electrolyte demonstrated outstanding anodic stability of 3.8 V vs. Mg^{2+}/Mg .⁹¹ Following this strategy, Luo *et al.*⁸⁹ synthesized Mg perfluorinated pinacolatoborate (FPB) for MMB electrolytes, which depicted outstanding anodic stability of 4.0 V vs. Mg^{2+}/Mg . However, it should be pointed out that the synthesis of boron-based Mg salts generally requires harsh conditions under inert environments. Complicated synthetic routes impose a potential risk for the practical application of these boron-

Table 1 Comparison of developed MMB electrolytes

Electrolyte name	APC ⁷⁹	Mg-HMDS ⁸⁸	MACC ^{81,82}	Mg(BR _n) ₂ (ref. 89)
Main precursors	PhMgCl, AlCl ₃	Mg(HMDS) ₂ , MgCl ₂	MgCl ₂ , AlCl ₃	Mg(BH ₄) ₂ , C ₆ H ₂ F ₁₂ O ₂
Cations and anions	 Mg _x Cl _y ⁺ and Ph _x AlCl _{4-x} ⁻	 Mg ₂ Cl ₃ ⁺ and HMDSAAlCl ₃ ⁻	 Mg ₂ Cl ₃ ⁺ and AlCl ₄ ⁻	 Mg ²⁺ and B(O ₂ C ₂ (CF ₃) ₄) ₂ ⁻
Anodic stability	2.5 V vs. Mg ²⁺ /Mg	2.8 V vs. Mg ²⁺ /Mg	3.5 V vs. Mg ²⁺ /Mg	4.0 V vs. Mg ²⁺ /Mg
Coulombic efficiency	~100%	99%	99%	95%
Advantages	High coulombic efficiency	Good cathode compatibility	Simple synthesis, high concentration	High anodic stability
Drawbacks	Low anodic stability	Low anodic stability	Conditioning required	Complicated synthetic process

based electrolytes. A summary of the main features of developed Mg electrolytes is presented in Table 1.

With the demonstrated anode–electrolyte chemistries, searching compatible cathodes represents the main task to establish suitable full-device chemistries. The large charge density of Mg²⁺ and its strong binding to Cl⁻ and solvent molecules rule out many recognized cathode materials in other battery systems. The first demonstrated MMB cathode with decent performance is the Chevrel-phase Mo₆S₈.⁷⁴ Theoretical studies suggest that the Chevrel phase surface can significantly accelerate the desolvation and dissociation of Mg₂Cl₃⁺ in THF, reducing the dissociation energy of Mg₂Cl₃⁺ from 3.0 eV to 0.2 eV.⁹² For this reason, the Chevrel phase is one of a few inorganic materials that can be used as cathodes of MMBs without structure modification or special conditions (*e.g.*, elevated temperature).

Besides, TMOs are considered promising materials for energy storage due to their high theoretical capacities and operation potentials. Apart from classic Mg²⁺ intercalation, TMO can also store charge through the conversion mechanism.

The charge storage mechanism is determined by the type of TMOs and the nature of electrolytes.^{93–95} However, TMO cathodes for MMBs suffer from large voltage hysteresis and sluggish intercalation kinetics. These issues can be assigned to the strong electrostatic interactions between O atoms in TMOs and Mg²⁺.⁹⁶ In addition, the compatibility of TMOs with chloride-containing electrolytes is poor, making the fabrication of MMBs with TMO cathodes a great challenge.⁹⁴ Another class of MMB cathodes is TMDs, which display better Mg²⁺-intercalation kinetics than TMOs in light of the weak electrostatic interactions between chalcogenide atoms and Mg²⁺. Unlike TMOs, TMDs are compatible with chloride-containing electrolytes. However, the main issue associated with TMDs is their much lower theoretical capacities and redox potentials than those of TMOs. The charge storage mechanism was shown to be either intercalation reaction or intercalation/conversion reaction with Mg²⁺, MgCl⁺, or [Mg(DME)₃]²⁺ as charge-carrier species (Fig. 4).

2.3 Al-metal batteries

Trivalent Al³⁺ and the high abundance of Al resources make Al-metal batteries (AMBs) to be promising candidates for large-scale energy storage. However, electrochemical Al stripping and plating is challenging in both organic and ionic liquid electrolytes. The large charge density of Al³⁺ induces the strong coulombic anion–cation interactions in Al salts (*e.g.*, Al(TFSI)₃ and Al(OTf)₃), which further results in the low solubility of Al salts in common carbonate solvents. On the other hand, although ether-based solvents (*e.g.*, DME and diglyme) can dissolve Al salts, these solvents exhibit strong interactions with cations, leading to high solvation energies.^{97,98} To achieve facile Al stripping/plating, the commonly used chemistry takes use of Al₂X₇⁻ (X is Cl or Br), as shown in eqn (3).^{99–102} The Al plating chemistry was first discovered in high-temperature (140–180 °C) molten salts, such as AlCl₃–LiCl and AlCl₃–NaCl–KCl.^{100,101} However, the requirement of high temperature would greatly restrict the practical application of AMBs in energy storage

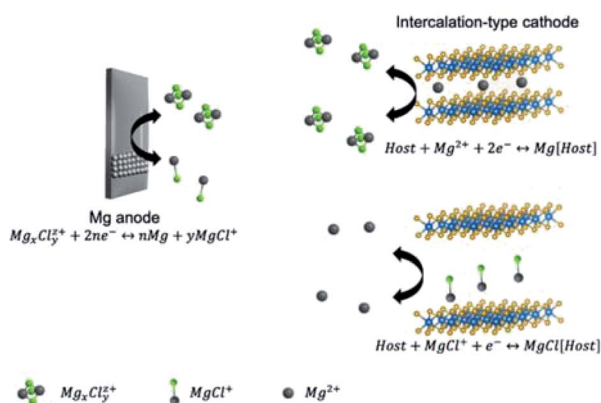
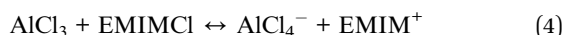
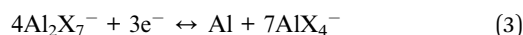
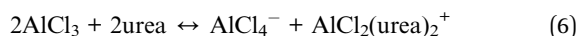


Fig. 4 Schematic illustration showing the charge storage mechanism of MMBs.

devices. To this end, room-temperature ionic liquids with low viscosity are employed for AMBs. The most commonly used ionic liquids are mixtures of AlCl_3 and 1-ethyl-3-methylimidazolium chloride (EMIMCl). To achieve Al plating, the AlCl_3 : EMIMCl molar ratio should be higher than 1 to ensure the presence of Al_2Cl_7^- through the reactions of eqn (4) and (5). The standard reduction potential of Al_2Cl_7^- is -0.7 V vs. SHE (eqn (3)), which is almost 1.0 V higher than the direct reduction of Al^{3+} (-1.66 V vs. SHE).¹⁰³



Besides, mixtures of AlCl_3 with amides (e.g., urea and acetamide) can serve as economical alternatives for ionic liquid-based electrolytes.^{104,105} In these cases, AlCl_4^- , Al_2Cl_7^- , and AlCl_2^+ are formed through the reactions in eqn (5) and (6). Thermodynamically, Al plating can also be achieved through the reduction of AlCl_2^+ . However, calculations showed that the large energy barrier associated with the dissociation of Al-amide bonds restricted this reaction (Fig. 5).¹⁰⁴ This fact could explain why electrochemical Al stripping/plating occurs only with the presence of Al_2Cl_7^- . While amide/ AlCl_3 -based electrolytes are appealing for replacing ionic liquid-based electrolytes from a cost perspective, they suffer from high viscosity and low ionic conductivity. These drawbacks result in the inferior performance of AMBs with amide/ AlCl_3 electrolytes, compared with AMBs with EMIMCl/ AlCl_3 electrolytes.¹⁰⁵



Intercalation of large-charge-density Al^{3+} usually leads AMB cathodes to poor cyclability and low-rate capability. For example, inorganic cathode materials (e.g., TiO_2 ,²⁹ TiS_2 ,¹⁰⁶ Co_9S_8 ,¹⁰⁷ and V_2O_5 (ref. 108)), with charge storage involving Al^{3+} , demonstrate significant capacity fading during the first few cycles. In addition to the sluggish Al^{3+} intercalation, the high dissociation energy of Al_2Cl_7^- to Al^{3+} (eqn (7)) is another important reason for the low rate capability and large charge/discharge voltage hysteresis of AMBs with Al^{3+} storage. Recently, Yang *et al.*¹⁰⁹ reported that the dissociation rate of $\text{Al}_2\text{Cl}_6\text{Br}^-$, prepared by mixing AlCl_3 with EMIMBr, was 15-fold

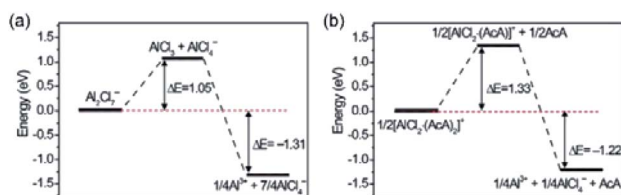


Fig. 5 Energy profiles of the dissociation reactions of (a) Al_2Cl_7^- and (b) $[\text{AlCl}_2(\text{acetamide})_2]^+$. Reprinted with permission from ref. 104. Copyright 2018 Elsevier.

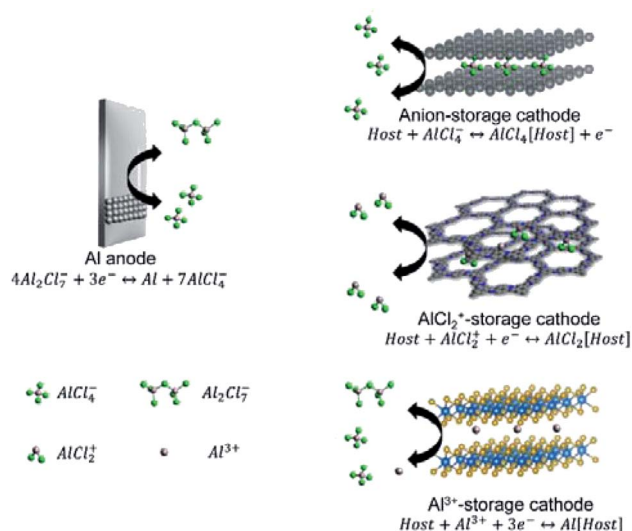
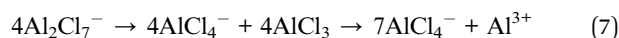


Fig. 6 Schematic illustration showing the charge storage mechanism of AMBs.

faster than that of Al_2Cl_7^- . However, the voltage window of this $\text{Al}_2\text{Cl}_6\text{Br}^-$ -based electrolyte exhibited a narrow potential window, which was only suitable for low-potential cathodes, such as TiS_2 (ref. 106) and TiO_2 .²⁹ Other Al-based species, such as AlCl_2^+ and AlCl_4^- , generally act as favourable charge carriers for AMB cathodes (Fig. 6).^{21,110,111} In detail, AlCl_4^- can serve as the charge carrier for graphite and amine compounds.^{21,112,113} On the other hand, n-type organic electrodes (e.g., pyrazine,¹¹⁴ polyaniline,¹¹⁵ and phenanthrenequinone¹¹⁰) can store charges through redox reactions with AlCl_2^+ . Compared with Al^{3+} , AlCl_2^+ as the charge carrier allows cathodes with higher charge/discharge rates and better cyclability. The intercalation of Al^{3+} was disclosed to be challenging in most materials, pushing towards the development of new n-type and p-type organic materials for $\text{AlCl}_2^+/\text{AlCl}_4^-$ storage.



3. Layered cathode materials for MVMBs

Layered materials present 2D topologies with flat planes, forming a bulk structure through the weak vdW interaction. They have been widely used for both cation and anion storage due to their potentially high theoretical capacities and favourable 2D ion transport channels.^{41,44,46} Specifically, efficient cation/anion storage in layered materials can be promoted by large interlayer spacing, weak interactions between intercalating ions and host lattices, and the electronic conductivity of layered materials.^{116,117} Therefore, both intrinsic properties of layered materials and the applied structure modification have a prominent effect on the charge storage capability. In this section, we present the current state-of-the-art layered cathode materials used for non-aqueous MVMBs. The materials in this section are divided into four major groups, layered TMOs,

TMDs, graphite-based materials, and 2D COFs. We analyse the proposed structure modification approaches and their influence on both the intrinsic physicochemical properties and the electrochemical performance enhancement of layered materials.

3.1 Layered transition metal oxides

TMOs include a broad class of materials with diverse structural frameworks, which exhibit excellent stability, environmental friendliness, and simple synthetic routes.^{117–120} The multiple valence states of transition metal elements arise from the coordination of the transition metal with highly electronegative oxygen, empowering TMOs with the superior charge storage capability (e.g., superior specific capacity). In addition, the high ionic feature of M–O bonds results in relatively high electrochemical redox potentials.³⁷ However, the oxygen atoms of TMOs impose strong interactions with charge carrier ions (e.g., Zn²⁺, Mg²⁺, and Al³⁺), which leads to the limited ion-storage kinetics and poor structural stability of TMOs used in MVMBs.^{25,121} In this sense, layered TMOs allow solid-state ion diffusion through the 2D interlayer space, providing efficient ion transport pathways.¹²² Furthermore, structure modification of layered TMOs aims at weakening the interaction between intercalating ions and oxygen atoms. So far, several layered TMOs have been explored for MVMB cathodes, including manganese oxide, vanadium oxide, and vanadyl phosphate (VOPO₄).

3.1.1 Manganese oxides. Manganese oxides have two layer-structure phases, namely, ϵ - and δ -phase MnO₂. The δ -phase MnO₂ (birnessite) is believed to provide more efficient pathways for cation diffusion than the ϵ -phase MnO₂.¹²³ Both MnO₂ phases are composed of Mn⁴⁺ ions surrounded by six oxygen atoms, creating [MnO₆] octahedral units. The [MnO₆] units are linked *via* edge corners to form the layer structure.^{124–127} Birnessite MnO₂ exhibits an interlayer distance of 7.24 Å, with a crystal water layer between two [MnO₆] octahedral layers. It is promising battery cathode material in light of the high specific capacity (308 mA h g⁻¹ for Mn³⁺/Mn⁴⁺ transition), nontoxicity, and low cost.

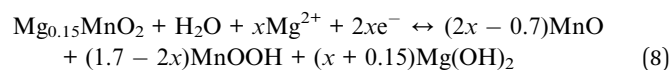
Due to the high specific capacity of MnO₂,⁵⁸ extensive researches have been conducted to use MnO₂ as cathodes for aqueous ZMBs. Recently, Han *et al.*⁶⁶ studied the charge storage performance of the δ -MnO₂ cathode using Zn(TFSI)₂ in AN as the electrolyte. δ -MnO₂ was prepared by the reaction between KMnO₄ and MnSO₄, displaying a nanofloret-like morphology with an interlayer spacing of 7 Å. The Zn²⁺-intercalation mechanism of δ -MnO₂ nanoflorets was studied using *ex situ* X-ray diffraction (XRD) and scanning transmission electron microscopy energy dispersive X-ray spectroscopy (STEM-EDS). After the first discharge, the (001) and (002) peak intensity of δ -MnO₂ was significantly decreased, indicating the loss of long-range order in the layer direction. This was caused by the structural transformation of δ -MnO₂ to the non-layered polymorph. The structural change caused the specific capacity increase to 123 mA h g⁻¹ at 12.3 mA g⁻¹ during the first 20 cycles. After 30 cycles, the specific capacity started to decay,

reaching 55 mA h g⁻¹ after 125 cycles. The decrease was attributed to the severe electrolyte decomposition and the formation of the passivation layer on the anode.

MnO₂ was also studied as the cathodes of MMBs in light of its high redox potential *vs.* Mg²⁺/Mg. However, Mg²⁺ intercalation into layered MnO₂ was not feasible with the electrolyte consisting of anhydrous Mg(ClO₄)₂ in AN.¹²⁸ Therefore, the water-containing electrolyte was prepared using Mg(ClO₄)₂·xH₂O with the H₂O : Mg²⁺ ratio of 6. After the addition of water, Mg²⁺ intercalation was improved from a ratio of <0.2 Mg²⁺ per Mn for anhydrous Mg(ClO₄)₂ to a ratio of 0.7 Mg²⁺ per Mn (Fig. 7a). Interestingly, cycling with the water-containing electrolyte acted as an activation step of MnO₂. The activated MnO₂ maintained the good Mg²⁺-storage performance in the anhydrous electrolyte. The authors claimed that, during the discharge/charge cycling in the water-containing electrolyte, a slight structure re-orientation occurred, causing the activation of MnO₂. However, due to the low crystallinity of the sample, the exact phase transition was not detected.

To further understand the role of water in MnO₂, Sun *et al.*⁹⁵ investigated Mg²⁺ intercalation into Mg_{0.15}MnO₂·0.9H₂O (Fig. 7b). Using Karl Fischer titration, it was disclosed that water molecules in the Mg_{0.15}MnO₂·0.9H₂O structure were removed during the first 20 cycles. Remarkably, the first 20 cycles were also the cycles required for the full conditioning of the Mg_{0.15}-MnO₂·0.9H₂O cathode (Fig. 7c and d). The activation was also necessary for the water-containing electrolyte, suggesting that the activation is related to the structural change of Mg_{0.15}-MnO₂·0.9H₂O. X-ray photoelectron spectroscopy (XPS) measurements detected the existence of MnOOH, MnO, and Mg(OH)₂ in the electrode at different charged states (Fig. 7e). In detail, the original electrode contained 77% Mn⁴⁺, 20% Mn³⁺, and 3% Mn²⁺, which was indicative of the chemical formula Mg_{0.15}MnO₂·0.9H₂O. At the discharged state, peaks corresponding to MnOOH and MnO were observed. At the charged state, MnO was still detected, indicating that the electrochemical process was partially reversible. These results indicated that the magnesianation process of Mg_{0.15}MnO₂·0.9H₂O was accompanied by the conversion reaction, as shown in eqn (8). Moreover, the small specific capacity of 135 mA h g⁻¹ after 20 cycles suggested that the electrochemical charge storage reaction was limited to the surface of Mg_{0.15}MnO₂·0.9H₂O.

Overall, water molecules in the electrolyte or the crystal structure of MnO₂ play a vital role in promoting the initial intercalation of Mg²⁺ into MnO₂. After the pre-cycling in the water-containing electrolyte, MnO₂ undergoes structural changes, and the water-containing electrolyte can be replaced by the anhydrous electrolyte. Since Mg metal is not stable in the water environment, water removal is an important step for the full Mg//MnO₂ cell.



3.1.2 Vanadium oxides. Orthorhombic vanadium pentoxide (V₂O₅) is a typical layered material with an interlayer

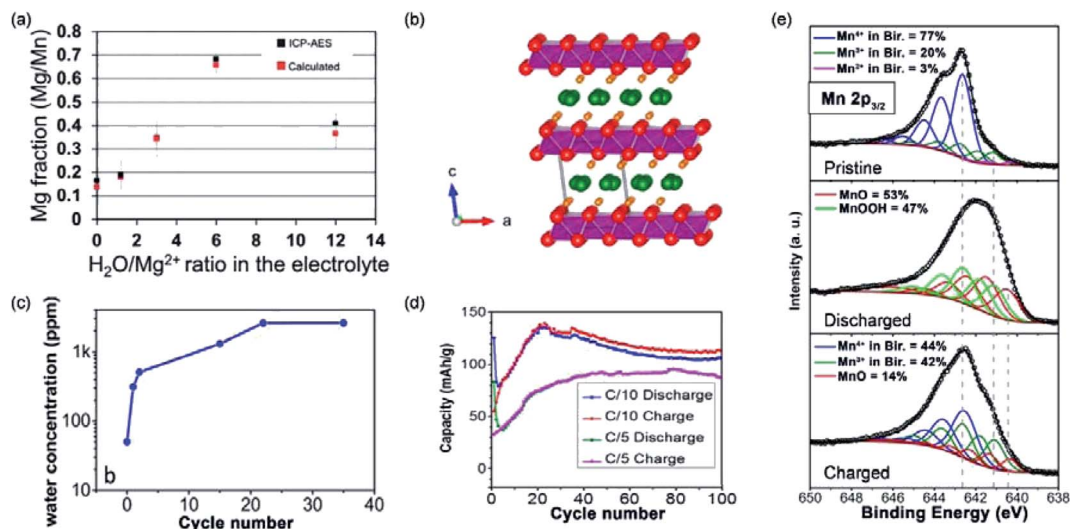


Fig. 7 (a) Inductively coupled plasma-atomic emission spectroscopy Mg : Mn ratios of MnO_2 nanowire electrodes discharged at -0.4 V vs. Ag/AgCl for 15 minutes in electrolytes with various $\text{H}_2\text{O}/\text{Mg}^{2+}$ ratios and expected Mg : Mn ratios which were calculated based on the total accumulated charges. Error bars indicate 95% confidence intervals. Reproduced from ref. 128 with permission from the PCCP Owner Societies. (b) Birnessite crystal structure showing a water monolayer between the MnO_2 sheets. (c) The water content of the electrolyte as determined by Karl Fischer titration, showing the full water release after 20 cycles. (d) Cycling performance of $\text{MnO}_2 \cdot 0.9\text{H}_2\text{O}$ at C/10 and C/5. (e) Mn $2p_{3/2}$ XPS spectra of the pristine, discharged, and charged Mg-birnessite/carbon cloth electrodes; fits are shown in colour as labelled. Reprinted with permission from ref. 95. Copyright 2016 American Chemical Society.

spacing of 4.37 \AA .¹²⁹ The layer is composed of $[\text{VO}_5]$ pyramids connected *via* edge-sharing. $[\text{VO}_5]$ pyramids show two types of bonds, namely, the $\text{O}=\text{V}$ double bond and the $\text{V}-\text{O}-\text{V}$ bond.¹³⁰ The $\text{V}^{5+}/\text{V}^{4+}$ redox couple empowers V_2O_5 with a high theoretical specific capacity of 295 mA h g^{-1} . In addition, V_2O_5 displays a high redox potential of ~ 3.2 V vs. Li^+/Li , making V_2O_5 a promising cathode material for MVMB cathodes.¹³¹

Novák and Desilvestro,¹³³ for the first time, demonstrated the intercalation of Mg^{2+} into V_2O_5 by adding water to the $\text{Mg}(\text{ClO}_4)_2$ in AN electrolyte. The intercalation kinetics of Mg^{2+} was significantly improved through the shielding effect of water. Inspired by this study, several studies showed that the incorporation of water into the V_2O_5 structure could attain a similar shielding effect. For example, An *et al.*¹³² synthesized the $\text{V}_2\text{O}_5 \cdot 1.4\text{H}_2\text{O}$ nanowire/graphene hybrid (denoted VOG), which presented greatly improved conductivity and Mg^{2+} -intercalation kinetics (Fig. 8a and b). VOG delivered a large specific capacity of 330 mA h g^{-1} at 50 mA g^{-1} and high capacity retention of 80% after 200 cycles. For comparison, VOG without crystal water was subsequently prepared *via* annealing. The annealed VOG exhibited a very limited Mg^{2+} -intercalation performance with a small specific capacity of $<75 \text{ mA h g}^{-1}$ at 100 mA g^{-1} (Fig. 8c). Remarkably, XRD patterns showed only a small difference between the interlayer distance of VOG (11 \AA) and the annealed VOG (10 \AA). It implied that, compared with the expanded interlayer spacing, the shielding effect of water molecules played the dominant role in promoting the Mg^{2+} -storage kinetics (Fig. 8d). Significantly, water molecules were located at the interstitial sites of $\text{V}_2\text{O}_5 \cdot 1.4\text{H}_2\text{O}$, and kept confined within the V_2O_5 lattice during charge/discharge, even at elevated temperatures.^{132,134} It thereby explained the excellent

capacity retention of VOG over the prolonged cycling (100 mA h g^{-1} after 200 cycles at 1 A g^{-1}).

Metal atom incorporation into V_2O_5 interlayers (*e.g.*, Mg, Mn, or Na)¹³⁵⁻¹³⁹ represents another effective strategy to promote the stability of layered V_2O_5 . For instance, Mg incorporation was achieved through electrochemically discharging V_2O_5 nanowires to 0.2 V vs. Mg^{2+}/Mg .¹³⁶ Near edge X-ray absorption fine

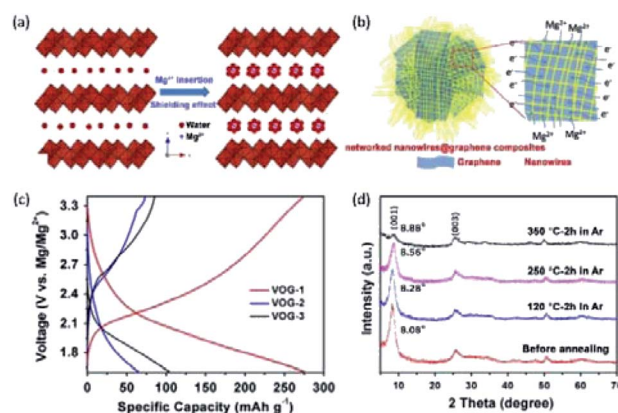


Fig. 8 (a) Shielding effect of water in $\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$. The strong polarization of divalent Mg^{2+} could be significantly reduced by solvating with crystal water molecules. (b) Schematic illustration of the $\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ /graphene nanocomposite with bi-continuous electron/ion transport pathways, large area of electrode–electrolyte interface, and facile strain relaxation during Mg^{2+} insertion/extraction. (c) Charge/discharge curves of hydrate $\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ (VOG-1), $\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ after heating in Ar (VOG-2) and in air (VOG-3) at $350 \text{ }^\circ\text{C}$ for 2 h. (d) XRD spectra of $\text{V}_2\text{O}_5 \cdot 1.35\text{H}_2\text{O}$ before and after annealing in Ar. Reprinted with permission from ref. 132. Copyright 2015 Elsevier.

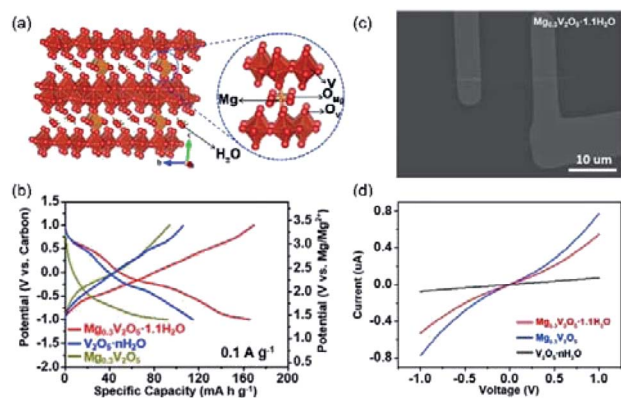


Fig. 9 (a) Schematic showing the crystal structure of $\text{Mg}_{0.3}\text{V}_2\text{O}_5 \cdot 1.1\text{H}_2\text{O}$. (b) Charge–discharge curves of $\text{Mg}_{0.3}\text{V}_2\text{O}_5 \cdot 1.1\text{H}_2\text{O}$, $\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$, and $\text{Mg}_{0.3}\text{V}_2\text{O}_5$. (c) Scanning electron microscope images of the $\text{Mg}_{0.3}\text{V}_2\text{O}_5 \cdot 1.1\text{H}_2\text{O}$ single-nanowire devices. (d) I – V curves of $\text{Mg}_{0.3}\text{V}_2\text{O}_5 \cdot 1.1\text{H}_2\text{O}$, $\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$, and $\text{Mg}_{0.3}\text{V}_2\text{O}_5$. Reprinted with permission from ref. 135. Copyright 2019 Elsevier.

structure (NEXAFS) of V K -edge revealed that the edge position of the Mg-incorporated V_2O_5 was close to that of VO_2 standard, indicating a stoichiometry of MgV_2O_5 for the Mg-incorporated V_2O_5 . Moreover, the decreased intensity of the pre-edge peak suggested a local reordering of the V environment upon Mg incorporation. Significantly, the obtained MgV_2O_5 electrode exhibited a high specific capacity of 160 mA h g^{-1} at 20 mA g^{-1} . Nevertheless, the electrochemical performance of pristine V_2O_5 was not presented, making it difficult to quantify the contribution of Mg incorporation. Mg can also be incorporated into the crystal structure of V_2O_5 during the material synthesis. Xu *et al.*¹³⁵ synthesized $\text{Mg}_{0.3}\text{V}_2\text{O}_5 \cdot 1.1\text{H}_2\text{O}$ nanowires through the reaction between V_2O_5 and $\text{C}_4\text{H}_6\text{O}_4\text{Mg} \cdot 4\text{H}_2\text{O}$. The $[\text{MgO}_6]$ octahedra species acted as pillars and enhanced the structural stability of V_2O_5 , while water molecules improved the Mg^{2+} -intercalation kinetics (Fig. 9a). The $\text{Mg}_{0.3}\text{V}_2\text{O}_5 \cdot 1.1\text{H}_2\text{O}$ electrode delivered a high specific capacity of 164 mA h g^{-1} (Fig. 9b), which is substantially higher than those of $\text{V}_2\text{O}_5 \cdot 1.1\text{H}_2\text{O}$ (114 mA h g^{-1}) and $\text{Mg}_{0.3}\text{V}_2\text{O}_5$ (91 mA h g^{-1}). Impressively, the $\text{Mg}_{0.3}\text{V}_2\text{O}_5 \cdot 1.1\text{H}_2\text{O}$ electrode also showed a superior cycling life with 80% capacity retained after 10 000 cycles at a current density of 1 A g^{-1} , which remarkably outclassed $\text{V}_2\text{O}_5 \cdot 1.1\text{H}_2\text{O}$ and $\text{Mg}_{0.3}\text{V}_2\text{O}_5$ (fast capacity decay over 200 cycles). The incorporation of Mg into the structure was uncovered to improve the conductivity of $\text{Mg}_{0.3}\text{V}_2\text{O}_5 \cdot 1.1\text{H}_2\text{O}$ (Fig. 9c and d), which contributed to the superior rate performance. XRD studies further observed the slight decrease by 0.5 \AA in the interlayer spacing of $\text{Mg}_{0.3}\text{V}_2\text{O}_5 \cdot 1.1\text{H}_2\text{O}$ after charging. This result indicated that the $[\text{MgO}_6]$ sites as pillars alleviated the electrode structure change during the charge/discharge process, further accounting for the excellent cycle stability of $\text{Mg}_{0.3}\text{V}_2\text{O}_5 \cdot 1.1\text{H}_2\text{O}$.^{135,137}

Besides, ammonium¹⁴⁰ or poly(ethylene oxide) (PEO)¹⁴¹ incorporated between vanadium oxide layers can also promote the Mg^{2+} -intercalation kinetics. Impressively, $\text{NH}_4\text{V}_4\text{O}_{10}$ exhibited the initial specific capacity of 175 mA h g^{-1} in the first

cycle, and the specific capacity increased to $\sim 250 \text{ mA h g}^{-1}$ in the second cycle. The boosted specific capacity was assigned to the irreversible de-ammoniation process occurring at the first charge, which created additional sites for Mg^{2+} storage. This de-ammoniation process was identified by the irreversible oxidation peak in the first cyclic voltammetry cycle and the disappearance of the N 1s XPS peak after the first charge. Similarly, PEO-incorporated $\text{V}_2\text{O}_5 \cdot 1.5\text{H}_2\text{O}$ displayed a superior specific capacity of 100 mA h g^{-1} , which substantially outweighed the low specific capacity of $\text{V}_2\text{O}_5 \cdot 1.5\text{H}_2\text{O}$ (20 mA h g^{-1} at 10 mA g^{-1}).¹⁴¹ In addition, the specific capacity of PEO-incorporated $\text{V}_2\text{O}_5 \cdot 1.5\text{H}_2\text{O}$ was stabilized at $\sim 90 \text{ mA h g}^{-1}$ after 20 cycles, in contrast to the fast capacity decay of $\text{V}_2\text{O}_5 \cdot 1.5\text{H}_2\text{O}$ (4.3 mA h g^{-1} after 35 cycles). The improved specific capacity of PEO-incorporated $\text{V}_2\text{O}_5 \cdot 1.5\text{H}_2\text{O}$ was assigned to the interlayer spacing expansion from 11.6 \AA for $\text{V}_2\text{O}_5 \cdot 1.5\text{H}_2\text{O}$ to 12.6 \AA for PEO-incorporated $\text{V}_2\text{O}_5 \cdot 1.5\text{H}_2\text{O}$.

The Mg^{2+} -intercalation kinetics of pristine vanadium oxide can also be improved by the charge/discharge at elevated temperatures. Rastgoo-Deylami *et al.*¹⁴² showed that the capacity of $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ was boosted from 80 mA h g^{-1} to 231 mA h g^{-1} when the temperature was increased from $25 \text{ }^\circ\text{C}$ to $60 \text{ }^\circ\text{C}$. Moreover, initial cycling of the electrode at the elevated temperature was also explored as an activation step for further cycling at room temperature.⁹³ To activate the cathode, commercial $\alpha\text{-V}_2\text{O}_5$ was discharged/charged at $110 \text{ }^\circ\text{C}$ with the electrolyte of $0.5 \text{ M Mg}(\text{TFSI})_2$ in 1-butyl-1-methyl-pyrrolidinium TFSI ($\text{Py}_{14}\text{TFSI}$). EDS and STEM analysis were used to evaluate the effect of the activation step on the structure of $\alpha\text{-V}_2\text{O}_5$. First, the $\alpha\text{-V}_2\text{O}_5$ cathode after discharge at $110 \text{ }^\circ\text{C}$ exhibited the uniform distribution of V and Mg, implying that the charge storage mechanism of $\alpha\text{-V}_2\text{O}_5$ was high-kinetics Mg^{2+} intercalation. STEM images of $\alpha\text{-V}_2\text{O}_5$ at the discharged state revealed the considerable delamination of $\alpha\text{-V}_2\text{O}_5$, which lead to the greatly reduced domain size (3.5 nm). The specific capacity of $\alpha\text{-V}_2\text{O}_5$ without activation was only 16 mA h g^{-1} . Interestingly, after the temperature was increased to $110 \text{ }^\circ\text{C}$, the specific capacity increased to 295 mA h g^{-1} . Afterwards, the specific capacity could be stabilized at 96 mA h g^{-1} after the temperature recovered to room temperature. It should be noted that the activation step of the cathode would be a high-cost step in the battery fabrication process, thus restricting the real-life application of the assembled devices.

Although preliminary studies demonstrated the feasible Mg^{2+} storage of layered vanadium oxides in electrolytes like $\text{Mg}(\text{TFSI})_2$ or $\text{Mg}(\text{ClO}_4)_2$ in AN and ionic liquids, these electrolytes are generally not compatible with Mg metal anodes. To enable full $\text{Mg}/\text{V}_2\text{O}_5$ cell, more efforts are needed to develop electrolytes compatible with both V_2O_5 cathodes and Mg metal anodes.

Unlike MMB electrolytes, metal anode-compatible AMB electrolytes (*e.g.*, $\text{AlCl}_3/\text{EMIMCl}$) are also suitable for oxide cathodes. AMBs composed of Al metal, V_2O_5 nanowires, and $\text{AlCl}_3/\text{EMIMCl}$ (molar ratio: 1.1) were assembled.¹⁴³ As revealed, the V_2O_5 cathode delivered a high specific capacity of 305 mA h g^{-1} in the first cycle with a voltage plateau of around 0.5 V . The specific capacity kept 273 mA h g^{-1} after 20 cycles,

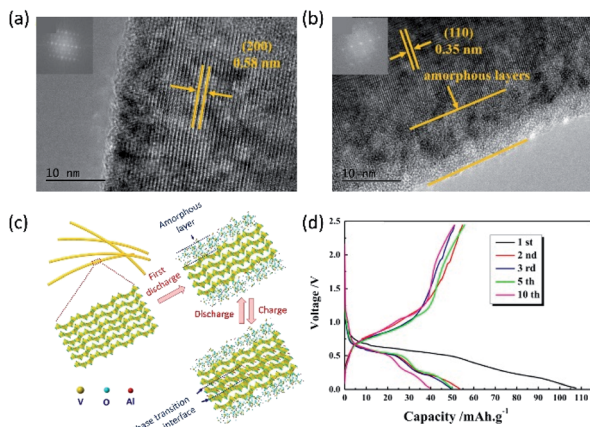


Fig. 10 (a and b) HRTEM images of the V_2O_5 nanowire (a) before cycling, and (b) at the fully discharged state (insets: fast Fourier transform images). (c) Schematic diagram showing the electrochemical Al^{3+} insertion/extraction of crystallized V_2O_5 nanowires. (d) Galvanostatic charge/discharge profiles of the V_2O_5 nanowire cathode. Reprinted with permission from ref. 108. Copyright 2017 Elsevier.

suggesting decent capacity retention of the V_2O_5 cathode. Recent studies have indicated that stainless steel exhibited nonnegligible electrochemical activity in $AlCl_3/EMIMCl$ electrolyte.¹⁴⁴ This electrochemical activity could provide false interpretation of the obtained results. To further understand the intercalation of Al^{3+} into V_2O_5 , Gu and co-workers¹⁰⁸ conducted the high-resolution TEM (HRTEM) analysis on V_2O_5 nanowires at different charge/discharge stages. They found that the intercalation of Al^{3+} led to the formation of 10 nm amorphous layers on the outer shell of V_2O_5 nanowires. After deintercalation of Al^{3+} , a new V_2O_5 phase appeared between the outer amorphous layer and the core of nanowires (Fig. 10a–c). The structural evolution suggested that the charge storage of V_2O_5 nanowires occurred only at the surface, and the charge storage mechanism was a combination of intercalation and phase transition. Furthermore, *ex situ* XPS measurements revealed that the oxidation state of V was not fully converted back to V^{5+} during the charging process. In addition, XPS also indicated the presence of Al after charging. These XPS results were consistent in several studies of AMBs with V_2O_5 cathodes.^{108,145} Due to the irreversible electrochemical process, the

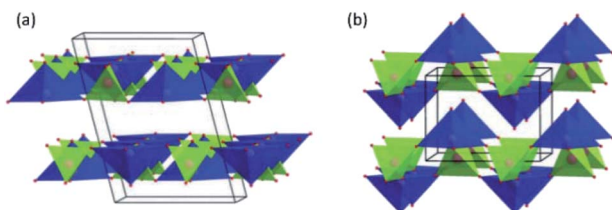


Fig. 11 Representation of (a) the α_1 - $VOPO_4$ structure ($C2/m$, $a = 8.73187(14)$ Å, $b = 6.20548(5)$ Å, $c = 6.20902(4)$ Å and $\beta = 104.448(3)^\circ$ at $280^\circ C$) and (b) the α_2 - $VOPO_4$ structure ($P4/n$, $a = 6.0156(3)$ Å, $c = 4.4375(3)$ Å at RT). Reproduced from ref. 147 with permission from The Royal Society of Chemistry.

specific capacity of V_2O_5 decayed fast during cycling, retaining only 40 mA h g^{-1} after 10 cycles (Fig. 10d). The compatibility of the AMB electrolytes with V_2O_5 will motivate further investigations to improve both the Al^{3+} -intercalation kinetics and the cycling stability of V_2O_5 via diverse structure engineering strategies.

3.1.3 Vanadyl phosphate. Layer-structure $VOPO_4$ has several phases, such as α_1 -, α_2 -, γ -, δ -, and ω - $VOPO_4$. The common ones for electrochemical intercalation are α_1 - $VOPO_4$ and α_2 - $VOPO_4$ with a $P4/n$ space group.¹⁴⁶ Both phases are based on the corner-sharing $[PO_4]$ tetrahedra and strongly distorted vanadium octahedra. The difference between α_1 - $VOPO_4$ and α_2 - $VOPO_4$ is the position of oxygen atoms in vanadyl groups. The oxygen atoms of α_1 - $VOPO_4$ are located within the layer, while the oxygen atoms of α_2 - $VOPO_4$ are not in the same plane as V (Fig. 11).¹⁴⁷ $VOPO_4$ has attracted significant attention as a possible cathode material due to the large specific capacity, high redox potential, and stable cyclability.¹⁴⁸ Impressively, $VOPO_4$ can deliver a high theoretical specific capacity of 166 mA h g^{-1} for the one-electron redox couple V^{4+}/V^{5+} and 331 mA h g^{-1} for the two-electron redox couple V^{3+}/V^{5+} .¹⁴⁹ Due to the enhanced ionic character of V–O bonds when $(PO_4)^{3-}$ anions are introduced, $VOPO_4$ possesses a much higher redox potential ($3.95 \text{ V vs. Li}^+/Li$) than that of V_2O_5 ($2\text{--}3.4 \text{ V vs. Li}^+/Li$).^{37,150}

$VOPO_4$ suffers from significant voltage decay during cycling in aqueous Zn electrolytes, which can be assigned to the decomposition of $VOPO_4$ into VO_x . Several studies suggested that low amounts of water additive would not cause the decomposition of $VOPO_4$.^{59,151} Recently, Wang *et al.*¹⁵¹ compared the Zn^{2+} -storage performance of $VOPO_4$ and $VOPO_4 \cdot 2H_2O$ in both water-free and water-containing electrolytes. $VOPO_4 \cdot 2H_2O$ was synthesized by the reaction between V_2O_5 and concentrated H_3PO_4 under the reflux condition. Subsequently, $VOPO_4$ was prepared through the calcination of $VOPO_4 \cdot 2H_2O$ at $550^\circ C$ in the air. The electrochemical performance was evaluated using 0.1 M Zn(OTf)_2 in AN with/without water. When the water content in the electrolyte was 0.5%, the performance of $VOPO_4$ showed only slight improvement. By contrast, the specific capacity of $VOPO_4$ was increased by 3-fold, when the water content reached 1%. The performance improvement was explained by the chemical co-intercalation of free water molecules and the formation of $VOPO_4 \cdot xH_2O$ (Fig. 12a), which was supported by the XRD pattern (Fig. 12b). Besides, the electrochemical performance of $VOPO_4 \cdot 2H_2O$ was evaluated in AN with and without 1% water. Interestingly, the addition of water to the electrolyte can apparently improve the performance of $VOPO_4 \cdot 2H_2O$. The specific capacities in the water-free electrolyte are 10 and 80 mA h g^{-1} at 20 mA g^{-1} for $VOPO_4$ and $VOPO_4 \cdot 2H_2O$, respectively. When 1% water was added, the specific capacities were increased to 122 and 135 mA h g^{-1} at 20 mA g^{-1} for $VOPO_4$ and $VOPO_4 \cdot 2H_2O$, respectively (Fig. 12c). XRD analysis revealed that water molecules were extracted from $VOPO_4 \cdot 2H_2O$ to the electrolyte, thus restricting the solid-state diffusion of Zn^{2+} (Fig. 12d and e). Apart from the increase of specific capacity, $VOPO_4 \cdot 2H_2O$ in the water-containing electrolyte exhibited an increase of the discharge voltage by $\sim 0.2 \text{ V}$ and

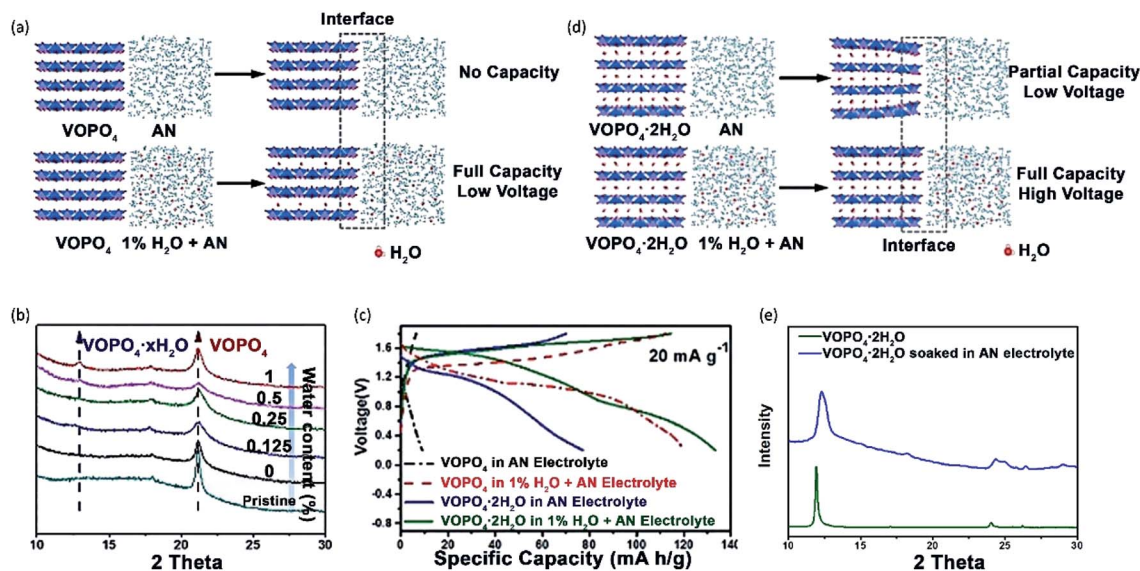


Fig. 12 (a) Schematic illustrations of VOPO_4 in 0.1 M $\text{Zn}(\text{OTf})_2$ dissolved in AN without water and with 1% H_2O . (b) XRD patterns of VOPO_4 soaked in different electrolytes for 24 h. (c) The charge/discharge profiles of VOPO_4 and $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ between 0.2 V and 1.9 V at 20 mA g^{-1} . (d) Schematic illustrations of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ in 0.1 M $\text{Zn}(\text{OTf})_2$ dissolved in AN without water and with 1% H_2O . (e) XRD patterns of the pristine $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ soaked in the electrolyte of 0.1 M $\text{Zn}(\text{OTf})_2$ dissolved in AN for 24 h. Reprinted with permission from ref. 151. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

superior cycling capabilities with 100 mA h g^{-1} retained after 25 cycles at 20 mA g^{-1} .

To further improve the cyclability of VOPO_4 , Verma *et al.*⁵⁹ synthesized a polypyrrole-incorporated VOPO_4 (PPy- VOPO_4). Polypyrrole between VOPO_4 layers induced the partial reduction of V^{5+} to V^{4+} , thus reducing the charge transfer resistance. The capacity retention of PPy- VOPO_4 was increased from 25% for the pristine VOPO_4 to 90% after 30 cycles at 30 mA g^{-1} . In addition, the cyclability was further improved by adding 10% volume of water to the electrolyte, thus enabling $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with pronouncedly enhanced capacity retention (60 mA h g^{-1} after 350 cycles at 100 mA g^{-1}). The improved stability was ascribed to the presence of polypyrrole, which prevented the distortion of the lattice structure. In contrast, $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ without polypyrrole suffered from the fast capacity decay caused by the extraction of crystal water.

VOPO_4 was also studied as the Mg^{2+} -intercalation cathodes, and their performance showed strong dependence on both the interlayer spacing of VOPO_4 and the water content in the electrolyte. Ji *et al.*¹⁵² studied the effect of water molecules in both the VOPO_4 structure and the electrolyte on the Mg^{2+} -intercalation performance of VOPO_4 . Interestingly, only when the $\text{VOPO}_4 \cdot \text{H}_2\text{O}$ cathode with water-containing electrolyte was used, the significant capacity enhancement could be observed. Theoretical calculation indicated that the energy barrier of Mg^{2+} -intercalation was reduced from 1.56 eV for VOPO_4 to 0.48 eV for $\text{VOPO}_4 \cdot \text{H}_2\text{O}$. Such a pronounced difference resulted in that the diffusion coefficient of $\text{VOPO}_4 \cdot \text{H}_2\text{O}$ was 1.2×10^{18} times higher than that of VOPO_4 . In addition, the calculated formation energies of different $[\text{Mg}(\text{PC})_n(\text{H}_2\text{O})_{6-n}]^{2+}$ ($n \leq 6$) species in the PC electrolyte without water were much more negative than those in the water-containing PC electrolyte (Fig. 13a). The difference in formation energies revealed the

immense desolvation energy of $[\text{Mg}(\text{PC})_6]^{2+}$. Additionally, the improved Mg^{2+} -intercalation kinetics contributed to reducing the charge/discharge mid-voltage hysteresis from 1.15 V for

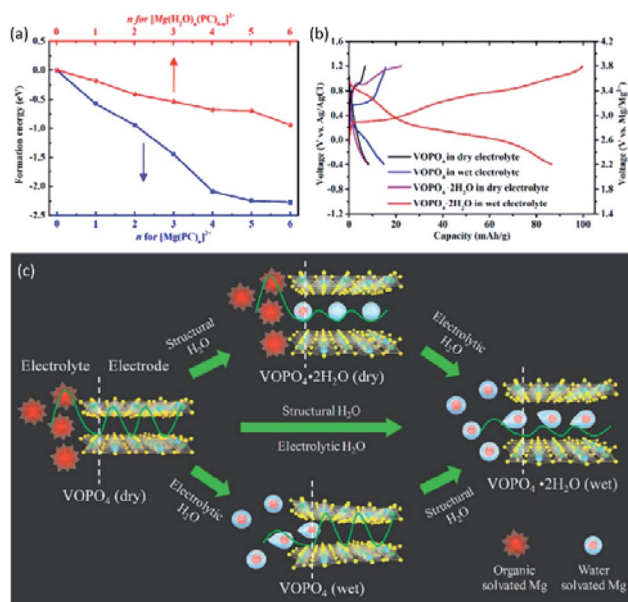


Fig. 13 (a) Formation energies of $[\text{Mg}(\text{PC})_n]^{2+}$ and $[\text{Mg}(\text{PC})_n(\text{H}_2\text{O})_{6-n}]^{2+}$ ($n \leq 6$). (b) Voltage profiles of VOPO_4 and $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ in the water-free (0.1 M $\text{Mg}(\text{ClO}_4)_2$ in PC) and water-containing (0.1 M $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in PC) electrolytes at 5 mA g^{-1} in a three-electrode cell with Ag/AgCl and active carbon as the reference and counter electrode, respectively. (c) Schematic illustrating the charge storage mechanism of $\text{VOPO}_4 \cdot n\text{H}_2\text{O}$ in the water-free and water-containing electrolytes. The green curves indicate the activation energy barriers, and the white dash lines represent the electrode/electrolyte interface. Reprinted with permission from ref. 152. Copyright 2018 American Chemical Society.

VOPO₄ in the water-free electrolyte to 0.49 V for VOPO₄·2H₂O in the water-containing electrolyte (Fig. 13b). The average equilibrium voltages in electrolytes with various water contents were also calculated for the V⁵⁺/V⁴⁺ redox stage (Mg_{0.5}VOPO₄) and the V⁴⁺/V³⁺ redox stage (MgVOPO₄). The V⁴⁺/V³⁺ stage displayed a pronounced dependence on the water content in electrolytes compared with the V⁵⁺/V⁴⁺ stage. The voltage plateau improved from 1.79 V to 2.19 V, when the water activity was increased from 10⁻⁶ to 10⁻². To clarify the influence of water, Fig. 13c illustrates how Mg²⁺ intercalation into VOPO₄ and VOPO₄·2H₂O in both water-free and water-containing electrolytes.

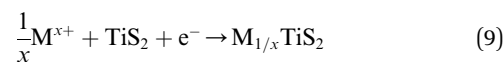
As mentioned earlier, water-containing electrolytes are not compatible with the Mg metal anode owing to the formation of the passivation layer on the Mg surface. By incorporating phenylamine molecules between VOPO₄ layers (denoted PA-VOPO₄), efficient Mg²⁺ intercalation in a water-free electrolyte was achieved.¹⁵³ PA-VOPO₄ was prepared by the exfoliation and self-assemble of VOPO₄·2H₂O nanosheets in a phenylamine solution (Fig. 14a). Phenylamine enabled VOPO₄ with apparent layer expansion (interlayer distance: 7.4 vs. 14.2 Å). The large interlayer distance of PA-VOPO₄ reduced the electrostatic interaction between the intercalating Mg²⁺ and VOPO₄. Meanwhile, the interlayer expansion also boosted the charge-storage kinetics of VOPO₄ by promoting the intercalation of MgCl⁺ (Fig. 14b–d).^{153,154} Impressively, PA-VOPO₄ kept 87% of the initial specific capacity after 500 cycles at 100 mA g⁻¹, which was superior to that of VOPO₄·2H₂O (40% after 150 cycles). Moreover, PA-VOPO₄ showed a decent rate performance with high

specific capacities of 275 and 109 mA h g⁻¹ at 50 and 2000 mA g⁻¹, respectively (Fig. 14e). The excellent cycling stability of PA-VOPO₄ is rather unique, given the APC electrolyte is known to be incompatible with oxides. Recently, Hu *et al.*¹⁵⁵ suggested that the incorporated PA molecules could improve the stability of VOPO₄ in aqueous ZMBs due to the increased hydrophobicity of PA-VOPO₄. It is highly desirable to understand the stability of PA-VOPO₄ in the APC electrolyte with future efforts. In addition, the low charge/discharge voltages and the higher specific capacities of PA-VOPO₄ than the theoretical value should be further clarified.

3.2 Transition metal dichalcogenides

Transition metal dichalcogenides, sharing the formula MX₂, are made of transition metal (M = Ti, V, Nb, Mo, W, *etc.*) and chalcogen (X = S, Se, and Te) atoms. The TMD layer has a three-atom-thick configuration of X–M–X. Stacked layers are connected by weak vdW interactions, allowing the exfoliation of bulk TMD into single-layer and few-layer TMD nanoflakes.⁴² TMDs have three polytypes, namely, trigonal prismatic, octahedral, and distorted octahedral, which differ in the metal atom coordination configuration and stacking orders. The electronic properties of TMDs (metallic, semiconducting, and insulating) are determined by the different polytypes and chalcogen types.^{41,156} The weaker electrostatic interactions between chalcogenide anions and the intercalating cations account for the better multivalent metal ion-intercalation kinetics of TMD cathodes than that of TMO cathodes.¹⁵⁷ Generally, TMDs exhibit the intercalation mechanism at potentials above ~1.0 V vs. Li⁺/Li. Under a low cut-off voltage (below ~1.0 V vs. Li⁺/Li), the specific capacities of TMDs are substantially enhanced due to the involved conversion reactions.

3.2.1 Ti-based TMDs. Titanium disulphide (TiS₂) and titanium diselenide (TiSe₂) show tetragonal symmetry and metallic properties, exhibiting layer spacings of 5.65 Å and 6.00 Å, respectively. TiS₂ depicts a theoretical specific capacity of 239 mA h g⁻¹ for the one-electron Ti³⁺/Ti⁴⁺ reaction, as shown in eqn (9). Compared with TiS₂, TiSe₂ has a lower theoretical specific capacity of 130 mA h g⁻¹, but better cation-intercalation kinetics.¹⁵⁷ The superior cation-intercalation kinetics of TiSe₂ originates from the unique hybridization between Ti 3d orbitals and Se 4p orbitals, which boosts the electron delocalization and reduces the electrostatic interactions between the intercalating cations and TiSe₂ (Fig. 15a and b).^{157,158} In addition, TiSe₂ displays the lowest charge rehybridization upon Mg²⁺ intercalation in comparison with TiS₂ and TiO₂, further implying the lowest Mg²⁺-diffusion barrier of TiSe₂ (Fig. 15c).¹⁵⁷



Several strategies were applied to improve the Mg²⁺-intercalation performance of Ti-based TMDs, such as particle size optimization, temperature increase, and interlayer expansion. Tao *et al.*¹⁵⁹ studied the Mg²⁺-intercalation behaviours of the TiS₂ nanotubes and large-flake TiS₂ (20 μm). TiS₂ nanotubes

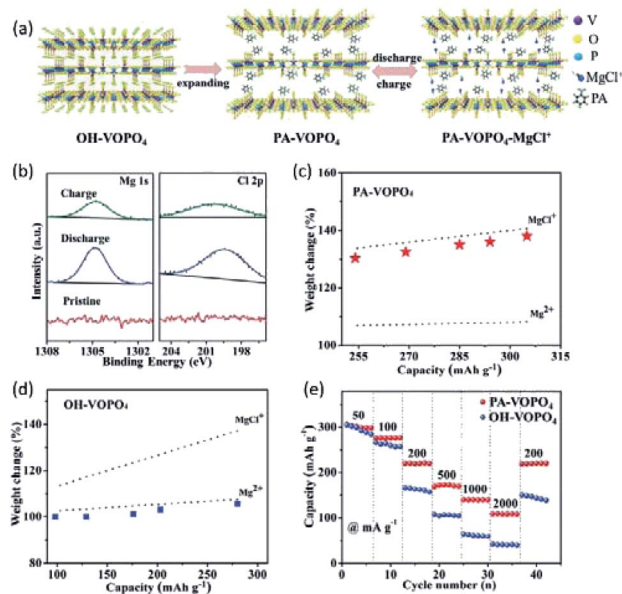


Fig. 14 (a) Schematic illustration of the experimental approach and proposed mechanism of PA-VOPO₄ nanosheets as the Mg-storage material. (b) Mg 1s and Cl 2p XPS spectra of PA-VOPO₄ nanosheets at the fully charged/discharged states. Mass change of the electrodes upon discharge when (c) PA-VOPO₄ nanosheets and (d) VOPO₄·2H₂O bulk served as cathode materials. (e) Rate capability of VOPO₄·2H₂O bulk and PA-VOPO₄ nanosheets. Reprinted with permission from ref. 153. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

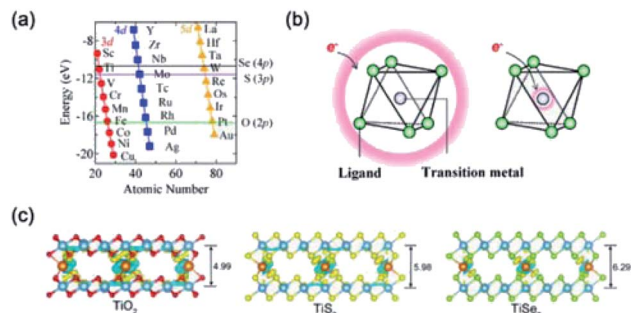


Fig. 15 (a) Energy diagram of atomic orbitals. Red circles, blue squares and orange triangles represent the energy levels of 3d-, 4d- and 5d-orbitals of each transition metal, respectively. The horizontal lines display the energy level position of O 2p-orbital, S 3p-orbital and Se 4p-orbital, respectively. (b) A schematic illustration of charge distribution in the electronic state with strong d–p hybridization. Electrons are accommodated in the delocalized state, which extends over transition metal and ligand atoms as schematically shown by the red framework. Reprinted with permission from ref. 158. Copyright 2015, Springer Nature. (c) Charge rehybridization upon the diffusion of Mg^{2+} between layers of TiO_2 , TiS_2 , and TiSe_2 with layer spacing (unit Å). Charge accumulation is shown in yellow, while depletion is shown in blue. Oxygen atoms are shown as small red spheres, sulfur as small yellow spheres, selenium as small kelly spheres, Ti as large sapphire spheres, and Mg at the center as an orange sphere. The isovalue number used for displaying the differential charge density is 0.003. Reprinted with permission from ref. 157. Copyright 2019 American Chemical Society.

(234 mA h g^{-1}) delivered more than double the capacity of the large-flake TiS_2 (96 mA h g^{-1}) at 10 mA g^{-1} (Fig. 16). In addition to the particle size, the Mg^{2+} -intercalation kinetics of TiS_2 was shown to be highly temperature-dependent. For example, Sun *et al.*¹⁶⁰ demonstrated efficient Mg^{2+} intercalation into TiS_2 using the APC electrolyte at 60 °C. The TiS_2 electrode at 60 °C exhibited the initial specific capacity of 270 mA h g^{-1} at 12 mA g^{-1} and a reversible capacity of 160 mA h g^{-1} in the following cycles. Interestingly, a fast decay of the specific capacity (to $\sim 110 \text{ mA h g}^{-1}$ after 40 cycles) suggested that neither TiS_2 nor the Mg anode was stable during cycling at high temperatures. To understand the Mg^{2+} -intercalation mechanism of TiS_2 , *in situ* XRD revealed the appearance of several new phases during the discharge process of TiS_2 . At the initial

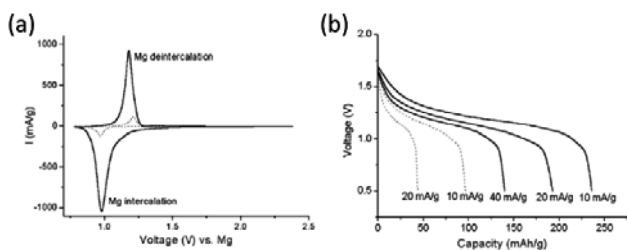


Fig. 16 (a) Cyclic voltammograms at 0.5 mV s^{-1} of TiS_2 nanotube (solid) and polycrystalline powder (dots) electrodes at 20 °C. (b) Discharge curves of TiS_2 nanotubes (solid) and polycrystalline TiS_2 (dots) at various current densities and 20 °C. Reproduced from ref. 159 with permission from The Royal Society of Chemistry.

discharge stage, partially irreversible interlayer expansion (c parameter increase) occurred, followed by the reversible increase in the a parameter. The increase in the c parameter was explained by Mg^{2+} intercalation into the octahedral sites of TiS_2 , while the change in the a parameter indicated Mg^{2+} intercalation into the tetrahedral sites.

Yoo *et al.*,¹⁵⁴ reported the electrochemical intercalation of organic Py_{14}^+ cations into TiS_2 interlayers, which remarkably improved the Mg^{2+} -intercalation kinetics and promoted Mg-Cl^+ intercalation. In this case, Py_{14}Cl ionic liquid was added to the APC electrolyte. Py_{14}^+ cations were intercalated into TiS_2 at a low rate (5 mA g^{-1}), causing the irreversible interlayer expansion of TiS_2 (Fig. 17a). As a result, the specific capacity of TiS_2 was remarkably increased from $\sim 25 \text{ mA h g}^{-1}$ to 239 mA h g^{-1} at 24 mA g^{-1} (Fig. 17b). Moreover, the specific capacity of 239 mA h g^{-1} was boosted to 400 mA h g^{-1} at a high temperature of 60 °C, corresponding to the intercalation of two Mg-Cl^+ species per Ti atom. N 1s XPS spectra revealed that only Py_{14}^+ cations were intercalated into TiS_2 at the beginning of the first discharge. Cl 2p and Mg 2s XPS signals appeared at a later stage of the discharge, which indicated the intercalation of MgCl^+ after the expansion of the interlayer distance by Py_{14}^+ . Besides, Mg K -edge NEXAFS of Mg^{2+} -intercalated TiS_2 displayed a similar onset energy with tetra-coordinated $[\text{Mg}_2\text{Cl}_2 \cdot 4\text{THF}]^{2+}$, implying that the intercalated Mg^{2+} was tetra-coordinated with one Cl atom and three S atoms. MgCl^+ acting as charge carriers improved the intercalation kinetics due to its lower charge density than that of Mg^{2+} . Additionally, MgCl^+ avoided the Mg-Cl dissociation step, and exhibited weaker binding to S than Mg^{2+} (Fig. 17c and d).

Besides, the Al^{3+} intercalation kinetics into TiS_2 shows a strong dependency on the temperature and the particle size of TiS_2 . Geng *et al.*¹⁶⁶ compared the Al^{3+} intercalation into TiS_2 at room temperature and 50 °C. As revealed, the specific capacity of TiS_2 at room temperature achieved 50 mA h g^{-1} in the initial cycle and decayed to 30 mA h g^{-1} after 50 cycles at 5 mA g^{-1} . By contrast, the specific capacity of TiS_2 at 50 °C reached 45 mA h g^{-1} and increased to 70 mA h g^{-1} after 50 cycles. The authors claimed that cycling at high temperatures altered the crystal structure of TiS_2 , thus facilitating Al^{3+} intercalation. Hawkins *et al.*¹⁶¹ showed that TiS_2 nanobelts, cycled at 50 °C, displayed a superior specific capacity of 150 mA h g^{-1} even at a high current density of 240 mA g^{-1} . It was suggested that both Al^{3+} and AlCl_4^- could be intercalated into TiS_2 nanobelts, which also accounted for the improved intercalation kinetics.^{30,108,162–164}

3.2.2 V-based TMDs. Vanadium disulphide (VS_2) and vanadium diselenide (VSe_2) exhibit metallic properties, tetragonal symmetry, and layer spacings of 5.74 Å and 6.10 Å, respectively.¹⁶⁵ The one-electron $\text{V}^{4+}/\text{V}^{3+}$ redox reaction enables VS_2 and VSe_2 with theoretical specific capacities of 233 mA h g^{-1} and 128 mA h g^{-1} , respectively. Nevertheless, the strong orbital hybridization in VSe_2 accounts for the superior cation-intercalation kinetics of VSe_2 to that of VS_2 . Therefore, pristine VSe_2 exhibited higher specific capacity than pristine VS_2 (Fig. 18).¹⁵⁷ Apart from intercalation, reversible conversion mechanism was also observed for VS_2 and VSe_2 in alkali metal-

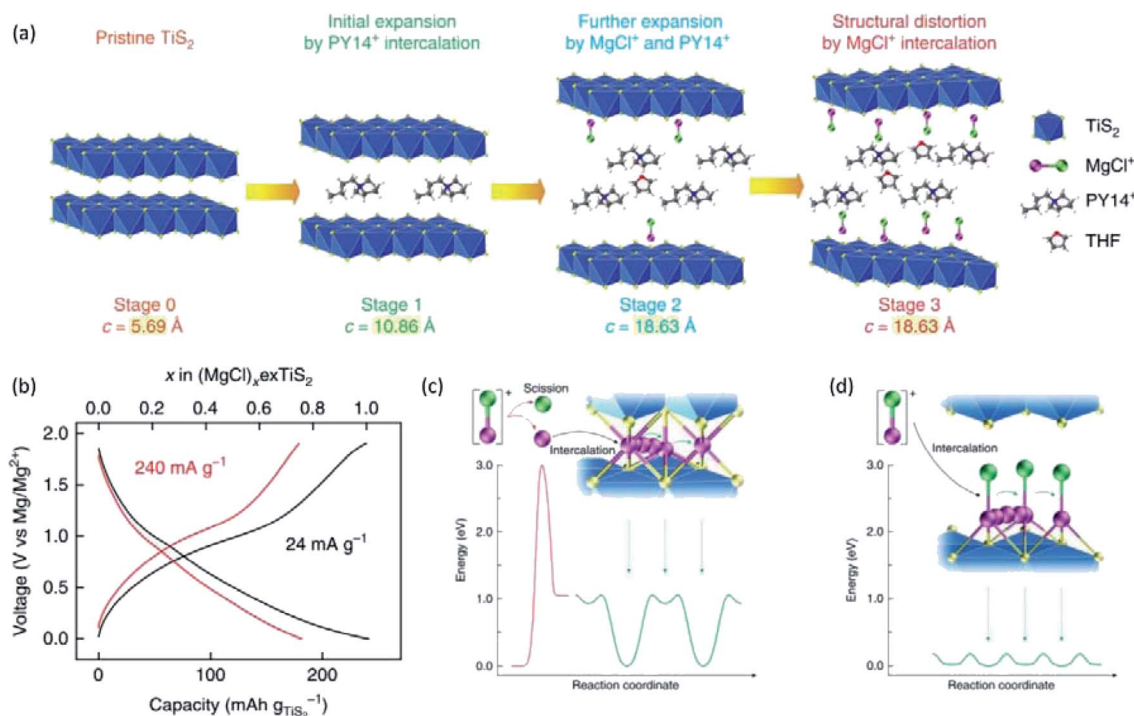


Fig. 17 (a) A schematic illustrating the structural evolution of TiS_2 at different stages of intercalation. (b) Galvanostatic voltage profiles of the exfoliated TiS_2 electrode at 24 and 240 mA g^{-1} at 25°C . The number of MgCl^+ intercalation per exfoliated TiS_2 is also shown in the top axis. (c and d) Energy diagrams for the intercalation and diffusion of Mg^{2+} and MgCl^+ . (c) Typical intercalation of Mg^{2+} involves the scission of MgCl^+ ions into Mg^{2+} and Cl^- , which requires substantial activation energy of 3 eV at least. Subsequent diffusion of divalent Mg^{2+} also has a high-migration energy barrier of 1.06 eV, which results in the limited level of intercalation at room temperature. (d) Intercalation of MgCl^+ bypasses the sluggish scission of the $\text{Mg}-\text{Cl}$ bond at the electrolyte–cathode interface. Afterwards, MgCl^+ diffuses fast in the expanded interlayers due to the fairly low-migration energy barrier of 0.18 eV. Mg and Cl atoms are shown as purple and green spheres, respectively. Reprinted with permission from ref. 154. Copyright 2017, Springer Nature.

ion batteries, empowering them with high specific capacities ($>700 \text{ mA h g}^{-1}$).^{41,166}

To improve the Mg^{2+} -intercalation kinetics of VS_2 , several interlayer expansion strategies were developed for VS_2 . For example, Xue *et al.*¹⁶⁷ synthesized VS_2 through a solvothermal reaction employing 2-ethylhexylamine as the solvent. Consequently, 2-ethylhexylamine molecules were incorporated into the VS_2 structure during the synthesis, obtaining interlayer-expanded VS_2 nanoflowers (Fig. 19a). The single-step preparation of the expanded VS_2 is vital for practical application, as the industry could not rely on elaborated post-synthesis steps. The combined XRD and Fourier transform infrared results verified

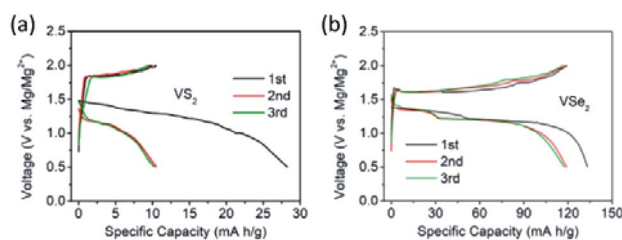


Fig. 18 Mg^{2+} intercalation into (a) pristine VS_2 and (b) pristine VSe_2 at 5 mA g^{-1} . Reprinted with permission from ref. 157. Copyright 2019 American Chemical Society.

that 2-ethylhexylamine molecules were located between VS_2 interlayers, rather than on the surface of VS_2 . Impressively, the fabricated VS_2 exhibited a large interlayer spacing of 9.93 \AA , which contrasted with the small interlayer distance of the annealed VS_2 (5.73 \AA). The expanded VS_2 showed superior electrochemical performance with a high specific capacity of 245 mA h g^{-1} at 100 mA g^{-1} and 77% capacity retention after 100 cycles. Moreover, an excellent rate capability of the expanded VS_2 was evidenced by the high specific capacities of 140 and 102 mA h g^{-1} at current densities of 1 and 2 A g^{-1} , respectively (Fig. 19b and c). XPS spectra of the expanded VS_2 electrode at different discharge stages presented both Mg 2s and Cl 2p signals with an Mg : Cl ratio >1 , implying both Mg^{2+} and MgCl^+ intercalation. The diffusion coefficient of $\text{Mg}^{2+}/\text{MgCl}^+$ in the expanded VS_2 was calculated to be in the range of 7.58×10^{-11} to $6.03 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$, which was substantially higher than the Mg^{2+} -diffusion coefficient of pristine VS_2 ($4.20 \times 10^{-23} \text{ cm}^2 \text{ s}^{-1}$). The *ex situ* XRD and HRTEM measurements showed that a conversion reaction occurred at a low voltage range ($<0.4 \text{ V vs. Mg}^{2+}/\text{Mg}$), forming MgS and V (Fig. 19d and e). MgS and V were not observed when the expanded VS_2 was charged back to 2.2 V, indicating the good reversibility of the conversion reaction.

Another method to increase the interlayer distance of VS_2 relies on the irreversible electrochemical intercalation of ionic

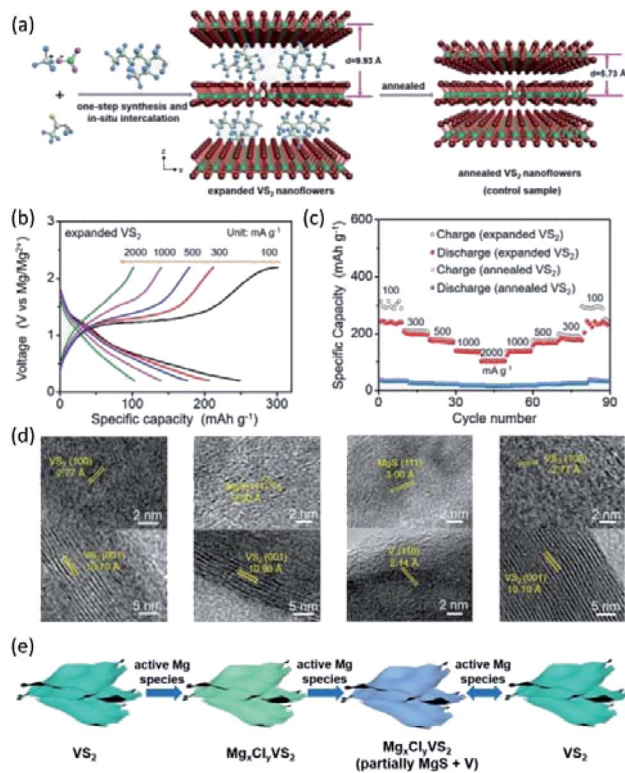


Fig. 19 (a) Schematic illustration of the one-step synthesis and *in situ* intercalation process of the expanded VS₂ nanoflowers and annealed VS₂ nanoflowers. (b) Galvanostatic discharge/charge profiles at various current densities. (c) Rate capabilities of the expanded VS₂ and annealed VS₂ electrodes at the current densities from 100 to 2000 mA g⁻¹. (d) HRTEM images of the expanded VS₂ nanoflowers at different discharge/charge states (from left to right): discharged to 0.6 V, discharged to 0.4 V, fully discharged to 0.2 V, and fully charged to 2.2 V. (e) Schematic of the reversible storage mechanism of active Mg species in the expanded VS₂ nanoflowers. Reprinted with permission from ref. 167. Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

liquid cations.^{80,154} Recently, Zhao *et al.*⁸⁰ used PP₁₄Cl as an electrolyte additive to enable PP₁₄⁺ intercalation between VS₂ layers. During the electrochemical activation at 20 mA g⁻¹, PP₁₄⁺ was intercalated between VS₂ nanosheets. *Ex situ* XPS analysis of the VS₂ electrode showed no change in the N 1s signal after the first discharge, indicating the irreversibility of PP₁₄⁺ intercalation. After the activation, VS₂ nanosheets exhibited high specific capacities of 299 and 214 mA h g⁻¹ at 50 and 2000 mA g⁻¹, respectively. Moreover, a high energy density of 152 W h kg⁻¹ at a power density of 1600 W kg⁻¹ was achieved by VS₂ nanosheets. It should be pointed out that a significant amount of capacity was detected at the low voltage range (*e.g.*, 150 mA h g⁻¹ between 0.5–0.01 V at 20 mA g⁻¹). The contribution of the capacity at the low voltage range was considerably low, and the low voltage was shown to affect the cyclability of TMDs in alkali metal batteries due to the occurring conversion reaction.^{168,169}

Compared to Mg²⁺ intercalation, Li⁺ intercalation generally shows higher kinetics owing to the low charge density.^{157,165} In

this regard, Sun *et al.*¹⁷⁰ reported hybrid devices combining Mg stripping/plating anodes and Li⁺-intercalation VS₂ cathodes. Such Mg–Li hybrid device exploited both the stable Mg stripping/plating on the anode, and the efficient Li⁺-intercalation into VS₂ cathode. Impressively, the specific capacity of the VS₂ cathode was increased by 10 folds (from <25 to 250 mA h g⁻¹ at 0.5C) by adding LiCl to the APC electrolyte. EDS mapping of VS₂ nanosheets after discharge showed no Mg signal, confirming the negligible intercalation of Mg²⁺ into VS₂. The galvanostatic intermittent titration technique (GITT) verified that the diffusion coefficient of Li⁺ in VS₂ was around 10⁻¹³ cm s⁻¹ even at a high Li content (*e.g.*, Li₂VS₂). By contrast, the diffusion coefficient of Mg²⁺ in VS₂ dropped from 10⁻¹⁴ to 10⁻¹⁵ cm s⁻¹ along with the slight change of Mg²⁺ content from Mg_{0.025}VS₂ to Mg_{0.04}VS₂. Thereby, the specific capacity improvement was thus ascribed to the higher diffusivity of Li⁺ in VS₂ than that of Mg²⁺. This study opens up an interesting direction for Mg–alkali metal hybrid batteries, which can be extended to constructing other energy storage systems, such as Mg–Na, Mg–K hybrid batteries. Still, alkali ions were consumed during the discharge process of VS₂. Such a fact requires the use of a large volume of electrolyte to assemble the device, consequently reducing the overall device performance.

V-based TMDs were also used as cathode materials for Al³⁺ intercalation. Wu *et al.*¹⁷¹ investigated the use of VS₂ and graphene-composited VS₂ (G-VS₂) as cathodes for AMBs. VS₂ was prepared using a hydrothermal method, and G-VS₂ was prepared by sonicating graphene together with VS₂. The G-VS₂ and VS₂ electrodes achieved specific capacities of 186 and 145 mA h g⁻¹ in the initial cycle at 100 mA g⁻¹, and maintained 50 and 25 mA h g⁻¹ after 50 cycles, respectively. The reversible Al³⁺ intercalation was identified by the *in situ* XRD analysis of G-VS₂, in which the intensity of VS₂ peaks decreased and increased reversibly during discharge and charge. The improved performance of the G-VS₂ cathode was associated with the reduced charge transfer resistance of G-VS₂ in comparison with VS₂. Furthermore, Lei *et al.*¹⁷² investigated single-crystal VSe₂ as the cathodes for AMBs. The XPS analysis indicated that AlCl₄⁻ served as the dominant charge carrier for VSe₂. The VSe₂ cathode exhibited the initial capacity of 650 mA h g⁻¹ at 100 mA g⁻¹, which decayed to 50 mA h g⁻¹ after 100 cycles. The rapid decay in the specific capacity of VS₂ and VSe₂ needs to be further clarified in the future.

3.2.3 Mo-based TMDs. Both molybdenum disulphide (MoS₂) and molybdenum diselenide (MoSe₂) show the hexagonal symmetry with two possible stacking configurations, namely, the 2H and 3R phases. The interlayer distances of the 2H phases are 6.15 and 6.7 Å for MoS₂ and MoSe₂, respectively. The 3R MoS₂ and MoSe₂ phases exhibit larger interlayer distances of 6.12 and 6.7 Å, respectively. In addition, the most common monolayer polytypes are semiconducting trigonal prismatic (2H) and metallic octahedral (1T). The 2H phase is thermodynamically favourable, and phase transition from 2H to 1T can occur during the electrochemical/chemical processes, such as intercalation and exfoliation.^{173,174} The theoretical capacities associated with the Mo³⁺/Mo⁴⁺ transition are 168 and 106 mA h g⁻¹ for MoS₂ and MoSe₂, respectively.¹⁷⁵ Nevertheless,

below ~ 1.1 V vs. Li^+/Li , both MoS_2 and MoSe_2 can undergo reversible conversion reactions, allowing high specific capacities of >700 mA h g^{-1} .

Due to the large interlayer spacing, MoS_2 can enable efficient Mg^{2+} intercalation. Liang *et al.*¹⁷⁶ assembled devices composed of Mg nanoparticles as the anodes and highly exfoliated graphene-like MoS_2 (G- MoS_2) as the cathodes. G- MoS_2 exhibited an enlarged interlayer spacing of 6.5–7 Å in comparison with bulk MoS_2 (B- MoS_2 , 6.3 Å). The reduced particle size, together with the enlarged lattice spacing, increased the Mg^{2+} -intercalation kinetics of G- MoS_2 . As a result, G- MoS_2 exhibited a superior specific capacity of 170 mA h g^{-1} at 20 mA g^{-1} , which was significantly higher than the specific capacity of B- MoS_2 (71 mA h g^{-1} , Fig. 20a) and comparable with the calculated theoretical specific capacity of 223.2 mA h g^{-1} (Fig. 20b). Interestingly, the excellent specific capacity highly depended on the anode configuration as well. In specific, with the bulk Mg anode, the specific capacity of the G- MoS_2 cathode was two-time lower (90 mA h g^{-1}) than the specific capacity of G- MoS_2 with the Mg nanoparticle anode (170 mA h g^{-1}). The authors proposed that the formation of a thin passivation layer on the Mg nanoparticle anode promoted the Mg^{2+} diffusion across the particle surface. Yet, no experimental evidence was provided to identify the formation of the passivation film and the amount of electrolyte that is consumed during the film formation. In addition, the formation of passivation layers is usually avoided in the chlorine-containing electrolyte.

To improve the cyclability of the MoS_2 cathodes for MMBs, polyvinylpyrrolidone (PVP) was incorporated between MoS_2 layers during the hydrothermal synthesis of MoS_2 .¹⁷⁷ The interlayer spacings of the expanded MoS_2 with and without PVP were determined to be 9.7 Å and 9.4 Å, respectively. Additionally, PVP-incorporated MoS_2 exhibited a new XRD peak at 18.4°, implying the new lamellar phase constructed from PVP and MoS_2 monolayers, with an interlayer spacing of 4.8 Å. An initial specific capacity of 143.3 mA h g^{-1} at the first discharge and 92% capacity retention after 100 cycles were reached by PVP-incorporated MoS_2 . In contrast, expanded MoS_2 without PVP

delivered a specific capacity of 131.9 mA h g^{-1} , but retained only 52% of the initial capacity after 100 cycles.

In addition to the interlayer expansion, altering the Mg-cation intercalating species was used to improve the electrochemical performance of MoS_2 . Li *et al.*¹⁷⁴ showed that $[\text{Mg}(\text{DME})_3]^{2+}$ intercalation into porous 2H- MoS_2 @C exhibited superior kinetics to the Mg^{2+} -intercalation kinetics. The mixture of $\text{Mg}(\text{BH}_4)_2$ and hexafluoroisopropanol in DME was employed as the electrolyte (denoted MgBOR/DME), in which $[\text{Mg}(\text{DME})_3]^{2+}$ cations acted as the charge carrier ion. $[\text{Mg}(\text{DME})_3]^{2+}$ intercalation was confirmed using the STEM-EDS analysis, which uncovered similar distribution of O and Mg in the outer layer of 2H- MoS_2 @C. Moreover, the XPS peak analysis revealed that 2H- MoS_2 underwent a phase transition to 1T- MoS_2 during the initial activation process (20 cycles at 20 mA g^{-1}). HRTEM image of the 2H- MoS_2 @C cathode after 30th discharge cycles showed an amorphous outer layer, which indicated the fragmentation and structural distortion of MoS_2 during extended $[\text{Mg}(\text{DME})_3]^{2+}$ intercalation/de-intercalation. Fig. 21 illustrates the charge storage process of 2H- MoS_2 @C, including the intercalation of large $[\text{Mg}(\text{DME})_3]^{2+}$ ions, 2H–1T phase transition, and the fragmentation and structural distortion. The effect of $[\text{Mg}(\text{DME})_3]^{2+}$ on the electrochemical performance of 2H- MoS_2 @C was assessed in different Mg electrolytes, such as MgBOR/DME, APC, and $\text{Mg}(\text{HMDS})_2/\text{MgCl}_2/\text{AlCl}_3$. The MgBOR/DME electrolyte enabled 2H- MoS_2 @C with the highest specific capacity of 95 mA h g^{-1} at 50 mA g^{-1} , in comparison with the APC (85 mA h g^{-1}) and $\text{Mg}(\text{HMDS})_2/\text{MgCl}_2/\text{AlCl}_3$ (45 mA h g^{-1}) electrolytes. This work highlighted a new electrochemical method for boosting the efficient Mg^{2+} intercalation in MoS_2 .

Several studies explored MoS_2 as cathodes for AMBs, where Al^{3+} served as the intercalating species with the $\text{AlCl}_3/\text{EMIMCl}$ electrolyte.^{111,178,179} For example, Li *et al.*¹¹¹ reported that MoS_2 spheres delivered a high specific capacity of 254 mA h g^{-1} at 20 mA g^{-1} in the initial cycle, but exhibited poor cyclability with

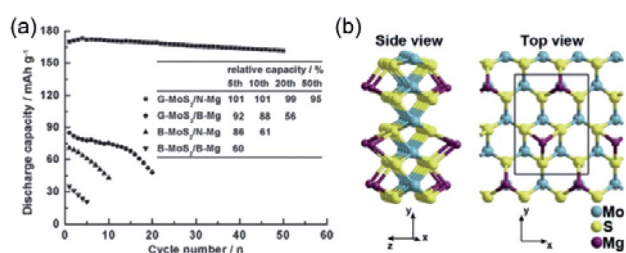


Fig. 20 (a) Typical cycling behaviour of the cells fabricated with B- MoS_2 or G- MoS_2 cathodes and bulk- or nanoparticles-Mg anodes with a discharge rate of 20 mA g^{-1} . In the inset table, the relative capacity at a certain cycle refers to the ratio of the discharge capacity of the cells at the corresponding cycle to that at the first cycle. (b) Graphical illustrations of theoretically modelled Mg adsorption on MoS_2 single-layered nanoribbon. Reprinted with permission from ref. 176. Copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

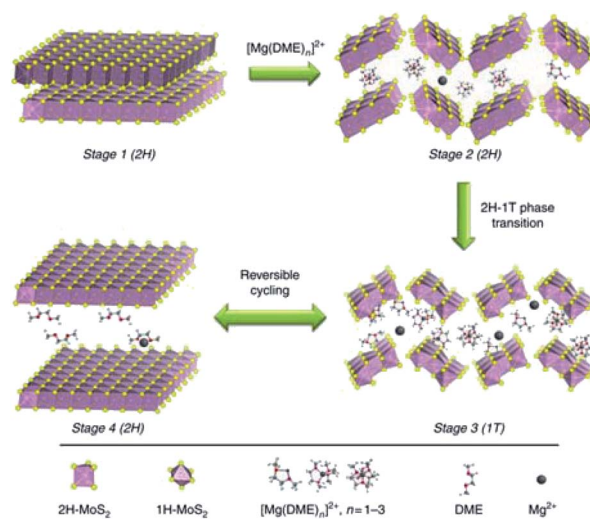


Fig. 21 Schematic illustration of the $[\text{Mg}(\text{DME})_3]^{2+}$ storage mechanism in MoS_2 structures with the MgBOR/DME electrolyte. Reprinted with permission from ref. 174. Copyright 2018, Springer Nature.

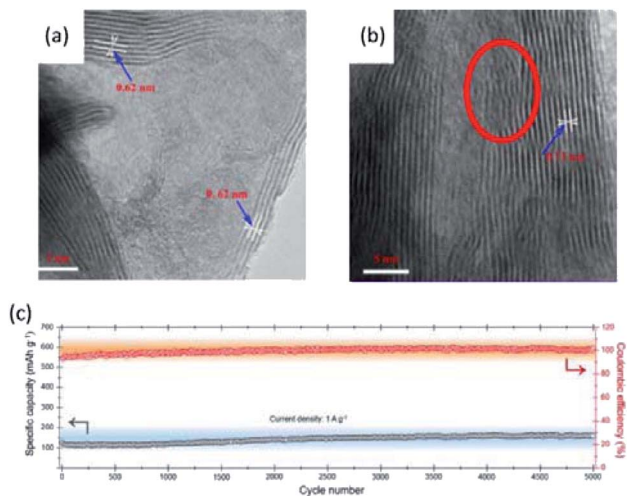


Fig. 22 TEM images of MoS₂ microspheres (a) before and (b) after cycling. Reprinted with permission from ref. 111. Copyright 2018 American Chemical Society. (c) The cycling performance and corresponding coulombic efficiency of MoSe₂@C at 1 A g⁻¹. Reprinted with permission from ref. 180. Copyright 2019 American Chemical Society.

67 mA h g⁻¹ retained after 100 cycles at 40 mA g⁻¹. XRD spectra revealed that the intercalation of Al³⁺ into MoS₂ spheres resulted in apparent interlayer expansion from 6.2 Å to 7.3 Å and obvious lattice stripe distortion (Fig. 22a and b). The XPS analysis showed that partial Al³⁺ intercalation into the MoS₂ spheres was irreversible, which also accounted for the inferior cycling performance.

To further improve the electrochemical performance, MoS₂ and MoSe₂ were hybridized with carbon materials.^{178,180} Yang *et al.*¹⁷⁸ fabricated MoS₂ nanostructure-incorporated free-standing carbon fibres through an electrospinning method. The highly conductive carbon fibres provided efficient encapsulation for MoS₂ nanostructures. The specific capacity of the carbon fiber-MoS₂ electrode achieved 293 mA h g⁻¹ in the initial cycle, and maintained 125 mA h g⁻¹ after 200 cycles at 100 mA g⁻¹. Moreover, Zhao *et al.*¹⁸⁰ prepared MoSe₂@C using a multistep synthetic route. First, dopamine hydrochloride as the carbon precursor was mixed with ammonium molybdate to create a homogenous mixture. Afterwards, the mixture was calcinated and selenized to obtain MoSe₂@C. The MoSe₂@C cathode for AMBs showed a high specific capacity of 267 mA h g⁻¹ at 100 mA g⁻¹ with no noticeable capacity fading for up to 5000 cycles at 1 A g⁻¹ (Fig. 22c). Interestingly, the specific capacities of both MoS₂ and MoSe₂ were higher than the theoretical value based on the intercalation mechanism. This phenomenon suggested that the conversion mechanism was involved in the charge-storage process.

3.3 Graphite-based materials

Graphite-based cathode materials are appealing due to the abundant resource, low cost, and environmental friendliness. The unique redox amphoteric feature allows graphite to host both cations (*e.g.*, Li⁺, K⁺, and Py₁₄⁺) and anions (*e.g.*, Br⁻, Cl⁻, BF₄⁻, FSI⁻, PF₆⁻, TFSI⁻, TOF⁻, and AlCl₄⁻). In particular, anion

intercalation into graphite occurs at a high potential (~1.75 V vs. SHE), which is beneficial for the construction of high-voltage energy storage devices.^{44,45,181} Anion intercalation of graphite-based materials is based on a staging mechanism. The stage number represents the number of graphite layers between intercalating anions (Fig. 23).¹⁸² Different intercalation stages can be detected by distinctive voltage plateau during charge/discharge and the spectroscopy analysis (*e.g.*, XRD and Raman). For example, the intercalation stage can be extracted from the peak position ratio of the two most dominant peaks, (00*n* + 1) and (00*n* + 2). Anion-intercalation graphite-based materials are widely employed to construct dual-ion MVMBs. During charging, metal cations are deposited on the anodes, and anions are intercalated into the graphite-based cathodes. Owing to the consumption of electrolyte ions, dual-ion batteries with graphite cathodes generally require the use of large-amount or high-concentration electrolytes.⁵⁰

In contrast to ZMBs constructed with commonly used cathodes (*e.g.*, V₂O₅ and MnO₂), ZMBs based on the graphite cathodes (denoted graphite-ZMBs) can depict high average voltages of above 2 V. However, most organic electrolytes of ZMBs (*e.g.*, Zn(TfO)₂ and Zn(TFSI)₂ in ionic liquid) have low anodic stable potential windows (<2.6 V vs. Zn²⁺/Zn), which cannot fulfil the high potential requirement of anion intercalation into graphite.^{23,24,68,183} For example, graphite-ZMBs charged to a cut-off voltage of 2.6 V vs. Zn²⁺/Zn only demonstrated a specific capacity of 50 mA h g⁻¹.⁶⁸ Recently, Wang *et al.*²⁴ showed that adding LiPF₆ into the Zn electrolyte composed of Zn(TFSI)₂ in AN can greatly enhance the anodic stability. It was shown that 1 M Zn(TFSI)₂ in AN started to decompose at ~2.3 V vs. Zn²⁺/Zn. The presence of LiPF₆ efficiently suppressed the anodic dissolution and the decomposition of Zn(TFSI)₂ electrolyte. The mixed electrolyte (0.5 M Zn(TFSI)₂ + 2 M LiPF₆) depicted a high stable potential of more than 4 V vs. Zn²⁺/Zn (Fig. 24a). The floating test at 3 V exhibited negligible leakage currents (<10⁻³ mA cm⁻²), which contrasted with the high leakage currents of the 1 M Zn(TFSI)₂ electrolyte (>30 mA cm⁻², Fig. 24b).¹⁹ F NMR identified the co-intercalation of PF₆⁻ and TFSI⁻ into graphite during charging. Density functional theory (DFT) calculations

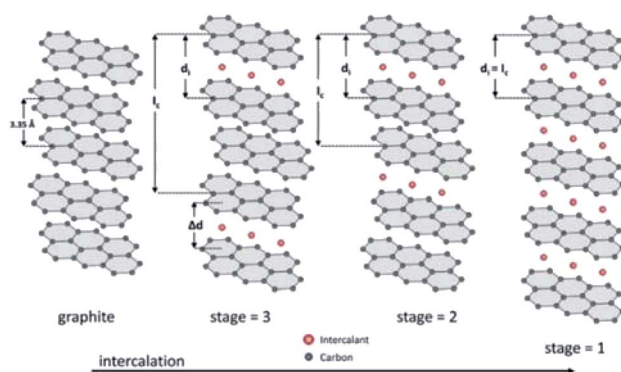


Fig. 23 Schematic illustration of the staging mechanism of intercalant guest species into graphite: l_c = periodic repeat distance; d_i = intercalant gallery height; Δd = gallery expansion. Reprinted with permission from ref. 182. Copyright 2013 Elsevier.

showed that PF_6^- had a lower diffusion energy barrier than TFSI^- , thus suggesting the higher diffusion rate of PF_6^- (Fig. 24c and d). Graphite-ZMB with the LiPF_6 additive could be charged to a high voltage of 2.8 V vs. Zn^{2+}/Zn , depicting large specific capacities of 105 and 97 mA h g^{-1} at 100 and 2000 mA g^{-1} , respectively (Fig. 24e). In addition, the superior cyclability of graphite-ZMB was demonstrated with nearly 100% retention after 2000 cycles at 1000 mA g^{-1} . Recently, Wang *et al.*²³ demonstrated that Zn metal would react with PF_6^- , forming dissolved Zn^{2+} in the electrolyte. The reaction between PF_6^- and Zn also led to the formation of a solid electrolyte interface on Zn, which was composed of ZnF_2 and LiF . With an electrolyte of 2.5 M LiPF_6 in EMC, graphite-ZMB exhibited a high specific capacity of 95 mA h g^{-1} at 200 mA g^{-1} . It is highly desirable to find alternative metal- PF_6 salts and avoid the use of Li salts.

AMBs are the most studied battery system with anion-intercalation graphite cathodes. Although the Al stripping and plating electrochemistry in the ionic liquid mixture containing Al_2Cl_7^- anions has been well known for several decades,⁹⁹ Dai *et al.*²¹ was the first to show AMBs constructed with the AlCl_4^- intercalation graphite cathodes in 2015. The optimal AMBs were assembled in the electrolyte with an $\text{AlCl}_4^-/\text{Al}_2\text{Cl}_7^-$ ratio of ~ 2.33 , which was prepared by mixing AlCl_3 and EMIMCl in a molar ratio of 1.3. The AlCl_4^- -intercalation chemistry allowed pyrolytic graphite with a specific capacity of 60 mA h g^{-1} at 66 mA g^{-1} and an average cell voltage of 2 V. However, the large size of AlCl_4^- anions led to the unsatisfactory rate capability (only 20 mA h g^{-1} retained at 264 mA g^{-1}) of the pyrolytic graphite cathode. To address these issues, the graphitic foam was used to replace pyrolytic graphite, delivering a specific capacity of 60 mA h g^{-1} at a high current density of 5 A g^{-1} . More impressively, the pouch-cell batteries assembled with the graphitic foam cathodes achieved high capacity retention of 100% after 7500 cycles with high coulombic efficiencies ($>97\%$).

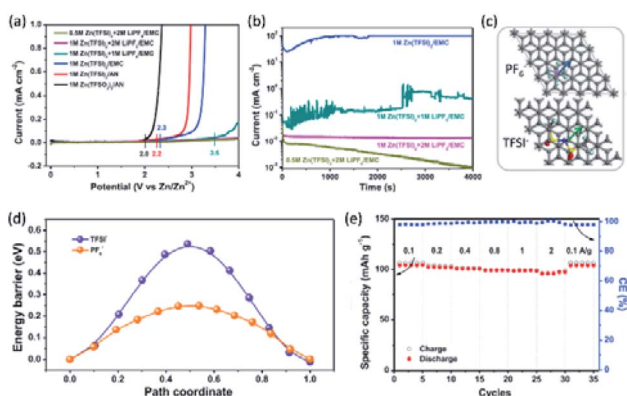


Fig. 24 (a) Linear sweep voltammetry curves at 2 mV s^{-1} of different electrolytes on stainless steel electrode within Zn//stainless steel cells. (b) Floating test of electrolytes at 3 V. Sensitivity is 0.01 A V^{-1} . (c) The optimized anion diffusion path in the graphite layers. (d) The optimized anion diffusion energy barriers in the graphite layers. (e) Rate performance of Zn//graphite dual-ion battery. Reprinted with permission from ref. 24. Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Ex situ XRD measurements provided significant insights into the AlCl_4^- -intercalation mechanism of graphite. In detail, the (002) peak of graphite vanished in the fully charged cathode, while two new peaks, assigned to lattice spacings of 3.15 and 3.77 \AA , appeared. In the fully discharged cathode, the graphite (002) peak reappeared with a broad shoulder, which was indicative of an irreversible change in the stacking of graphite layers. AlCl_4^- intercalation into graphite was determined to be a stage-4 process. Besides, the same group also found that free-standing natural graphite film employed as the AMB cathode depicted superior cyclability ($\sim 100\%$ retention after 6000 cycles), good coulombic efficiencies ($\sim 98\%$), and importantly considerably enhanced specific capacity (110 mA h g^{-1} at 99 mA g^{-1}).¹¹³

To further improve the rate performance, AlCl_4^- -intercalated graphite was subjected to rapid thermal expansion at 1000 $^\circ\text{C}$ and subsequently transferred to water for electrolysis.¹¹² The electrolysis process produced massive amounts of hydrogen gas, which further introduced large porosity into the expanded graphite. The obtained porous graphite was comprised of microparticles ($\sim 1 \mu\text{m}$) with 4–5 graphene layers, presenting superior rate performance with a specific capacity of 60 mA h g^{-1} at 12 A g^{-1} (18 seconds charge). Moreover, Zhang *et al.*¹⁸⁴ studied the AlCl_4^- -intercalation behaviours of four different graphitic materials, namely, large-size graphite (L-graphite) and graphene (L-graphene), small-size graphite (S-graphite) and graphene (S-graphene). At a low current density of 60 mA g^{-1} , the specific capacities of L-graphite and L-graphene were both $\sim 85 \text{ mA h g}^{-1}$ with two apparent voltage plateaus. In contrast, S-graphite and S-graphene showed a relatively low specific capacity of $\sim 72 \text{ mA h g}^{-1}$ without distinctive voltage plateaus. In addition, L-graphene showed the best rate capability among four samples, retaining 90% of the initial capacity at a large current density of 4.8 A g^{-1} (Fig. 25a). The excellent rate capability originated from both the high conductivity and structural flexibility of L-graphene, which could well endure the structural stress during the repeat AlCl_4^- intercalation/deintercalation (Fig. 25b). Interestingly, the good crystallinity of graphitic materials contributed to the high specific capacity of L-graphite. The carboxyl and hydroxyl groups on the edge of S-graphene caused the repulsive interaction with the intercalating AlCl_4^- , thus imposing a specific

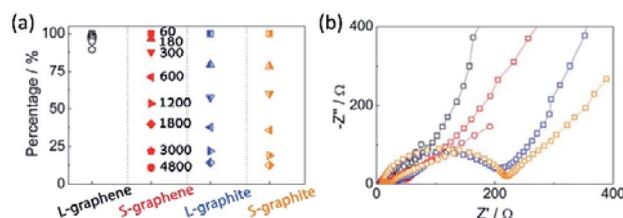


Fig. 25 (a) Rate capability from 60 to 4800 mA h g^{-1} of L-graphene (black), S-graphene (red), L-graphite (blue), and S-graphite (orange). (b) Electrochemical impedance spectra (circle represents high voltage and square represents low voltage). Reprinted with permission from ref. 184. Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

activation energy for AlCl_4^- -intercalation.^{184,185} In addition, slight performance degradation was detected for L-graphene during the continuous charge/discharge cycles, which significantly contrasted with the notable performance degradation of S-graphene caused by the apparent structural change.¹⁸⁴

High-performance cathodes relying on simple and robust preparation methods are highly pursued for practical applications. In this regard, Hu *et al.*¹⁸⁶ reported a simple acid treatment strategy, which greatly improved the rate performance of commercial carbon nanofibers (CNFs). The acid treatment cleaved the outer graphitic layer of CNFs, creating edge-rich graphitic nanoribbons interconnected by the nanofiber core (Fig. 26a). In the original CNFs, the intercalation of AlCl_4^- was blocked due to the dense outer wrapping graphite layer. By contrast, the inner graphitic carbon was sufficiently exposed after the cleavage of the outer layer, enabling the superior AlCl_4^- -intercalation kinetics (Fig. 26b). In addition, the cleaved nanoribbons increased the charge-transport capability of the

electrode by serving as conductive ties to link the stacked nanofibers. Raman spectra confirmed that the graphitic structure of the cleaved nanoribbons was not destroyed by the acid treatment. Additionally, the acid treatment increased the specific surface area from $23.2 \text{ m}^2 \text{ g}^{-1}$ for the pristine CNFs to $55.3 \text{ m}^2 \text{ g}^{-1}$ for the cleaved CNFs. DFT calculations suggested that the edge-rich graphene structure (2.45 eV) had a stronger binding with AlCl_4^- than the edge-less graphene structure (2.21 eV). Furthermore, the AlCl_4^- binding energies in the bilayer structures are -3.14 eV , -1.66 eV , and -1.17 eV for the edge-less graphene, the centre of edge-rich graphene, and the edge of edge-rich graphene, respectively (Fig. 26c–h). These calculation results supported that the intercalation of AlCl_4^- was preferred with edge-rich graphene. This conclusion was also consistent with a recent study,¹⁸⁷ disclosing that the voids in few-layers graphene promoted the stage-2 and stage-1 AlCl_4^- intercalation. After the acid treatment, the cleaved CNFs presented a high specific capacity of 126 mA h g^{-1} at 1 A g^{-1} , which significantly contrasted with the pristine CNFs (15 mA h g^{-1}). Besides, excellent rate performance and cyclability were demonstrated for the cleaved CNFs with high specific capacities of 95 mA h g^{-1} at 50 A g^{-1} and 105 mA h g^{-1} ($\sim 100\%$ retention) after 5000 cycles at 10 A g^{-1} (Fig. 26i and j).

As discussed earlier, low-cost amides or amines can be used to replace the ionic liquid in the AMB electrolytes. For example, mixing AlCl_3 with urea,¹⁰⁵ triethylamine hydrochloride (Et_3NCl),¹⁸⁸ or acetamide¹⁰⁴ can form AlCl_4^- , AlCl_2^+ , and Al_2Cl_7^- in electrolytes. The charge/discharge electrode reaction in the $\text{AlCl}_3/\text{urea}$ electrolyte is the same as in the $\text{AlCl}_3/\text{EMIMCl}$ electrolyte, involving the Al_2Cl_7^- reaction (eqn (3)) at the anode side and AlCl_4^- intercalation at the cathode side.¹⁰⁴ However, the high viscosity of $\text{AlCl}_3/\text{urea}$ led the graphite cathode in the $\text{AlCl}_3/\text{urea}$ electrolyte to exhibit poor performance.¹⁰⁵ The specific capacity decreased from 73 mA h g^{-1} at 100 mA g^{-1} to 50 mA h g^{-1} at 200 mA g^{-1} . In addition, the average discharge voltage of graphite in the $\text{AlCl}_3/\text{urea}$ electrolyte was 1.73 V , which was 0.27 V lower than the graphite cathode in the $\text{AlCl}_3/\text{EMIMCl}$ electrolyte. To overcome the viscosity issue, Xu *et al.*¹⁸⁸ showed a device combining the $\text{Et}_3\text{NAlCl}_4$ electrolyte and the graphene aerogel cathode. The cathode was fabricated through freeze-drying and subsequent annealing of graphene oxide. In spite of the high viscosity of the electrolyte, the favourable porosity of the graphene aerogel cathode enabled an excellent rate performance. A specific capacity of nearly 110 mA h g^{-1} was reached at a current density of 5 A g^{-1} . Besides, the graphene aerogel was charged to a high voltage due to the high cut-off voltage of the $\text{Et}_3\text{NAlCl}_4$ electrolyte (2.62 V). Charging the graphene aerogel to 2.51 V resulted in a high energy density of $\sim 260 \text{ W h kg}^{-1}$ at a power density of 3 kW kg^{-1} . Nevertheless, Al-based dual-ion batteries require further electrolyte development to improve the anodic stability, as no commercial current collector can be used for the cathodes.

Anion intercalation provides a good strategy to avoid the drawback associated with the intercalation of multivalent Zn^{2+} , Mg^{2+} , and Al^{3+} . In addition, the anion-intercalation chemistry has been extensively studied in Li^+ -based systems, which accumulate insightful experience for constructing MVMB devices. In

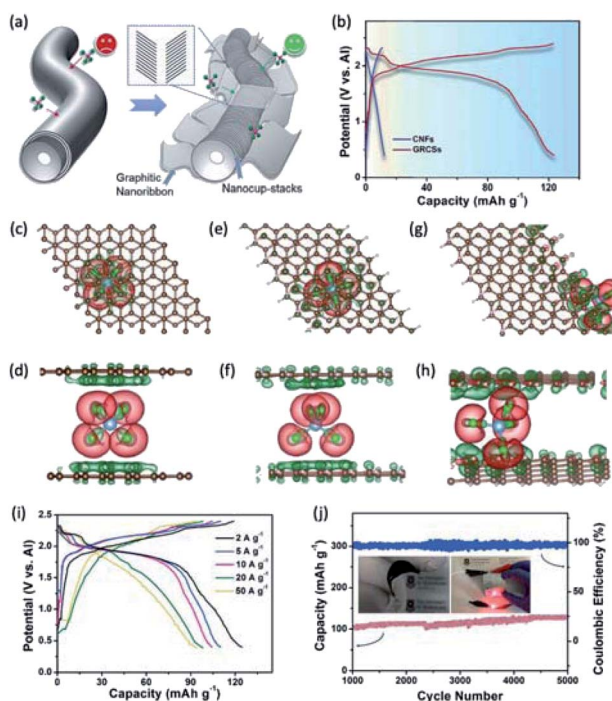


Fig. 26 (a) Schematic comparison of anion intercalation/deintercalation in commercial CNFs and cleaved CNFs. (b) Representative charge/discharge curves of CNFs and cleaved CNFs. (c–h) Calculated charge density differences of the AlCl_4^- in different graphene structures: the (c) top and (d) side views of the bilayer edge-less graphene with one AlCl_4^- ion placed between the two layers; the (e) top and (f) side views of the bilayer edge-rich graphene with one AlCl_4^- ion placed in the middle area; and the (g) top and (h) side views of bilayer edge-rich graphene with one AlCl_4^- ion placed near the edge, between two layers. An isosurface level of $0.0007 \text{ e}\text{\AA}^{-3}$ has been used in all images. (i) Charge/discharge curves of cleaved-CNFs at current densities from 2 to 50 A g^{-1} . (j) Long-term stability of cleaved-CNFs with coulombic efficiency and discharge specific capacity versus the cycle number at a current density of 10 A g^{-1} . The inset in d shows a flexible cleaved-CNFs electrode and a flexible AIB lighting a light emitting diode. Reproduced from ref. 186 with permission from The Royal Society of Chemistry.

this direction, the development of suitable electrolytes with wide stable potential windows and efficient metal stripping and plating will be highly desired for MVMBs.

3.4 Two-dimensional covalent organic frameworks

Two-dimensional covalent organic frameworks are a class of crystalline and porous 2D polymers, which are constructed with dynamic covalent bonds in the layer and stacked by non-covalent aromatic π -interactions. Interestingly, 2D COFs are equipped with one-dimensional channels along the c -crystallographic direction, allowing efficient mass transport through the material. Recently, 2D COFs have attracted intensive research attention as a group of multifunctional materials.^{189–192} Importantly, the regular porosity, large specific surface area, and the tailorable chemistries/topologies empower 2D COFs with versatile opportunities for energy storage by periodically organizing redox-active sites into porous frameworks.¹⁹³ According to the redox potentials, many organic groups are potentially suitable for constructing redox-active 2D COFs, such as quinone,^{194–200} phenazine,^{201,202} triphenylamine,^{203,204} cyano,^{205,206} bipyridine,^{114,207} pyridinic nitrogen,²⁰⁸ and phenanthrenequinone.^{20,110,209} At present, the energy-storage investigation on 2D COFs is still at the primary stage, and basic electrochemistry understanding is accumulating with dominant efforts devoted to the exploration of 2D COFs for LIBs. It should be noted that the electrochemical behaviours of organic groups are expected to be quite different for the applications of LIBs and MVMBs due to the change of charge carrier ions. For example, hexaazatriphenylene was demonstrated to exhibit a high specific capacity of ~ 400 mA h g⁻¹ for Li⁺ storage based on the accommodation of two Li⁺ ions in each bipyridine site. In the case of Mg²⁺ storage, two bipyridine sites would accommodate only one Mg²⁺, displaying inferior capacity and rate performance.¹¹⁴

Recently, some pioneering studies attempted to demonstrate the application of 2D COFs in MVMBs. Distinct from inorganic

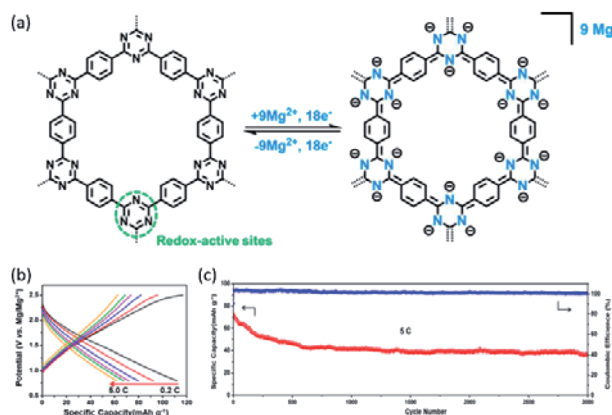


Fig. 27 (a) Chemical structure and possible electrochemical redox mechanism of the triazine-based COF. (b) Discharge/charge curves of electrodes at different rates. (c) Long-term cycling performance of the 2D COF at 5C. Reprinted with permission from ref. 208. Copyright 2019 American Chemical Society.

cathodes for MVMBs, 2D COFs provide flexible Mg²⁺ diffusion pathways and superior electrochemical reaction kinetics. Recently, Sun *et al.*²⁰⁸ synthesized a triazine-based 2D COF for Mg²⁺ storage (Fig. 27a). The 2D COF was synthesized through the polymerization of 1,4-dicyanobenzene by annealing with ZnCl₂ at 400 °C. An impressive rate performance was exemplified with a specific capacity of 110 mA h g⁻¹ and more than 50% capacity retention when the current density was increased from 50 to 1300 mA g⁻¹ (Fig. 27b). In addition, the 2D COF presented impressive cyclability, retaining a specific capacity of ~ 40 mA h g⁻¹ after 5000 cycles at 1300 mA g⁻¹ (Fig. 27c). Based on the proposed structure in Fig. 27a, the high density of active triazine sites enabled the 2D COF with a high theoretical specific capacity of 419 mA h g⁻¹, considerably higher than the measured value (110 mA h g⁻¹). XPS measurements detected changes in the signal of pyridinic-N in triazine during charge/discharge, indicating that charge storage occurred through interaction between Mg²⁺ and $\text{C}=\text{N}$ in triazine rings. However, pyrrolic-N and graphitic-N could not contribute to the charge storage, which explained the low specific capacity.

Apart from cation-storage 2D COFs, anion-storage 2D COFs were also demonstrated for MVMBs, which delivered high voltage and large specific capacity. Lu *et al.*²¹⁰ synthesized a bipyridine-containing COF (denoted TpBpy-COF) through the reaction between 5,5'-diamino-2,2'-bipyridine and triformylphloroglucinol (Fig. 28a). Importantly, TpBpy-COF exhibited a high crystallinity with a large specific surface area of 1794 m² g⁻¹ and regular porosity with pore sizes of ~ 2.1 nm. The TpBpy-COF cathode for AMBs exhibited an exceptionally high specific capacity of 307 mA h g⁻¹ at 125 mA g⁻¹ (Fig. 28b), close to its theoretical value of 369.7 mA h g⁻¹. Additionally, a high specific capacity of 150 mA h g⁻¹ was retained after 13 000 cycles at a high current density of 2 A g⁻¹. *Ex situ* XRD reflected that TpBpy-COF well retained its crystalline structure during repeat

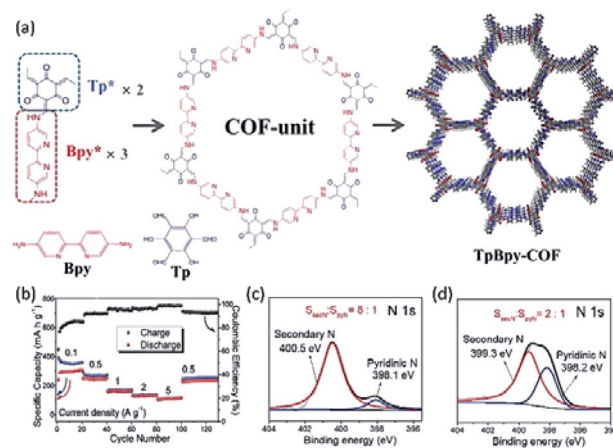


Fig. 28 (a) Synthetic reaction and structure illustration of 2D COF fabricated from 5,5'-diamino-2,2'-bipyridine and triformylphloroglucinol. (b) Galvanostatic discharge/charge curves under different current densities in the potential range 0.01–2.3 V. 1 s XPS spectra of electrodes (c) charged to 2.3 V and (d) discharged to 0.1 V at 2 A g⁻¹. Reprinted with permission from ref. 210. Copyright 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Table 2 Summary of layered cathode materials for non-aqueous ZMBs^a

Material	Electrolyte	Specific capacity	Average discharge voltage	Energy density based on the cathode	Cyclability	Ref.
Bilayered hydrated V ₂ O ₅	0.5 M Zn(TFSI) ₂ in AN	196 mA h g ⁻¹ at 14.4 mA g ⁻¹	0.9 V	176 W h kg ⁻¹	170 mA h g ⁻¹ after 120 cycles at 14.4 mA g ⁻¹	65
V ₃ O ₇ ·H ₂ O nanofibers	0.25 M Zn(OTf) ₂ in AN	175 mA h g ⁻¹ at 5 mA g ⁻¹	0.75 V	131 W h kg ⁻¹	175 mA h g ⁻¹ after 50 cycles at 5 mA g ⁻¹	61
δ-MnO ₂ nanoflorets	0.5 M Zn(TFSI) ₂ in AN with 10% water	123 mA h g ⁻¹ at 12.3 mA g ⁻¹	1.37 V	169 W h kg ⁻¹	55 mA h g ⁻¹ after 125 cycles at 12.3 mA g ⁻¹	66
PPy-intercalated VOPO ₄	1 M Zn(OTf) ₂ in AN	67 mA h g ⁻¹ at 30 mA g ⁻¹	1.3 V	87 W h kg ⁻¹	60 mA h g ⁻¹ after 350 cycles at 100 mA g ⁻¹	59
Natural graphite	0.2 M Zn(OTf) ₂ in EMImOTf	33.7 mA h g ⁻¹ at 200 mA g ⁻¹	2.0 V	65.1 W h kg ⁻¹	20 mA h g ⁻¹ after 100 cycles at 200 mA g ⁻¹	183
Graphite powder	2 M LiPF ₆ + 0.5 M Zn(TFSI) ₂ in EMC	105 mA h g ⁻¹ at 100 mA g ⁻¹	2.2 V	231 W h kg ⁻¹	96 mA h g ⁻¹ after 2000 cycles at 1 A g ⁻¹	24
Natural graphite	2.5 M LiPF ₆ in EMC/TMS (4 : 1)	98 mA h g ⁻¹ at 100 mA g ⁻¹	2.2 V	216 W h kg ⁻¹	82 mA h g ⁻¹ after 1200 cycles at 300 mA g ⁻¹	23

^a TMS – tetramethylene sulfone.

charge/discharge cycles, accounting for the excellent cyclability. Furthermore, Fourier-transform infrared measurements suggested that AlCl₄⁻ storage altered the environment of nitrogen atoms ($\nu_{\text{C}=\text{N}}$ and $\nu_{\text{C}-\text{N}}$ signals) in TpBpy-COF upon charging. N 1s peak related to the secondary N (-NH-) shifted from 399.2 eV to higher binding energy of 400.5 eV upon the charge, and shifted back to 399.3 eV after the discharge. Meanwhile, the ratio between secondary N and pyridinic N changed from 1 : 1 to 8 : 1 upon the charge and recovered to 2 : 1 after the discharge (Fig. 28c and d). These XPS results indicated that the C-N and C=N groups were involved in the p-type oxidation with AlCl₄⁻.²¹⁰

4. Summary and outlook

To sum up, MVMBs, using highly available multivalent metal as anodes, have emerged as promising alternatives for LIBs, particularly in large-scale and stationary energy storage applications. Currently, MVMBs are still at the preliminary research stage, and the whole community focuses on exploiting suitable “anode–electrolyte–cathode” systems for potential practical applications. In this review, we briefly introduced the cell configuration and the so-far developed “anode–electrolyte” chemistries for non-aqueous MVMBs, including ZMBs, MMBs, and AMBs. Particularly, we put the emphasis on discussing the recent progress in the development of layered cathode materials (including layered TMOs, TMDs, graphite, and 2D COFs) for non-aqueous MVMBs (also summarized in Tables 2–4). It should be noted that Ca-metal batteries are also promising alternative MVMBs. However, the development of Ca metal-compatible electrolytes is still the main challenge of Ca-metal batteries, resulting in rare studies on the Ca²⁺ intercalation of layered materials.²¹¹ Therefore, Ca-metal batteries are not discussed in this review. Among layered materials, layered TMOs (e.g., MnO₂ and V₂O₅) demonstrate auspicious specific capacities and redox potentials, but display sluggish multivalent

metal ion-storage kinetics (e.g., Zn²⁺ and Al³⁺) and compatibility issues with MVMB electrolytes (e.g., MMB electrolytes). In comparison with TMOs, TMDs show good electrolyte compatibility with efficient cation intercalation and superior rate capabilities. Nevertheless, inferior discharge voltages lead to the low energy densities of MVMBs constructed with TMD cathodes. Graphite-based materials with the anion-intercalation chemistry exhibit high redox potentials (e.g., ~1.75 V vs. SHE), avoiding the drawbacks related to multivalent metal ion intercalation. However, graphite-based materials are limited by the low theoretical capacity, as well as the insufficient electrolyte studies for ZMBs and MMBs. In addition, 2D COFs provide a unique material platform for exceptional active site engineering at the molecular level, providing many opportunities for both cation and anion storage. Fig. 29 compares the average discharge voltages and specific capacities of recently developed layered cathodes for ZMBs, MMBs, and AMBs. It provides an unambiguous picture about the advantages and limitations of different layered materials for different MVMBs. In light of the unique vdW interaction between layers, the structure of layered materials can be easily engineered *via* versatile strategies to tailor their intrinsic properties and ion-storage kinetics. In this sense, interlayer expansion strategies represent the most employed one to facilitate the efficient ion diffusion and promote the intercalation of new charge carrier species (e.g., MgCl⁺ in MMBs). Besides, guest species incorporation strategies can enhance the intrinsic conductivity and structural stability of layered materials, while imposing a shielding effect on the interaction of charge carrier ions and cathodes. Given the remarkable progress achieved in this research direction, there are many challenges to be addressed in the near future, which are highlighted below.

Although many material engineering strategies have been reported to modify the structures of layered materials, their side effects on the electrochemical performance were not adequately addressed in the previous studies. For example, guest species

Table 3 Summary of layered cathode materials for MMBs^a

Material	Electrolyte	Specific capacity	Average discharge voltage	Energy density based on the cathode	Cyclability	Ref.
V ₂ O ₅ on CNFs	1 M Mg(ClO ₄) ₂ in AN	160 mA h g ⁻¹ at 20 mA g ⁻¹	0.6 V	96 W h kg ⁻¹	120 mA h g ⁻¹ after 50 cycles at 30 mA g ⁻¹	136
α-V ₂ O ₅	0.5 M Mg(TFSI) ₂ in PY ₁₄ TFSI	295 mA h g ⁻¹ at 15 mA g ⁻¹ (110 °C)	0.0 V vs. AC (2.0 V vs. Mg ²⁺ /Mg)	N/A	200 mA h g ⁻¹ after 50 cycles at 59 mA g ⁻¹ (110 °C)	93
V ₂ O ₅ -PEO nanocomposites	0.5 M Mg(ClO ₄) ₂ in AN	100 mA h g ⁻¹ at 10 mA g ⁻¹	~1.4 V	~140 W h kg ⁻¹	90 mA h g ⁻¹ after 35 cycles at 10 mA g ⁻¹	141
Graphene-decorated V ₂ O ₅	0.5 M Mg(TFSI) ₂ in AN	320 mA h g ⁻¹ at 50 mA g ⁻¹	-0.4 V vs. AC (2.0 V vs. Mg ²⁺ /Mg)	N/A	95 mA h g ⁻¹ after 200 cycles at 1 A g ⁻¹	132
V ₃ O ₇ ·H ₂ O NWs	0.5 M Mg(ClO ₄) ₂ in AN	231 mA h g ⁻¹ at 10 mA g ⁻¹ (at 60 °C)	-0.75 V vs. AC (1.75 V vs. Mg ²⁺ /Mg)	N/A	132 mA h g ⁻¹ after 100 cycles at 40 mA g ⁻¹ (60 °C)	142
NH ₄ V ₄ O ₁₀	0.5 M Mg(ClO ₄) ₂ in AN	174.8 mA h g ⁻¹ at 42 mA g ⁻¹	-0.19 V vs. AC (2.19 V vs. Mg ²⁺ /Mg)	N/A	36.8 mA h g ⁻¹ after 100 cycles at 210 mA g ⁻¹	140
Mn _{0.04} V ₂ O ₅ ·1.17H ₂ O NBs	0.3 M Mg(TFSI) ₂ in AN	140 mA h g ⁻¹ at 50 mA g ⁻¹	-0.2 V vs. AC (2.2 V vs. Mg ²⁺ /Mg)	N/A	70 mA h g ⁻¹ after 10 000 cycles at 2 A g ⁻¹	138
Mg _{0.3} V ₂ O ₅ ·1.1H ₂ O NWs	0.3 M Mg(TFSI) ₂ in AN	162 mA h g ⁻¹ at 100 mA g ⁻¹	-0.25 V vs. AC (2.25 V vs. Mg ²⁺ /Mg)	N/A	108 mA h g ⁻¹ after 10 000 cycles at 1 A g ⁻¹	135
Mg _x V ₅ O ₁₂ ·nH ₂ O NFs	0.3 M Mg(TFSI) ₂ in AN	160 mA h g ⁻¹ at 50 mA g ⁻¹	0.0 V vs. AC (2.0 V vs. Mg ²⁺ /Mg)	N/A	68 mA h g ⁻¹ after 10 000 cycles at 2 A g ⁻¹	137
Na ₂ V ₆ O ₁₆ ·1.63H ₂ O NWs	0.5 M Mg(TFSI) ₂ in DME	175 mA h g ⁻¹ at 50 mA g ⁻¹	-0.4 V vs. AC (2.0 V vs. Mg ²⁺ /Mg)	N/A	46 mA h g ⁻¹ after 450 cycles at 200 mA g ⁻¹	139
Free-standing MnO ₂ NWs film	0.1 M Mg(ClO ₄) ₂ in PC	120 mA h g ⁻¹ at 246 mA g ⁻¹	N/A	N/A	92 mA h g ⁻¹ after 100 cycles at 246 mA g ⁻¹	128
MnO ₂	0.25 M Mg(TFSI) ₂ in diglyme	135 mA h g ⁻¹ at 25 mA g ⁻¹	1.4 V	N/A	90 mA h g ⁻¹ after 100 cycles at 125 mA g ⁻¹	95
MoO ₃	0.5 M Mg(ClO ₄) ₂ in AN	220 mA h g ⁻¹ at N/A	1.8 V	N/A	N/A	221
PA-VOPO ₄	APC in THF	275 mA h g ⁻¹ at 100 mA g ⁻¹	1 V	275 W h kg ⁻¹	192 mA h g ⁻¹ after 500 cycles at 100 mA g ⁻¹	153
VOPO ₄ ·2H ₂ O	0.1 M Mg(ClO ₄) ₂ ·6H ₂ O in PC	91.7 mA h g ⁻¹ at 5 mA g ⁻¹	0.1 V vs. Ag/AgCl (2.7 V vs. Mg ²⁺ /Mg)	N/A	N/A	152
TiS ₂ nanotubes	1 M Mg(ClO ₄) ₂ in AN	236 mA h g ⁻¹ at 10 mA g ⁻¹	1.2 V	N/A	184 mA h g ⁻¹ after 80 cycles at 10 mA g ⁻¹	159
TiSe ₂ nanocrystal	0.25 M Mg(AlCl ₂ EtBu) ₂ in THF	110 mA h g ⁻¹ at 5 mA g ⁻¹	0.9 V	99 W h kg ⁻¹	~100 mA h g ⁻¹ after 50 cycles at 5 mA g ⁻¹	158
TiS ₂	APC in tetraglyme	160 mA h g ⁻¹ at 12.5 mA g ⁻¹ (60 °C)	~0.7 V	~112 W h kg ⁻¹	~115 mA h g ⁻¹ after 40 cycles at 25 mA g ⁻¹ (60 °C)	160
Layer-expanded TiS ₂	APC in THF with 0.25 M Py ₁₄ Cl	239 mA h g ⁻¹ at 24 mA g ⁻¹	0.7 V	176 W h kg ⁻¹	120 mA h g ⁻¹ after 500 cycles at 240 mA g ⁻¹	154
Pristine TiSe ₂	APC in THF	127 mA h g ⁻¹ at 5 mA g ⁻¹	1.25 V	159 W h kg ⁻¹	80 mA h g ⁻¹ after 40 cycles at 5 mA g ⁻¹	157
Pristine VSe ₂	APC in THF	115 mA h g ⁻¹ at 5 mA g ⁻¹	1.2 V	138 W h kg ⁻¹	86 mA h g ⁻¹ after 40 cycles at 5 mA g ⁻¹	157
2-Ethylhexylamine pillared VS ₂ nanoflowers	Mg(HMDS) ₂ -4MgCl ₂ in THF with PP ₁₄ TFSI	249 mA h g ⁻¹ at 100 mA g ⁻¹	0.7 V	174 W h kg ⁻¹	90 mA h g ⁻¹ after 600 cycles at 1 A g ⁻¹	167
VS ₂ NSs	APC in THF with 0.2 M PP ₁₄ Cl	348 mA h g ⁻¹ at 100 mA g ⁻¹	0.7 V	244 W h kg ⁻¹	200 mA h g ⁻¹ after 300 cycles at 1 A g ⁻¹	80
Graphene-like MoS ₂	Mg(AlCl ₃ Bu) ₂ in THF	170 mA h g ⁻¹ at 20 mA g ⁻¹	1.9 V	323 W h kg ⁻¹	162 mA h g ⁻¹ after 50 cycles at 20 mA g ⁻¹	176
MoS ₂ @C porous NRs	Fluorinated Mg alkoxyborate	120 mA h g ⁻¹ at 10 mA g ⁻¹	0.65 V	80 W h kg ⁻¹	56 mA h g ⁻¹ after 200 cycles at 100 mA g ⁻¹	174
PVP-incorporated MoS ₂	APC in THF	143.4 mA h g ⁻¹ at 20 mA g ⁻¹	~0.75 V	~108 W h kg ⁻¹	131.9 mA h g ⁻¹ after 100 cycles at 20 mA g ⁻¹	177
Expanded graphite	0.5 M Mg(TFSI) ₂ in Py ₁₄ TFSI	93 mA h g ⁻¹ at 100 mA g ⁻¹	1.83 V	174 W h kg ⁻¹	62 mA h g ⁻¹ after 500 cycles at 300 mA g ⁻¹	212
Triazine-based porous COF	0.5 M Mg(TFSI) ₂ in DME	102 mA h g ⁻¹ at 57 mA g ⁻¹	1.45 V	146 W h kg ⁻¹	30 mA h g ⁻¹ after 3000 cycles at 570 mA g ⁻¹	208

^a NFs – nanofibers, NW – nanowire, AC – active carbon, NB – nanobelts, NS – nanosheet, NR – nanorod.

Table 4 Summary of layered cathode materials for AMBs^a

Material	Electrolyte	Specific capacity	Average discharge voltage	Energy density based on the cathode	Cyclability	Ref.
V ₂ O ₅ NWs	AlCl ₃ : [EMIm]Cl molar ratio 1.1 : 1	305 mA h g ⁻¹ at 125 mA g ⁻¹	0.55 V	168 W h kg ⁻¹	273 mA h g ⁻¹ after 20 cycles at 125 mA g ⁻¹	143
Binder-free V ₂ O ₅	AlCl ₃ : [BMIm]Cl molar ratio 1.1 : 1	239 mA h g ⁻¹ at 44.2 mA g ⁻¹	0.6 V	143 W h kg ⁻¹	N/A	213
V ₂ O ₅ NWs	AlCl ₃ : [BMIm]Cl molar ratio 1.1 : 1	107 mA h g ⁻¹ at N/A	0.5 V	54 W h kg ⁻¹	40 mA h g ⁻¹ after 10 cycles	108
α-MoO ₃	AlCl ₃ : [EMIm]Cl molar ratio 1.1 : 1	100 mA h g ⁻¹ at 3 mA g ⁻¹	0.9 V	90 W h kg ⁻¹	12.5 mA h g ⁻¹ after 25 cycles at 10 mA g ⁻¹	214
TiS ₂	AlCl ₃ : [BMIm]Cl molar ratio 1.5 : 1	70 mA h g ⁻¹ at 5 mA g ⁻¹ (50 °C)	0.75 V	53 W h kg ⁻¹	70 mA h g ⁻¹ after 50 cycles at 5 mA g ⁻¹ (50 °C)	106
TiS ₂ NB	AlCl ₃ : [EMIm]Cl molar ratio 1.5 : 1	200 mA h g ⁻¹ at 240 mA g ⁻¹ (at 50 °C)	0.4 V	80 W h kg ⁻¹	150 mA h g ⁻¹ after 90 cycles at 240 mA g ⁻¹	161
Graphene-VS ₂ NS	AlCl ₃ : [EMIm]Cl molar ratio 1.3 : 1	186 mA h g ⁻¹ at 100 mA g ⁻¹	0.6 V	112 W h kg ⁻¹	50 mA h g ⁻¹ after 50 cycles at 100 mA g ⁻¹	171
VSe ₂	AlCl ₃ : [EMIm]Cl	419 mA h g ⁻¹ at 100 mA g ⁻¹	1.2 V	503 W h kg ⁻¹	50 mA h g ⁻¹ after 100 cycles at 100 mA g ⁻¹	172
MoS ₂ microspheres	AlCl ₃ : [EMIm]Cl molar ratio 1.3 : 1	253.6 mA h g ⁻¹ at 20 mA g ⁻¹	0.6 V	152 W h kg ⁻¹	66.7 mA h g ⁻¹ after 100 cycles at 40 mA g ⁻¹	111
Free-standing MoS ₂ /carbon NF	AlCl ₃ : [EMIm]Cl molar ratio 1.3 : 1	293.2 mA h g ⁻¹ at 100 mA g ⁻¹	~0.5 V	~147 W h kg ⁻¹	127 mA h g ⁻¹ after 200 cycles at 100 mA g ⁻¹	178
Flower-like MoS ₂ microspheres	AlCl ₃ : [EMIm]Cl molar ratio 1.3 : 1	154 mA h g ⁻¹ at 50 mA g ⁻¹	~0.4 V	~61 W h kg ⁻¹	112 mA h g ⁻¹ after 100 cycles at 50 mA g ⁻¹	179
Carbon paper	AlCl ₃ : [EMIm]Cl molar ratio 1.3 : 1	90 mA h g ⁻¹ at 50 mA g ⁻¹	1.8 V	162 W h kg ⁻¹	70 mA h g ⁻¹ after 100 cycles at 100 mA g ⁻¹	215
Graphitic foam	AlCl ₃ : [EMIm]Cl molar ratio 1.3 : 1	60 mA h g ⁻¹ at 5 A g ⁻¹	1.8 V	108 W h kg ⁻¹	60 mA h g ⁻¹ after 7500 cycles at 4 A g ⁻¹	21
Aligned graphene sheets	AlCl ₃ : [EMIm]Cl molar ratio 1.3 : 1	60 mA h g ⁻¹ at 12 A g ⁻¹	1.8 V	108 W h kg ⁻¹	60 mA h g ⁻¹ after 4000 cycles at 12 A g ⁻¹	112
Few-layer graphene	AlCl ₃ : [EMIm]Cl molar ratio 1.3 : 1	110 mA h g ⁻¹ at 100 mA g ⁻¹	2 V	220 W h kg ⁻¹	75 mA h g ⁻¹ after 1000 cycles at 3 A g ⁻¹	216
Natural graphite	AlCl ₃ : [EMIm]Cl molar ratio 1.3 : 1	132 mA h g ⁻¹ at 100 mA g ⁻¹	2 V	264 W h kg ⁻¹	132 mA h g ⁻¹ after 100 cycles at 100 mA g ⁻¹	217
Graphite powder	AlCl ₃ : urea molar ratio 1.3 : 1	73 mA h g ⁻¹ at 100 mA g ⁻¹	1.73 V	126 W h kg ⁻¹	~73 mA h g ⁻¹ after 200 cycles at 100 mA g ⁻¹	105
Natural graphite	AlCl ₃ : [EMIm]Cl molar ratio 1.3 : 1	110 mA h g ⁻¹ at 99 mA g ⁻¹	~1.9 V	209 W h kg ⁻¹	60 mA h g ⁻¹ after 6000 cycles at 600 mA g ⁻¹	113
Large-size few-layer graphene	AlCl ₃ : [PMIm]Cl molar ratio 1.3 : 1	85 mA h g ⁻¹ at 60 mA g ⁻¹	1.8 V	153 W h kg ⁻¹	80 mA h g ⁻¹ after 200 cycles at 60 mA g ⁻¹	184
Carbon nanoscrolls	AlCl ₃ : [EMIm]Cl molar ratio 1.3 : 1	104 mA h g ⁻¹ at 1 A g ⁻¹	1.5 V	156 W h kg ⁻¹	101 mA h g ⁻¹ after 55 000 cycles at 50 A g ⁻¹	218
Graphite powder	AlCl ₃ : [EMIm]Cl molar ratio 1.7 : 1	~110 mA h g ⁻¹ at 50 mA g ⁻¹ (at -10 °C)	~2 V (-10 °C)	~220 W h kg ⁻¹ (at -10 °C)	85 mA h g ⁻¹ after 1200 cycles at 100 mA g ⁻¹ (-20 °C)	219
Edge-rich graphene	AlCl ₃ : [EMIm]Cl molar ratio 1.3 : 1	128 mA h g ⁻¹ at 2 A g ⁻¹	1.8 V	230 W h kg ⁻¹	90 mA h g ⁻¹ after 20 000 cycles at 8 A g ⁻¹	220
Graphene aerogel	AlCl ₃ /Et ₃ NHCl molar ratio 1.5 : 1	112 mA h g ⁻¹ at 5 A g ⁻¹	~1.7 V	190 W h kg ⁻¹	109 mA h g ⁻¹ after 30 000 cycles at 5 A g ⁻¹	188
Edge-rich graphitic nanoribbons	AlCl ₃ : [EMIm]Cl molar ratio 1.3 : 1	126 mA h g ⁻¹ at 1 A g ⁻¹	1.91 V	241 W h kg ⁻¹	105 mA h g ⁻¹ after 20 000 cycles at 10 A g ⁻¹	186
Surface-perforated graphene	AlCl ₃ : [EMIm]Cl molar ratio 1.3 : 1	197 mA h g ⁻¹ at 2 A g ⁻¹	~1.75 V	~345 W h kg ⁻¹	147 mA h g ⁻¹ after 1000 cycles at 5 A g ⁻¹	187
TpBpy-COF	AlCl ₃ : [EMIm]Cl molar ratio 1.3 : 1	307 mA h g ⁻¹ at 100 mA g ⁻¹	~1.15 V	~353 W h kg ⁻¹	150 mA h g ⁻¹ after 13 000 cycles at 2 A g ⁻¹	210

^a NFs – nanofibers, TMS – tetramethylene sulfone, NW – nanowire, AC – active carbon, NB – nanobelts, NS – nanosheet, NR – nanorod, BMIM – 1-butyl-3-methylimidazolium, PMIM – 1-methyl-3-propylimidazolium chlorides, TpBpy – 1,3,5-triformylphloroglucinol + 2,2'-bipyridine-5,5'-diamine.

incorporation would bring the extraction of molecules (e.g., water) into the electrolyte, inducing the formation of the passivation layer on metal anodes. The incorporated molecules

would also induce the partial reduction of active sites, thus lessening the theoretical specific capacity. Moreover, interlayer expansion strategies would also lead to low discharge voltages

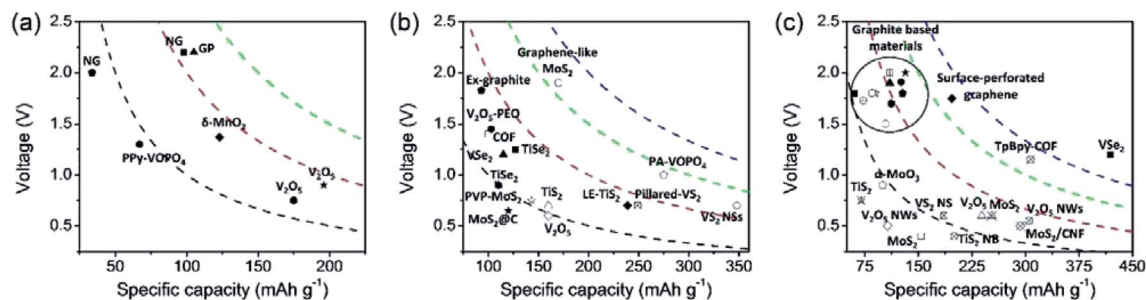


Fig. 29 Average discharge voltage vs. specific capacity of recently developed layered cathodes for (a) ZMBs,^{23,24,59,61,65,66,183} (b) MMBs,^{80,136,141,153,154,157,158,160,167,174,176,177,208,212} and (c) AMBs.^{21,105,106,108,111–113,143,161,171,172,178,179,184,186–188,210,213–220} The black (100 mA h g⁻¹), red (200 mA h g⁻¹), green (300 mA h g⁻¹), and blue (400 mA h g⁻¹) dash lines correspond to energy density at the same values.

compared with the theoretical values for pristine materials. New material structure engineering strategies at the molecule level are highly desired. In this sense, many approaches, which have been well demonstrated in alkali metal ion batteries (*e.g.*, defect engineering, artifice electrode/electrolyte interface construction), could be considered in future researches.

The sluggish charge-storage kinetics of MVMB cathodes associated with the multivalent metal ions as charge carriers represents one of the dominant factors restricting the performance. To this end, employing anion-storage cathodes (*e.g.*, graphite and p-type organic redox compounds) for MVMBs represents a feasible way to avoid the kinetics issue, because the low-charge-density anion-storage (*e.g.*, PF₆⁻, TFSI⁻, and AlCl₄⁻) chemistry allows cathode with high rate capability and high redox potentials. Anion-storage chemistries have been extensively explored in AMBs and preliminarily demonstrated in ZMBs. More future efforts are desired to further expand anion-storage chemistries to more MVMB devices, which will require the development of high-capacity anion-storage sites and wide-potential-window electrolytes. Besides, rationally constructing 2D COFs with dense p-type organic redox groups could be an effective approach to obtain superior anion-storage cathodes.

Furthermore, the dominant motivation to develop MVMBs comes from the advantages brought by the direct use of multivalent metal anodes (*e.g.*, superior volumetric capacity and dendrite-free stripping/plating). However, in many studies, the developed cathodes were evaluated in electrolytes that are incompatible with the metal anode chemistry (*e.g.*, the Mg(ClO₄)₂ in AN electrolyte for MMBs). In this regard, the acquired electrochemical data would not be the suitable reference for assembling MVMBs. In addition, various device parameters (*e.g.*, mass loading, electrode preparation method, and electrolyte) for the performance assessment of cathodes could significantly affect the electrochemical performance. Therefore, the comparison between cathodes evaluated in different device systems is somehow unjustified. Additionally, the cathode analysis focused primarily on the specific capacity and rate capability. Important parameters, such as energy density, energy efficiency, and power density, are often overlooked. Especially, in some cases, the specific capacities were measured at very low voltages, resulting in the negligible contribution to the energy. Therefore, it is essential for the

community to push forwards the standardization of electrode evaluation for MVMBs, which take under consideration the important parameters measured at agreed conditions.

Although the research on MVMBs is still at the primary research stage, commercialization is always the ultimate goal for new battery chemistries. Thus, we summarize some promising research directions of non-aqueous MVMBs in views of practical application as below. Zn metal stability in aqueous electrolytes is restricted by the severe dendrite growth, thus motivating the development of non-aqueous ZMBs with reversible and efficient anode electrochemistry. However, the intercalation kinetics of Zn²⁺ into layered TMO cathodes is sluggish in non-aqueous electrolytes. Learned from aqueous ZMBs, trace water additive holds the promise to greatly improve the performance of TMO cathodes for non-aqueous ZMBs. In this sense, additional efforts are required to explore the effect of the water additive on the Zn anode and fine-tune the amount of the water additive in organic solvents. As Mg has the lowest stripping/plating potential among the presented multivalent metals, it has great potential for constructing batteries with high energy and power densities. Among the possible cathode materials for MMBs, TMOs exhibit the most promising performance with large theoretical capacities, high redox potentials, and thus large theoretical energy densities. In addition, the demonstration of effective Mg²⁺ intercalation into TMOs and decent cyclability imply their potential as promising cathodes for MMBs. However, before the implementation of TMOs-based MMB devices can be made, considerable efforts should be devoted to developing compatible electrolytes for both the TMO cathodes and the Mg metal anode. Unlike TMOs, TMDs are fully compatible with currently developed Mg electrolytes. Nevertheless, large amounts of their capacities are at the low operation voltage range (<0.5 V), which is not feasible for practical applications. For AMBs, the intercalation of Al³⁺ causes the fast capacity degradation of most layered cathodes. Recent studies suggest other Al species, such as AlCl₂⁺, AlCl₂²⁺, and AlCl₄⁻, to be promising charge carriers for AMB cathodes. In this regard, carbon-based/carbon-rich materials, such as graphite, 2D COFs, and 2D conjugated metal-organic frameworks, are considered as the potential alternative cathodes for AMBs, as they enable new electrochemistries, high specific capacities, long-term

cyclability, and high operation voltage that other layered materials are lacking (e.g., TMOs and TMDs).

Finally, the assessment of the cathode performance alone could not promote the transition from research to practical application. Most reported studies focus only on evaluating cathodes with flood electrolytes and much over-capacity metal anodes, and the full-device demonstration for MVMBs is often missing in previous studies. When assembling full devices, the anode–electrolyte–cathode ratios could have a prominent effect on the performance. In addition, some MVMB electrolytes (e.g., APC for MMBs and $\text{AlCl}_3/\text{EMIMCl}$ for AMBs) used in previous studies are not compatible with the commonly used current collectors (e.g., Al, Cu, and stainless steel) due to the strong corrosive effect. In this sense, the fabrication of promising cathodes should go side-by-side with the development of suitable electrolytes. Furthermore, effort should also be directed to the development of simple procedures for cathodes material synthesis. Since most pristine layered materials display inefficient multivalent metal ion storage, post structure engineering (e.g., layer expansion) is commonly required to promote the ion-storage kinetics. However, such structure engineering steps could hinder their commercialization due to the high material processing cost.

Conflicts of interest

There are no conflicts to declare.

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