

Recent Progress and Challenges in the Optimization of Electrode Materials for Rechargeable Magnesium Batteries

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Rechargeable magnesium batteries (RMBs) have been regarded as one of the promising electrochemical energy storage systems to complement Li-ion batteries owing to the low-cost and high safety characteristics. However, the various challenges including the sluggish solid-state diffusion of highly polarizing Mg²⁺ ions in hosts, and the formation of blocking layers on Mg metal surface have seriously impeded the development of high-performance RMBs. In order to solve these problems toward practical applications of RMBs, a tremendous amount of work on electrodes and electrolytes has been conducted in the last few decades. Creative optimization strategies including the modification of cathodes and anodes such as shielding the charges of divalent Mg²⁺, expanding the layers of host materials, and optimizing the interface of electrode-electrolyte are raised to promote the technology. In this review, the detailed description of innovative approaches, representative examples, and facing challenges for developing high-performance electrodes are presented. Based on the review of these strategies, guidelines are provided for future research directions on improving the overall battery performance, especially on the electrodes.

1. Introduction

With the rapid growth of energy consumption, the depletion of fossil fuels is unavoidable and concerns over environmental pollution are growing.^[1–3] Renewable and clean energies (solar, wind, and tidal energy) have become a crucial topic in recent decades, and are regarded as promising alternatives to conventional fuels.^[4–6] Nevertheless, the new energy sources are intermittent and may not satisfy practical applications, leading to the urgent demand for advanced energy storage devices. Li-ion battery (LIB) technology has already achieved great success in the application of commercial portable electronic devices

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benefited from the characteristics of high energy density, high power density and environmental friendliness.^[7-10] Li has the lowest oxidation potential (-3.04 V vs SHE) among metals, thus Li metal is the most suitable anode to deliver the highest energy density for a battery system. However, the limited reserve of Li sources, safety issues and high cost restrict its further applications.^[11,12] Therefore, the exploration of other battery systems based on earth-abundance elements with good safety to complement LIBs is necessary, especially in large-scale applications. Na, Mg, Zn, and Al as anodes in rechargeable batteries have a similar operating mechanism as that of Li. Potential candidates as alternatives to LIBs can be rechargeable sodium-ion batteries, rechargeable magnesium batteries (RMBs), rechargeable zinc batteries and rechargeable aluminum-ion batteries. Metallic sodium is too active to handle safely and has

the similar problem of dendrite formation as lithium.^[13,14] In respect of multivalent batteries, the Mg, Zn, and Al metals are abundant in the earth and usually employed as the anode to deliver high specific capacity as well as energy density owing to the multielectron reactions.^[15–20] In addition, they have many unique properties, such as small ionic radius, and reasonably low deposition potential (**Table 1**). Certainly, they also have special opportunities and challenges when used as an anode in counterpart batteries. At the present stage, they are uncompetitive with LIBs in many aspects, and methods are being explored to enhance the ions storage performance, such as the optimization of cathode, anode, and electrolyte. There is no denying that multivalent battery systems still require much time and effort before achieving satisfactory results to narrow the gap with LIBs, or even surpass them.^[21]

Compared with Zn and Al metals, Mg metal possesses a lower redox potential (an advantage for high energy density). Moreover, the dendrite-free property (in specific conditions) and high coulombic efficiency in proper electrolytes make it more competitive.^[27–31] However, the divalent Mg²⁺ ions exhibit sluggish kinetics which originates from the strong polarizing nature and results in low or even no capacity in most cathode materials established for Li-storage.^[32–35] Choosing Mo₆S₈ as the cathode material is a breakthrough on the way to RMBs and it still surpasses many of cathodes even today, especially in cycling stability. The Chevrel phase (CP) compound was first

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Table 1. Theoretical key characteristics of Li, Mg, Zn, and Al.

Parameter	Li	Mg	Zn	Al
Valence	+	2+	2+	3+
Atomic weight ^[22]	6.94	24.31	65.41	26.98
Ionic radius [Å] ^[23,24]	0.76	0.72	0.74	0.54
Standard potential (V vs SHE) ^[25]	-3.07	-2.35	-0.76	-1.68
Specific capacity [mAh g ⁻¹]	3862	2205	819	2980
Specific capacity [mAh cm ⁻³]	2062	3832	5848	8046
Abundance [ppm] ^[26]	18	23 000	79	82 000

introduced in LIB in 1985, and also demonstrated high mobility of various ions (Ni²⁺, Zn²⁺, and Mg²⁺).^[36-38] Even the concept of RMB was raised in the early 1990, however, the prototype of Mg full cell was not demonstrated until 2000.[39-42] Assembled with Mg metal anode in Mg(AlCl₂BuEt)₂/tetrahydrofuran (THF) electrolyte, CP Mo₆S₈ cathode exhibited stable longcycling performance (over 2000 cycles) and reasonable kinetics of Mg ions. The CP Mo₆S₈ had been the benchmark of cathode materials for RMBs despite its low operating voltage (about 1 V vs Mg²⁺/Mg) and specific capacity (about 120 mAh g^{-1}) at low rate. Since then, many works (both experimental and theoretical investigations) are reported to improve the Mg-ion storage performance of CP-based RMBs. The simple unit of Chevrel structure is Mo_6T_8 (T = S, Se, and Te) blocks, which is separated by three different cation locations and two of them can store the intercalated Mg²⁺ ions in different coordination environments.^[11,43] The successful insertion of Mg²⁺ ions are benefited from the unique structure, and the changes of electron density can be easily compensated when the divalent Mg²⁺ is introduced in this structure.^[44-46] In the charging process, Mg trapping occurs due to the S surroundings and some researchers proposed the substitution of Se to S to avoid the trapping.^[11,47] Other types of CP compounds ($M_xMo_6T_8$, M = metal, T = S, Se) have exhibited similar kinetics and reversible Mg2+ intercalation/extraction when used as Mg host cathodes.[48-51] The CP compounds are promising cathode candidates, however, the low energy density and complex synthesis processes have hampered their commercial applications.^[34,44,47,52,53]

In recent years, many other compounds were also explored as the cathode materials of RMBs accompanied with optimization strategies. The transition metal oxides of V₂O₅,^[54,55] MoO₃,^[56-60] MnO2,^[61] and the Prussian blue analog of Na0,69Fe2(CN)6,^[62] K_{0.86}Ni[Fe(CN)₆]_{0.954}(H₂O)_{0.766}^[63] were specifically introduced as high voltage cathode materials for RMBs. The main problems of transition metal oxides and Prussian blue analog are sluggish electrode kinetics and the incompatibility with electrolytes where Mg is reversibly deposited/stripped.^[34,64,65] Most of the electrochemical tests were performed in three-electrode setups where the performance of Mg anode is overlooked. On the other hand, a number of transition metal chalcogenides (TiS₂,^[66,67] MoS₂,^[68,69] CuS,^[70,71] TiSe₂,^[72] WSe₂,^[73,74] and so on) have been investigated as the electrode of RMBs. The soft anion (sulfur or selenium) lattice contribute greatly to a weaker coulombic attraction between the intercalated Mg²⁺ ions and host structures.^[41] However, the disadvantage of chalcogenides is their low energy densities due to the low working voltage and

discharge capacity, leaving much room for improvement. The transition metal carbides such as Ti₃C₂ MXene^[75] and V₂C MXene^[76] were employed as electrode materials for Mg-storage, and the shortcoming of them is also the low energy density.[77] Many polyanion materials were introduced as RMBs cathodes, like MgFePO₄F,^[78] Mg_{0.5}Ti₂(PO₄)₃,^[79] and Na₃V₂(PO₄)₃.^[80] The intrinsic problem of polyanion materials is the poor electronic conductivity. Many works have been carried out to improve the conductivity of polyanion materials and further improve the Mg-storage performance. Several organic materials were also used for Mg-storage, such as 3,4,9,10-perylenetetracarboxylic dianhydride,^[81] 2,5-dimethoxy-1,4-benzoquinone,^[82] and anthraquinonyl-based polymers.^[83] Nevertheless, they suffer from either low specific capacity even at low current densities, or fast capacity fading during cycling.^[3,83] In terms of the anodes, Mg metal is an ideal candidate and has been the most commonly used anode in RMBs. Some groups have also conducted the optimization of Mg metal by minimizing the particle size to achieve better performance.^[33] Other anodes such as nanostructured Sn,^[84,85] SnSb alloys,^[86,87] Bi,^[88–90] Bi-based composite,^[91] and size-controlled Li₄Ti₅O₁₂^[92] were also reported.

All these reported electrode materials are far from practical applications due to the low voltage, specific capacity, and especially the sluggish Mg²⁺ kinetics.^[93,94] CP compounds and transition metal chalcogenides possess more favorable Mg²⁺ intercalation/deintercalation kinetics, but exhibit low energy densities. Most of other cathodes are presented in a threeelectrode cell system with very low current densities. For RMBs, low energy density is a significant and fundamental issue, especially for the full Mg cell system. Various innovative methods were proposed to overcome the remaining challenges. With a focus on the modification strategies for developing RMBs, we present the typical optimization approaches and the representative materials in the literature (**Figure 1** and **Table 2**), especially on the optimization of electrodes.

2. Optimization Strategies

In most cases, the poor electronic and ionic conductivity are intrinsic problems which strongly impede the realization of excellent performance, especially at high rates. Many approaches were employed to enhance the electrical conductivity and Mg²⁺ diffusivity to increase discharge capacity and rate performance. At the crystal structure level, optimization strategies such as doping ions, introducing vacancy defects, variation in the crystal form, and expanding the interlayer distance have been adopted to improve the electrochemical activity and obtain enhanced Mg-storage performance.^[95-97] To modify the divalent Mg²⁺ ions, water molecules are introduced to shield the strong polarizing nature and accelerate the intercalation/deintercalation kinetics of Mg2+.[34,98-100] The traditional methods of nanostructure construction and fabrication with carbon are widely used to shorten the Mg²⁺ transport route and optimize the conductivity of host materials, respectively. Recently, the newly developed strategy about the modification of electrode-electrolyte interface can tackle the impermeable passivation layers on Mg anode in conventional nonaqueous electrolytes. All these strategies are effective for some specific



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Figure 1. Energy densities and the corresponding modification strategies of the representative electrode materials.

host materials. In this review, the comprehensive knowledge of these optimization strategies and representative examples are provided.

2.1. Doping lons

 Mo_6T_8 with CP structure is one of the very few cathodes which are compatible with most of the present electrolytes. Figure 2a shows the crystal structure of CP, which is composed of Mo_6T_8 blocks. Inside each Mo₆T₈ unit, the molybdenum atoms form an octahedron on the cube faces and T anions take up the cor- $\operatorname{ners}^{[48,101,102]}$ In this way, three types of intercalation locations are provided. However, just the cavity 1 (has a large distance from Mo atom) and 2 (share faces and edges with Mo₆T₈ unit) can accommodate metal ions because the cavity 3 is locked by the severe electrostatic repulsions of Mo atoms. Benefited from this unique structure, about two Mg²⁺ ions can be intercalated into each formula unit.^[103] Moreover, the micro-sized Mo₆S₈ also can deliver outstanding Mg ions storage performance when used as practical cathode material for RMBs.^[40,104] Figure 2b shows the voltage profile with the intercalation of Mg²⁺ into Mo₆S₈. Two stages can be observed corresponding to two Mg²⁺ ions insertion. The first stage located on voltage plateau of about 1.4 V reflects the insertion of the first Mg²⁺ ion, which occupies the cavity 1 in the inner sites. The second stage located on voltage plateau of about 1.1 V exhibits the insertion of the second Mg²⁺ ion, which occupies the cavity 2 in the outer sites. Mitelman et al. extensively investigated the diffusion of Mg²⁺ in the crystal structure of Mg_xMo₆S₈.^[47] They gave the detailed theoretical evidence of Mg²⁺ trapping mechanism in the Mo₆S₈ and demonstrated the excellent reversibility of Mg²⁺ intercalation/deintercalation process with the substitution of Se to S. Before cavity 2 is filled, the inserted Mg²⁺ has an influence on the surrounded cation sites and causes a lower barrier for Mg²⁺ hop in the inner ring, and resulted in the easily trapped environment, especially in the existence of sulfide. In the charging process, Mg₂Mo₆S₈ is easily transformed to MgMo₆S₈ even at room temperature, however, the trapped Mg²⁺ in MgMo₆S₈ is

difficult to realize the extraction and only part of the them can be extracted even at elevated temperatures.^[104] The sluggish Mgextraction kinetics can be promoted through the replacement of small amount of Se to S, which will affect the crystal structure through providing a lower activation barrier, and thereby release some of the trapped Mg^{2+} .^[105,106] Besides, the Se²⁻ ion has a larger atomic radius than S²⁻ ion, which will increase lattice constants of the intercalation compounds and improve the ion movement.^[107] In this respect, the $Mo_6S_{8-x}Se_x$ host provides faster kinetics of Mg²⁺ compared with Mo₆S₈ in the charging process and reaches the theoretical capacity even at room temperature. Furthermore, Aurbach et al. also revealed the Cu (left in synthesis process) in Cu_vMo₆S₈ can alleviate the Mg²⁺ trapping in the binary phase of Mo₆S₈.^[108] With the slow scan rate cyclic voltammetry test combined with theoretical analysis, they concluded that the unique coupling between Mg²⁺ intercalation and Cu extrusion/reinsertion process occurred, leading to the various phases of Mg_xCu_yMo₆S₈. The new intercalation mechanism realizes the unusual high columbic efficiency of 100% without charge trapping limitations. Woo et al. also conducted experiments by doping Cu into Mo₆S₈ to enhance the electrochemical behavior.^[109] They studied the effect of doping with various amount of Cu element and found that the best doping amount is 1.3 molar Cu per formula unit, which gives much closer to the theoretical capacity. The existence of Cu will introduce Cu-Mg repulsion effect and result in improved reversible capacity. Apart from Chevrel structure, Cui et al. introduced Cu⁺ as the charge carrier to decouple Mg²⁺ and improve the electrochemical reaction.^[110] The Cu⁺ is generated from Cu₃Se₂ during conditioning process, which participated in the Cu₃Se₂ reaction as a charge carrier (reversible Cu⁺/Cu redox reaction) to accelerate the magnesiation of Cu_{2-x}Se. Benefited from the positive effect of Cu⁺, the copper selenide cathode exhibits high reversible capacity and improved rate capability. They also reported Cu metal foam effects on trapping polysulfide (polyselenide) in Mg-SeS₂ system, in which Cu was used as the interlayer between the SeS2 cathode and separator to promote reaction kinetics.^[111] Mai et al. demonstrated that Ni_{0.75}Fe_{0.25}Se₂ exhibits more active sites and improved Mg²⁺ diffusion kinetics

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Optimization strategy	Cathode anode	Electrolyte	Highest capacity [mAh g ⁻¹]	Average discharge voltage [V vs Mg ²⁺ /Mg]	Cycling stability [current density, cycle numbers, initial capacity/cycled capacity]	Ref.
Doping ions	Cu₃Se₂∥Mg	ВСМ	310	≈0.9	100 mA g ⁻¹ , 500 cycles, 310/250 mAh g ⁻¹	[110]
	SeS ₂ /CMK3 Mg	OMBB	1020	≈]	1125 mA g ⁻¹ , 230 cycles, ≈690/696 mAh g ⁻¹	[111]
	Ni _{0.75} Fe _{0.25} Se ₂ Mg	0.25 м Mg(AlCl ₂ EtBu) ₂ in THF	190	≈0.9	20 mA g ⁻¹ , 500 cycles, 190/148 mAh g ⁻¹	[112]
	Ti _{0.78-0.22} O _{1.12} F _{0.40} (OH) _{0.48} Mg	$(PhMgCl)_2-AlCl_3$ in THF	165	≈0.5	20 mA g ⁻¹ , 3 cycles, 165/155 mAh g ⁻¹	[114]
	eta -Cu $_2$ Se \parallel Mg	0.25 м Mg(AlCl ₂ EtBu) ₂ in THF	230	≈0.9	5 mA g ⁻¹ , 4 cycles, ≈260/≈220 mAh g ⁻¹	[117]
Variation in the crystal form $TiS_2 \parallel l$ $Ti_2S_4 \parallel$ $\alpha \cdot V_2O_5 \parallel$ $\zeta \cdot V_2O_5 \parallel$ $\lambda \cdot MnO_2 \parallel g$	TiS₂∥Mg	0.4 $\mbox{\sc m}$ (PhMgCl)_2–AlCl_3 in THF	270	≈0.6	24 mA g ⁻¹ , 40 cycles, ≈118/115 mAh g ⁻¹	[126]
	Ti₂S₄ ∥ Mg	0.4 м (PhMgCl) ₂ –AlCl ₃ in THF or G4	200	≈1.2	24 mA g ⁻¹ , 40 cycles, ≈188/140 mAh g ⁻¹	[41]
	<i>α</i> -V ₂ O ₅ ∥ AC	0.5 м Mg(ClO ₄) ₂ in ACN	180	≈2.5	–, 15 cycles, 180/150 mAh g ⁻¹	[60]
	<i>ζ</i> -V ₂ O ₅ AC	0.2 м Mg(TFSI) ₂ in PC	140	1.65	308 mA g ⁻¹ , 100 cycles, 140/90 mAh g ⁻¹	[134]
	<i>α</i> -MnO ₂ ∥ Mg	0.2 м Mg-HMDS in THF	280	≈].4	9 mA g ⁻¹ , 30 cycles, 280/≈83 mAh g ⁻¹	[142]
	λ -MnO ₂ graphite	0.5 м $MgCl_2$ in H_2O	545.6	≈0.5	136 mA g ⁻¹ , 300 cycles, ≈330/155.6 mAh g ⁻¹	[147]
	TiO ₂ anatase Mg	0.4 м (PhMgCl) ₂ –AlCl ₃ in THF	67	≈0.8	6.7 mA g ⁻¹ , 5 cycles, 67/≈55 mAh g ⁻¹	[123]
Charge shielding	Mg _{0.15} MnO ₂ · 0.9H ₂ O/C ∥ AC	0.5 м Mg(ClO ₄) ₂ + H ₂ O	150	≈2.4	500 mA g ⁻¹ , 160 cycles, 150/≈45 mAh g ⁻¹	[139]
	V ₂ O ₅ ·1.42H ₂ O @rGO ∥ AC	0.5 м Mg(TFSI) ₂ in can	330	≈2.1	1000 mA g ⁻¹ , 200 cycles, ≈120/≈97 mAh g ⁻¹	[164]
Charge shielding	$VOPO_4 \cdot 2H_2O \parallel AC$	0.1 м Mg(ClO ₄) ₂ in PC + H ₂ O	91.7	≈0.5	5 mA g ⁻¹ , 50 cycles, ≈89/≈91.7 mAh g ⁻¹	[171]
	$Mg_{0.3}V_2O_5\cdot1.1H_2O \parallel AC$	0.3 м Mg(TFSI) ₂ in can	176	≈2.2	100 mA g ⁻¹ , 500 cycles, 164/164 mAh g ⁻¹	[173]
	$Mn_{0.04}V_2O_5 \cdot 1.17H_2O \parallel AC$	0.3 м Mg(TFSI) ₂ in can	145	≈2.0	50 mA g ⁻¹ , 100 cycles, ≈145/≈145 mAh g ⁻¹	[174]
	Birnessite MnO ₂ Mg	0.5 м Mg(ClO ₄) ₂ in ACN + H ₂ O	231.1	2.8	500 mA g ⁻¹ , 500 cycles, ≈164/128.5 mAh g ⁻¹	[167]
Organic molecules preintercalation	exTiS₂ ∥ Mg	0.25 м (PhMgCl) ₂ –AlCl ₃ + 0.2 м PY14Cl in THF	239	≈0.6	240 mA g ⁻¹ , 400 cycles, ≈160/≈128 mAh g ⁻¹	[186]
	PA-VOPO ₄ Mg	0.25 м (PhMgCl) ₂ -AlCl ₃ in THF	310	≈0.8	100 mA g ⁻¹ , 500 cycles, ≈280/192 mAh g ⁻¹	[181]
	Expanded $VS_2 \parallel Mg$	Mg(HMDS) ₂ –4MgCl ₂ /2THF– PP ₁₄ TFSI	249	≈0.7	100 mA g ⁻¹ , 100 cycles, 116/191.1 mAh g ⁻¹	[182]
	VS_2 nanosheet \parallel Mg	0.4 м (PhMgCl) ₂ –AlCl ₃ + 0.2 M PY ₁₄ Cl in THF	350	≈0.8	1000 mA g ⁻¹ , 300 cycles, ≈260/200 mAh g ⁻¹	[188]
	Expanded VS₄@rGO∥ Mg	0.25 м (PhMgCl) ₂ –AlCl ₃ + 0.25 м [BMP]Cl in THF	268.3	≈0.8	50 mA g ⁻¹ , 100 cycles, 268.3/147.2 mAh g ⁻¹	[189]
	V ₂ O ₅ -PEO Mg	0.5 м Mg(ClO ₄) ₂ in can	125	≈1.5	10 mA g ⁻¹ , 35 cycles, 125/96 mAh g ⁻¹	[180]

Table 2. Summary of the representative electrode materials in terms of their electrochemical performance after modification.

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Flectrolyte

Table 2. Continued.

Ontimization

strategy			[mAh g ⁻¹]	voltage [V vs Mg ²⁺ /Mg]	density, cycle numbers, initial capacity/cycled capacity]	
	PEO ₂ -MoS ₂ Mg	0.25 м $[Mg_2Cl_3] + [AlPh_2Cl_2]^-$ in THF	75	≈0.5	5 mA g ⁻¹ , 30 cycles, 75/70.5 mAh g ⁻¹	[176]
	CuS-CTAB-2 Mg	0.3 м Mg[B(hfip) ₄] ₂ in DME	477	≈].]	560 mA g ⁻¹ , 1000 cycles, ≈30/111 mAh g ⁻¹	[71]
	Ti ₃ C ₂ T _x /CTAB ∥ Mg	0.4 м (PhMgCl) ₂ –AlCl ₃ in THF	100	≈0.5	50 mA g ⁻¹ , 100 cycles, 100/74 mAh g ⁻¹	[75]
Nanostructure construction	$WSe_2 \parallel Mg$	0.25 м Mg(AlCl ₂ EtBu) ₂ in THF	203	1.6	50 mA g ⁻¹ , 160 cycles, 203/203 mAh g ⁻¹	[74]
	Mn₃O₄ ∥ graphite	0.4 м (PhMgCl) ₂ –AlCl ₃ in THF	190	≈]	308 mA g ⁻¹ , 1000 cycles, ≈70/≈65 mAh g ⁻¹	[207]
Nanostructure construction	<i>α</i> -MoO₃ ∥ AC	0.1 м Mg(TFSI) ₂ in can	220	1.8	–, 10 cycles, ≈170/210 mAh g ⁻¹	[60]
	CoS Mg	0.25 м Mg(AlCl ₂ EtBu) ₂ in THF	125.3	≈1.0	50 mA g ⁻¹ , 60 cycles, 125.3/105.9 mAh g ⁻¹	[208]
	MgCoSiO₄ ∥ Mg	0.25 м Mg(AlCl ₂ EtBu) ₂ in THF	167	≈1.65	30.57 mA g ⁻¹ , 7 cycles, ≈124/≈163 mAh g ⁻¹	[210]
	Bi Mg	$Mg(BH_4)_2$ and $LiBH_4$ in THF	335	≈0.15	770 mA g ⁻¹ , 150 cycles, ≈330/≈307 mAh g ⁻¹	[89]
	Mo ₆ S ₈ ∥ Mg	0.4 м (PhMgCl) ₂ –AlCl ₃ in THF	123	≈].]	64 mA g ^{−1} , 500 cycles, ≈104/89 mAh g ^{−1}	[46]
	$G-MoS_2 \parallel Mg$	$Mg(AlCl_3Bu)_2$ in THF	170	≈1.8	20 mA g ⁻¹ , 50 cycles, 170/161.5 mAh g ⁻¹	[68]
Decoration with carbon	$MoS_2/C \parallel Mg$	0.4 м (PhMgCl) ₂ –AlCl ₃ in THF	213	≈0.4	50 mA g ⁻¹ , 50 cycles, 213/84.3 mAh g ⁻¹	[221]
	$Na_3V_2(PO_4)_3/C \parallel AC$	0.3 м Mg(TFSI) ₂ in MeCN	88.8	2.5	20 mA g ⁻¹ , 100 cycles, 88.8/77 mAh g ⁻¹	[80]
	MWNT/C/Mg _{1.03} Mn _{0.97} SiO ₄ Mg	0.25 м Mg(AlCl ₂ EtBu) ₂ in THF	303.6	≈1.55	63 mA g ⁻¹ , 6 cycles, ≈155/300 mAh g ⁻¹	[222]
	GO/V ₂ O ₅ Mg	0.25 м Mg(AlCl ₂ EtBu) ₂ in THF	178	≈1.25	60 mA g ⁻¹ , 20 cycles, 178/140 mAh g ⁻¹	[228]
Electrode-electrolyte interface optimization	S Mg	0.5 м Mg(TFSI) ₂ in DME	1165	≈1.5	168 mA g ⁻¹ , 10 cycles, ≈1165/≈548 mAh g ⁻¹	[231]
	$TiS_2 \parallel Mg$	0.4 м GeCl₄ and 0.5 м Mg(TFSI)₂ in DME	147	0.5	10 mA g ⁻¹ , 30 cycles, ≈147/≈86 mAh g ⁻¹	[232]
	$Ti_3C_2 \parallel Mg$	0.4 м GeCl₄ and 0.5 м Mg(TFSI)₂ in DME	162	≈0.4	50 mA g ⁻¹ , 30 cycles, ≈162/≈83 mAh g ⁻¹	[232]
	V₂O₅ ∥ Mg	0.5 м Mg(TFSI) ₂ /PC + H ₂ O	140	≈].]	29.4 mA g ⁻¹ , 40 cycles, ≈130/≈95 mAh g ⁻¹	[233]

Highest capacity

as well as electron transfer compared with NiSe₂.^[112] With the existence of Fe, Ni_{0.75}Fe_{0.25}Se₂ displays much better Mg-storage performance. Zhu et al. also investigated the appropriate molar ratio of iron/manganese in MgFe_xMn_{2-x}O₄ on the Mg-storage performance.^[113] With the varying of *x* (0.67, 1, 1.33, and 1.6), the authors concluded that MgFe_{1.33}Mn_{0.67}O₄ can effectively prevent the hydrogen/oxygen evolution during charging–discharging and has the fastest Mg²⁺ diffusion kinetics. As a result, MgFe_{1.33}Mn_{0.67}O₄ displays the best electrochemical performance, such as long-cycling performance (88.3 mAh g⁻¹)

after 1000 cycles) and rate performance (about 60 mAh g^{-1} at the current density of 2 A $g^{-1}).$

In another case, through the doping of anions to introduce vacancies as active sites is also an effective method. Damien et al. conducted the experiments of introducing titanium vacancies into TiO₂. Through the doping of monovalent anions (F^- and OH⁻), greatly enhanced capacities were achieved compared to the pure TiO₂.^[114] First, they used the density functional theory (DFT) to calculate the intercalation mechanism of F-doped TiO₂ and anatase TiO₂. With the monovalent doping of F⁻,



Ref

Cycling stability (current

Average discharge







Figure 2. a) The crystal structure of Mo_6T_8 . Reproduced with permission.^[48] Copyright 2006, American Chemical Society. b) The observed voltage curve and the insertion mechanism about two stages of Mo_6S_8 with the Mg insertion processes. Reproduced with permission.^[192] Copyright 2013, The Royal Society of Chemistry.

a great quantity of charge-compensating Ti vacancies will be introduced into the anatase TiO₂. The V_{Ti} sites (F-doped TiO₂) have much lower intercalation energy (-1.02 eV) for Mg²⁺ compared with that of anatase TiO₂ (-3.03 eV) and are promising for

the intercalation of Mg²⁺. To test the hypothesis, the authors synthesized the F⁻- and OH⁻-doped anatase TiO₂ to substitute part of the O²⁻. With 22% cationic vacancies, the sample is predicted with the formula of $Ti_{0.78-0.22}O_{1.12}F_{0.40}(OH)_{0.48}$. Figure 3a–d



Figure 3. a) High-resolution Cs-corrected TEM image of $Ti_{0.78-0.22}O_{1.12}F_{0.40}(OH)_{0.48}$ nanoparticles. b) The atomic-resolution image oriented along the [001] axis. c) Colored high-resolution transmission electron microscopy (HRTEM) image along a line of atoms. d) Calculated random HRTEM image of the structure. e,f) Charge/discharge profiles of TiO_2 and the doped TiO_2 at 0.02 A g⁻¹. g) Mg²⁺ diffusion mechanism in the two structures. h) The change of unit cell parameters and volume. i) The occupancy of titanium vacancy site (4a) and octahedral interstitial site (4b) with Mg²⁺. Reproduced with permission.^[114] Copyright 2017, Springer Nature.

shows the aberration-corrected TEM images which give direct observation of the Ti vacancies. As displayed in Figure 3b, the variation of atomic column intensity demonstrates the existence of vacancies, and the result is also identified through the colored image (Figure 3c).^[115] The calculated HRTEM image of Ti atomic occupancy with random distribution (Figure 3d) is corresponding well with the experimental image. The Mgstorage performance was tested via a three-electrode cell with Mg as the counter and reference electrode in APC electrolyte (Figure 3e,f). Ti_{0.78-0.22}O_{1.12}F_{0.40}(OH)_{0.48} delivers much higher reversible capacity (155 mAh g⁻¹) when compared with the pure TiO₂ (25 mAh g⁻¹). The galvanostatic intermittent titration technique (GITT) results also indicate higher Mg²⁺ diffusion coefficient (Figure 3g), which is comparable to that of Li⁺ diffusion. The authors conducted the pair distribution function (PDF) originated from the Fourier transformation of high-energy X-ray to give structural information about diffuse and Bragg intensities during magnesiation/de-magnesiation. Figure 3h shows the relative change of lattice constants and indicates little volume variation (less than 0.6%). Through the comparison of titanium vacancies and interstitial sites as hosting sites for the intercalated Mg²⁺ (Figure 3i), the authors concluded that the occupancy of Mg²⁺ ions in titanium vacancies are more promising during the whole insertion process. As a further step in the investigation of defects, Taniguchi et al. reported that the difference between anion sublattice structures can greatly affect the Mg-storage performance of copper sulfides $(Cu_{2-x}^{-}S)$.^[70,116,117] These works demonstrate a valuable approach to unlock the electrochemical activity in electrode materials for easy intercalation of Mg²⁺.

2.2. Variation in the Crystal Form

In terms of a given electrode material, the specific capacity and charge/discharge curves are highly related to the crystal structure, especially the crystal form. Take the VO₂ for example, VO₂(B) demonstrates excellent Li^[118–121] and Na^[122] storage performance, however, other structures of VO₂ are rarely reported as electrode material for energy storage systems. When the selected material has several crystal forms, the control of crystal form is also an important factor on the Mg-storage performance.^[123] The intrinsic phase structures have significant influence on ions diffusion kinetics and migration barriers.^[124,125] In this section, we will elaborate the typical comparison examples of different crystal structures about TiS₂, V₂O₅, and MoO₂.

2.2.1. TiS₂

The sulfide-based electrode, TiS_2 was first demonstrated for Mg-storage in Mg(ClO₄)₂/ACN electrolyte versus Mg anode by Tao et al. in 2004.^[67] However, the authors just investigated the first discharge processes at various current densities due to the passivation of Mg metal anode, which will impede the Mg²⁺ transport during subsequent cycles. To test the electrochemical performance of layered TiS₂ in Mg-full cell, Aurbach et al. conducted the experiments in Mg(AlCl₂BuEt)₂/THF electrolyte.^[66]

charge/discharge process (about 90 mAh g⁻¹) and decays rapidly at the second cycle. In recent years, Nazar et al. studied the electrochemical performance of layered TiS₂ and thiospinel Ti₂S₄ as the cathode for Mg batteries in APC electrolyte at 60 °C.^[41,126] Figure 4a,d shows the framework structure as well as the tetrahedral site and octahedral site of layered TiS₂ and thiospinel Ti₂S₄.^[127] When used as the cathode of Mg battery in APC electrolyte versus the Mg metal anode, the thiospinel Ti₂S₄ has a higher discharge capacity and average operating voltage than that of the layered TiS₂ at various rates (Figure 4b,e). In addition, the thiospinel Ti₂S₄ exhibits much more stable capacity (140 mAh g^{-1}) compared to that of layered TiS₂ (115 mAh g^{-1}) within 40 charge/discharge cycles (Figure 4c,f). The improved electrochemical performance is related to the lower Mg migration barriers of thiospinel Ti₂S₄ (about 1200 meV) than that of layered TiS₂ (about 800 meV).^[43,128] The authors also investigated the Mg-storage mechanism and confirmed the reversible intercalation of Mg²⁺ into layered TiS₂ and thiospinel Ti₂S₄.

2.2.2. V₂O₅

 $\rm V_2O_5$ is a most extensively investigated oxide material for Li, Na, Zn, and Mg-ions insertion in the literature as well as various modification strategies. It is well known as a high-capacity cathode. The abundance of V–O phase diagram shows the possibility of various metastable polymorphs which can provide great potential for the intercalation of Mg²⁺ ions.^[129,130] Among them, the orthorhombic phase of V₂O₅ is thermodynamically stable and can be easily obtained from the natural minerals.

The layered α -V₂O₅ was first compositionally isolated in 1868, and attracted much interest from researchers since the first work on the application as cathode of LIBs reported by Whittingham and co-workers.^[131] Figure 5a presents the structure of α -V₂O₅. It possesses many advantages to accommodate the inserted cations, such as a large interlayer spacing, the easily approached V-O couples and abundance of insertion sites. Pereira-Ramos et al. first demonstrated the intercalation of Mg²⁺ in V₂O₅ at elevated temperature of 150 °C from Mg(ClO₄)₂ dissolved in molten dimethylsulfone or sulfolane.^[54] Aurbach et al. used the vacuum deposition method to obtain the thin film V₂O₅ electrode and gave the detailed exploration of reversible reaction in nonaqueous electrolyte at room temperature.^[60] With the activated carbon (AC) cloth as reference and counter electrodes, the V2O5 exhibits a high capacity of 150 mAh g^{-1} (with the formation of Mg_{0.5}V₂O₅) in the electrolyte of 0.1 м Mg(TFSI)₂/ACN. Energy dispersive X-ray spectroscopy (EDS) gives further evidence of Mg-insertion into V₂O₅. They also demonstrated the reversible structural changes of V2O5 during the Mg ions insertion/extraction processes through X-ray diffraction (XRD) and Raman. To achieve better electrochemical performance, some researchers turned to the $\delta V_2 O_5$ and $\zeta V_2 O_5$. Figure 5b,c shows the structure of $\delta V_2 O_5$, which is obtained through the rotation of V2O5 layers along a-direction by a/2 of α -V₂O₅. Gautam et al. calculated Mg–V₂O₅ intercalation phase diagram and combined the first-principles calculations to extensively investigate the Mg²⁺ intercalation properties in orthorhombic α -V₂O₅ and δ -V₂O₅ phases.^[130] Compared with α -V₂O₅, the δ -V₂O₅ gets a moderate increase www.advancedsciencenews.com

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Figure 4. a) Crystal structure, tetrahedral and octahedral sites of layered TiS_2 . b) The discharge–charge profiles of layered TiS_2 at various rates in APC/tetraglyme. c) Capacity and coulombic efficiency of layered TiS_2 at C/10 in APC/tetraglyme. Reproduced with permission.^[126] Copyright 2016, The American Chemistry Society. d) Crystal structure, tetrahedral and octahedral sites of thiospinel MgTiS₂. Reproduced with permission.^[127] Copyright 2018, The American Chemistry Society. e) The discharge–charge curves of thiospinel Ti_2S_4 at different current densities in APC/THF. f) Cycling performance of thiospinel Ti_2S_4 at C/10 in APC/tetraglyme. Reproduced with permission.^[41] Copyright 2016, The Royal Society of Chemistry.

in the voltage, and the Mg-mobility is much faster, leading to the insertion of 0.66 Mg²⁺ in per formula δ -V₂O₅. They also concluded that the original host structure has the ability to be stable or metastable even with higher Mg concentration. However, an experimental proof directly revealed a much lower Mg insertion level of around 0.17.[60,132] Several studies also identified that the excess capacity was caused by the intercalation of proton cations.^[133] Banerjee et al. obtained a metastable ζ -V₂O₅ through the topochemical leaching of β phase vanadium oxide bronzes (tunnel structure, Figure 6a).^[134] After leaching, the one dimensional tunnel can be retained. The stabilized V-O framework can facilitate the kinetics of inserted ions and mitigate charge localizations. In this way, fast Mg²⁺ diffusion and polarons stabilization are realized (Figure 6b).^[130,135–137] With regard to the electrochemical performance, up to 0.33 Mg²⁺ can be inserted into per formula V_2O_5 with the average operating voltage of about 1.65 V versus Mg²⁺/Mg. It also exhibits highly

reversible intercalation of Mg^{2+} at various conditions, such as high voltage, nonaqueous, and aqueous electrolytes.

2.2.3. MnO₂

On the way to search for high-performance host materials, MnO_2 has been investigated as electrode material for various battery systems (Li, Na, Mg, Zn) and electronic supercapacitors benefited from the properties of low-cost, non-toxicity and high energy density. It possesses several different structures for the various arrangement of MnO_6 octahedra unit (shared by vertices and edges), such as layered structure, 1D, 2D, and 3D tunnel-type structures.^[138,139] As is known to all, the existed layer spacing in layered structure and the large tunnels can accommodate the inserted ions, offering much possibility for divalent Mg²⁺. As a result, a number of MnO_2 polymorphs



Figure 5. a) α and b) δ of orthorhombic V₂O₅ are displayed along the *c*-axis and c) along the *a*-axis. Reproduced with permission.^[130] Copyright 2015, The American Chemistry Society.







Figure 6. a) The topochemical leaching of vanadium oxide bronze with HCl to obtain the ζ -V₂O₅. b) The stabilized structure with the pseudosquare-pyramidal β site to accommodate inserted Mg²⁺. Reproduced with permission.^[134] Copyright 2018, Elsevier.

have been introduced as the cathode of RMBs. According to the literature, most researchers focused on the α - and λ -MnO₂.

Figure 7a shows the structure of α -MnO₂ with equivalent *a* and *b* axes which is a promising host material of Mg²⁺ ions. However, the reversible Mg²⁺ intercalation is unable to realize. In the initial discharging process, the high specific capacity of about 280 mAh g⁻¹ can be obtained with the operation voltage of 2.8 V versus Mg²⁺/Mg, but it decays rapidly to below 50 mAh g⁻¹ within 10 cycles.^[140,141] The rapid capacity loss is due to the decrease of the crystallinity of α -MnO₂. In order to perform a suitable optimization on α -MnO₂ cathode, extensive investigations on the initial discharge process has been conducted, including experimental and theoretical works. Matsui et al. pointed out that the irreversible capacity decay is resulted from the incomplete recovery of edge position of electrodes at

different states, which was confirmed through the X-ray photoelectron spectroscopy (XPS) and Mn K-edge X-ray absorption near edge structure (XANES) spectra.^[142] They also performed the extended X-ray absorption fine structure (EXAFS) analysis and revealed the unrecoverable collapse of some channel structures. Arthur et al. utilized the microscopic and spectroscopic techniques to determine the Mg-storage mechanism of α -MnO₂ is different from that of Li.^[143] They proposed a conversion reaction in magnesiation process for the unstable Mg_{0.5}MnO₂ (Figure 7b, initial product for the intercalation of Mg²⁺), i.e., the amorphous mixture of MgO, Mn₂O₃, and MnO are generated to form a core–shell product in the end. They concluded that the capacity loss can be attributed to the irreversible phase transformation reaction during magnesiation. Ling et al. revealed a more complicated mechanism in α -MnO₂ with



Figure 7. a) The structure of α -MnO₂. b) The structure of α -Mg_{0.5}MnO₂ with the intercalation of two Mg²⁺ in the same cavity. c) Two possible reaction routes. Reproduced with permission.^[140] Copyright 2018, Elsevier.





Figure 8. a) λ -MnO₂ crystal structure with the A atoms occupy the tetrahedral sites and Mn atoms occupy the octahedral sites. Reproduced with permission.^[145] Copyright 2015, The Royal Society of Chemistry. b) The crystal structure of LiMn₂O₄. c) λ -MnO₂ after the removal of Li⁺ d) MgMn₂O₄ after the intercalation of Mg²⁺. Reproduced with permission.^[147] Copyright 2014, Elsevier.

the intercalation of Mg^{2+,[140]} The authors used the DFT calculations to analyze the magnesiation mechanism (Figure 7c), and gave the detailed comparison of intercalation path (partial intercalation at first and then with a conversion reaction) and conversion path (direct conversion). The results demonstrated the feasibility of conversion routes in the thermodynamic view, in consistent with the reported experimental observation. Considering the troublesome reversibility of Mg intercalation, the α -MnO₂ cannot be used as a practical RMBs cathode at present.

Another type of MnO₂ polymorphs, λ -MnO₂, is an excellent alternative for Mg-cathodes owing to the high voltage, high discharge capacity and good structural stability. It can be obtained from the spinel-type structure of AMn₂O₄ (A represents intercalation ion). A ions and Mn ions located at the tetrahedral sites and the octahedral sites coordinated by oxygen (Figure 8a).^[144] Persson et al. used the first-principles calculations to extensively investigate the potential use of spinel structure in RMBs and concluded that Mn_2O_4 (one number of the λ -MnO₂ family) is a superior alternative.^[145] Mn₂O₄ displays a high theoretical working voltage of about 2.9 V with the high discharge capacity of 308 mAh g⁻¹. Munichandraiah et al. reported the conversion of LiMn₂O₄ to MgMn₂O₄ through replacing of Li⁺ by Mg²⁺ in the aqueous Mg(NO₃)₂ electrolyte.^[146] They conducted extensive analysis on the cyclic voltammetry curves of LiMn₂O₄ electrode in LiNO₃ and Mg(NO₃)₂ electrolytes. The results suggest the deintercalation of Li+ ions occurred on anodic sweep (0.71 and 0.85 V), leading to the formation of λ -MnO₂ and Mg²⁺ ions are inserted on the cathodic sweep, thus results in the formation of MgMn₂O₄. Further studies about the cycled

electrodes were conducted through inductively coupled plasma (ICP), XRD, and XPS investigations, which demonstrated the conversion of LiMn₂O₄ to MgMn₂O₄. The obtained spinel-MgMn₂O₄ displays the discharge capacity of \approx 35 mAh g⁻¹ (≈11% of the theoretical capacity) over 20 cycles. Cao et al. also studied the reaction process about the intercalation of Mg²⁺ into λ -MnO₂.^[147] They used an acid leaching method to remove the Li⁺ from LiMn₂O₄, and the main cubical structure is remained (Figure 8b,c). The intercalated Mg²⁺ ions occupy the octahedral sites (Figure 8d) with the valence change of Mn to coordinate the divalent charge. When employed as the cathode material of RMBs, it demonstrates a high discharge capacity of about 545 mAh g⁻¹ in aqueous MgCl₂ electrolyte, the obtained capacity is much higher than its theoretical capacity (may be stem from the higher voltage than water electrolysis, resulting in proton insertion). Similarly, Alcántara et al. used the electrochemical route to remove Mg²⁺ from MgMn₂O₄ in aqueous Mg(NO₃)₂ electrolyte to form λ -MnO₂ and studied its electrochemical performance as Mg-cathode in aqueous/nonaqueous electrolytes.^[148] In the 3 м Mg(NO₃)₂ aqueous electrolyte, it delivers the high specific capacity of about 150 mAh g⁻¹ in the initial cycle, however, the capacity slowly decreases to about 100 mAh g^{-1} within 20 cycles. In the nonaqueous electrolyte of 0.5 M Mg(ClO₄)₂/ACN electrolyte, with the Pt as reference electrode and V₂O₅ as the negative electrode, the reversible capacity based on the mass of MgMn₂O₄ is preserved at about 120 mAh g⁻¹ during 24 charge/discharge cycles. However, there are not enough structural characterizations to confirm the extraction of Mg from MgMn₂O₄.

The strategy of variation in the crystal form most focus on the TiS₂, V₂O₅, and MnO₂, for which have various structures and demonstrate reversible intercalation of Mg²⁺ ions. By changing the crystal structure, the Mg-storage mechanism and reversible capacity can be affected. The examples above demonstrate the importance of crystal form selection. Thus, the exploration of a most suitable crystal structure that can exhibit faster diffusion kinetics, higher specific capacity and operating voltage is of great importance.

2.3. Charge Shielding

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The divalent charge of Mg²⁺ ions resulted in a strong electrostatic interaction between them and the host cathodes, which caused sluggish kinetics in the same host when compared with Li⁺ and Na⁺. For this reason, Mg²⁺ insertion is seriously impeded and results in sluggish kinetics in many cathodes which are usually used in LIBs. To promote the intercalation kinetics of Mg²⁺ associated with the strong polarizing nature, a number of approaches have been implemented to alleviate the slow diffusion kinetics of Mg²⁺.^[149] Among the various strategies, introducing a small amounts of highly polar molecules (e.g., H₂O) within the electrolyte (through cointercalation with Mg²⁺) or host lattice (directly introduced in synthesis process) to shield the bivalency of Mg²⁺ ions is an effective way.^[43,150] With the charge screening effect of dipole molecules, the ionic interaction between Mg2+ and hosts can be mitigated, which contribute greatly to the enhancement of Mg transport and intercalation chemistry.^[151] The solvent shielding effect is also a well-known phenomenon in LIBs and NIBs.[152-155] In the following part, we have reviewed the research progress of the charge shielding effect in host structures for RMBs and discussed the influence of introduced polar molecules on the structure and electrochemical performance.

2.3.1. V₂O₅

As early as in 1993, Novák et al. have already discovered that the Mg²⁺ insertion capability into metal oxides and sulfides is largely depending on the ratio of H_2O with Mg^{2+} in $Mg(ClO_4)_2$ contained organic solvents electrolytes.^[55] The specific capacity of V2O5 in several organic solvents with different ratio of Mg(ClO₄)₂/H₂O were studied. With 1 м Mg(ClO₄)₂ and 1 м H₂O dissolved in ACN solution as electrolyte, V₂O₅ demonstrates an improved Mg-storage performance of 170 mAh g⁻¹ at room temperature, but its cycling stability is far from being practical. They conducted some experiments to identify the higher capacity in H₂O contained electrolyte and revealed that water molecules have a solvating effect on Mg²⁺ and then accelerate the insertion kinetics. Zhang et al. conducted the similar experiments on commercial V2O5 with various amount of H2O contained electrolyte of 0.1 M Mg(ClO₄)₂ in propylene carbonate (PC).^[156] The same effect was also realized by using a specific amount of water in electrolyte to improve the discharge capacity and electrochemical performance of V2O5. However, although both of the two works combined theoretical analysis with the fundamental results of XRD, CV, discharge/charge curves to

draw the conclusion, no specific evidence of cointercalation of H_2O with Mg^{2+} was provided, as well as the functional role of water molecules in electrolyte. In these two aspects, a great deal of theoretical and experimental investigations is still needed to give more details.

There are some problems in using the water contained electrolyte to shield the Mg²⁺ as cointercalation species, such as the undesirable reaction of H₂O with Mg metal anode, the big ionic groups of H_2O surrounded Mg^{2+} , and the low intercalation level in some specific hosts.^[34] For all these reasons, it is necessary and theoretically needed to synthesis or search for new structures which have already contained water. More importantly, the crystal water should be stable and will not leach out with the discharge/charge cycling processes in order to avoid the detrimental side effect. V2O5 xerogel has a chemical formula of $V_2O_5 \cdot xH_2O$ and is stacked by $[VO_6]$ octahedron bilayers (Figure 9). The large distance of about 11.5 Å is the closest approach between bilayers and can accommodate the intercalated molecules. While, the bilayer is made up of two $[VO_6]$ octahedron monolayers and the interbilayer spacing is close to 2.9 Å. When the $V_2O_5 \cdot H_2O$ is heated to about 350 °C, the structural H₂O will be cleared away with the irreversible phase transformation of xerogel to orthorhombic phase.^[157] The relatively stable structural water at room temperature in xerogel-V₂O₅ provides much possibility for shielding the divalent Mg²⁺ with low risk of leaching out. Inanura et al. first evaluated the Mg intercalation properties of xerogel-V2O5 via the sealed three-electrode setup with Mg(ClO₄)₂ dissolved in CAN as electrolyte, Mg ribbon as counter electrode, and Ag/AgNO3 as reference electrode.^[158,159] Compared to Li, a higher capacity for Mg insertion is indicated by the comparison of corresponding CV curves. After the initial cathodic sweep by 0.1 mV s⁻¹, the insertion of Mg is about 1.84 mol for per formula V₂O₅ (confirmed by ICP test), which is equivalent to discharge capacity of



Figure 9. The structure of V₂O₅ · nH_2O which is revealed by PDF analysis. The distances and water molecules are shown. Reproduced with permission.^[162] Copyright 2002, American Chemical Society.





Figure 10. The XRF maps of Mg, V and overlay of Mg with V about the sample discharged to 0.02 V. Reproduced with permission.^[160] Copyright 2015, American Chemical Society.

540 mAh g⁻¹. When cycled at a high current, it displays a high discharge capacity in the first charge/discharge cycle, but rapidly decays in the following few cycles. The XRD pattern and FTIR spectra show the similar results with other experimental and theoretical studies which suggested the reversible intercalation of Mg^{2+} .^[160,161] However, the detailed effect of crystal water is not mentioned.

To give more details about the water effect during the cycling, Tepavcevic et al. synthesized a unique bilayered V₂O₅ with large interlayer spacing and extensively investigated its influence on Mg intercalation properties.^[160] First, the authors removed the absorbed and hydrogen bonded water through annealing the samples at about 120 °C in vacuum to obtain a stoichiometry product of $V_2O_5 \cdot 0.6H_2O$. The decrease of weakly bounded water results in the smaller interlayer distance from 13.5 to 12 Å.^[162] The remained structural hydroxyl groups act as a lubricant for the divalent Mg²⁺ and is stable enough in the discharge/charge cycling. Thus, the cathode delivers a high specific capacity of 240 mAh g⁻¹ against the Mg metal anode. The X-ray fluorescence (XRF) images give direct evidence for the Mg insertion into the V₂O₅ sample (Figure 10) and the XANES spectra shows the change of V-oxidation states. The high HRTEM, high-angle annular dark field (HAADF) imaging, scanning transmission microscopy (STEM) were conducted to give more evidence of intercalated Mg and the structural evolution. The interlayer water not only maintains the interlayer spacing to allow the insertion of bigger solvated Mg groups (at least 6 Å) but also accommodates the inserted Mg²⁺ by cointercalation of dipole interactions.^[163] When the xerogel-V₂O₅ was annealed to above 350 °C to get rid of the structural water, the two functions will be reduced and lead to poor electrochemical performance.^[160] XRD, small-angle X-ray scattering (SAXS), and wide-angle X-ray scattering (WAXS) studies gave further investigation of the xerogel-V₂O₅ structure. The results indicate that V atomic surroundings in the bilayers has little change and the only altered is the decreasing of interlayer spacing with the insertion of Mg²⁺, which is consistent well with the reported literature.^[158]

However, the water content in the host is also an important factor. Yao et al. performed a facile reaction followed by

freeze-drying process and successfully synthesized the hydrated vanadium oxide/graphene nanowire composite.[164] The crystal water in the obtained sample was identified through thermogravimetric analysis (TGA) and the chemical formula of the sample is $V_2O_5 \cdot 1.42H_2O$. The shielding effect of water in crystal structure and the structural advantages for Mg-ion storage are displayed in Figure 11a,b. In order to study the influence of water on electrochemical performance, the sample was calcinated at 350 °C for 2 h in Ar (with much lower content of water) and air atmosphere (without water). The electrochemical performance of three samples were investigated via the three-electrode tube cell with AC cloth as both counter and reference electrode in 0.5 м MgTFSI₂/ACN electrolyte. The hydrated V₂O₅ shows an increased capacity from 210 to about 280 mAh g⁻¹ in the initial three cycles, the result is in accordance with the increased peak intensity at CV curves. However, the samples with little and no crystal water demonstrate much lower capacity of about 80 mAh g⁻¹ (Figure 11c,d). To give further evidence about the effect of crystal water, four samples (without graphene) treated at different temperatures in Ar atmosphere for 2 h were obtained. According to the TGA and XRD analysis, four samples had different content of crystal water (from 1.35 to 0.43) and gradually decreased interlayer spacing (the main peak shifted to higher angles). With the increase of *n* in $V_2O_5 \cdot nH_2O_5$. the specific capacity also improved from 60 to 210 mAh g⁻¹ (Figure 11e). In this way, the authors concluded that the content of crystal water can effectively reduce the diffusion barrier and further improving Mg-storage performance through shielding the divalent Mg²⁺.

Apart from the experimental results, Ceder et al. first conducted theoretical studies by combining the thermodynamic model with first-principles calculations to study the important role of water during Mg²⁺ insertion into nanocrystalline xerogel–V₂O₅.^[161] They used a Ni-intercalated bilayered V₂O₅ structure (**Figure 12**a,b) with $x_{Mg} = 0.5$ and $n_{H_2O} = 1$ as template to describe the Mg and H₂O (corresponding to the oxygen and hydrogen atoms) positions. The grand-potential phase diagrams (Figure 12c,d) were employed to give a direct observation about the stable Mg–xerogel V₂O₅ phases versus the water



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Figure 11. a) Shielding effect of Mg^{2+} in $V_2O_5 \cdot 1.42H_2O$. b) Schematic illustration of reversible Mg^{2+} insertion/extraction. c,d) Galvanostatic charge/ discharge profiles and cycling performance of three samples. e) Cycling performance of the samples treated at different temperatures in Ar atmosphere. Reproduced with permission.^[164] Copyright 2015, Elsevier.



Figure 12. a) Structure of $Mg_{0.5}V_2O_5 \cdot H_2O$ and b) $V_2O_5 \cdot H_2O$. c) Grand-potential phase diagram at 0 K of Mg-xerogel V_2O_5 in a different amount of water contained electrolyte. d) The average Mg intercalation voltage with low (red line) and high (blue line) Mg concentrations. Reproduced with permission.^[235] Copyright 2016, American Chemical Society.



levels in electrolyte. The authors concluded that the water shielding effect is thermodynamically preferable in wet electrolytes ($a_{\rm H_2O}$ is set to about 1) and water cointercalation only happens with $x_{\rm Mg} < 0.25$ in dry electrolytes ($a_{\rm H_2O}$ is about 10⁻⁴). However, there would be a strong driving force that stimulates all the H₂O in the structure leaching out and causes a slight change of the phase behavior on the whole system in the super dry electrolyte ($a_{\rm H_2O} < 10^{-7}$).¹⁶¹] In the condition of H₂O cointercalation with Mg²⁺, first-principles calculations demonstrate the increase of Mg intercalation voltage along with the increasing of $a_{\rm H_2O}$, which is well consistent with the experimental results.^{1162,165}] The extent and reversibility of H₂O/Mg coinsertion into V₂O₅ based cathodes, such as Mg_{0.1}V₂O₅ · nH₂O, also showed improved performance for the interlayer water, which is stable during cycling and shield the charge of Mg²⁺ ions.¹¹⁶⁰]

2.3.2. MnO₂

The shielding effect of a much lower H_2O content in electrolyte or crystal structure based on V_2O_5 cathode has been experimentally and theoretically investigated, so it provides an alternative strategy to another high performance cathode of MnO_2 . Lee et al. first demonstrated that the reversible Mg^{2+} insertion into

nanostructured MnO2 can be enhanced in water containing electrolyte.[151] The electrochemical performance was tested in three-electrode system with the synthesized free standing MnO₂ nanowire as the cathode, Ag/AgCl as the reference electrode, and platinum as the counter electrode in Mg(ClO₄)₂/PC containing water electrolyte. The authors determined the improved performance by CV curves (Figure 13a) in electrolytes with various water contents. Ex situ XPS (Figure 13b), STEM mapping and electron energy loss spectroscopy (EELS) (Figure 13c) give direct evidence about insertion of Mg²⁺ into MnO₂ and the uniformly distribution. The amount of intercalated Mg²⁺ ions with the cointercalated water molecules are determined via the combination of inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and electrochemical quartz crystal microbalance (EQCM) techniques. The coinserted mole ratio of H_2O and Mg^{2+} is in agreement with that of V_2O_5 (about 3:1).^[167] The difference in MnO₂ system is that the improved Mg²⁺ insertion behavior can be maintained even transferred to dry electrolyte after the initial cycling in water contained electrolyte, while the enhanced capacity is no longer observed in V_2O_5 system. The schematic of Mg²⁺ insertion mechanism into MnO₂ is presented in Figure 13d–f. In terms of cycling performance, it displays high specific capacity of about 160 mAh g⁻¹ in the first cycle and the capacity retention of is 67% after



Figure 13. a) CV curves of MnO₂ in various water contained electrolytes i) 0.1 M dry Mg(ClO₄)₂, ii) 0.1 M Mg(ClO₄)₂. $6H_2O$ with 0.4 M dry Mg(ClO₄)₂, iii) 0.1 M Mg(ClO₄)₂. $6H_2O$ with 0.1 M dry Mg(ClO₄)₂, iv) 0.1 M Mg(ClO₄)₂. $6H_2O$ b) Mg Is XPS spectra for MnO₂ at different states. c) STEM mapping of Mn, Mg, and Mg mapping image analyzed by EELS at a fully discharged state. d) Mg²⁺ insertion process in a dry electrolyte. e) Mg²⁺ insertion process in a wet electrolyte. f) Mg²⁺ insertion process in dry electrolyte after cycling in a wet electrolyte. Reproduced with permission.^[151] Copyright 2012, The Royal Society of Chemistry.

200 cycles at 1.6 C (1 C = 0.616 A g⁻¹) in 0.1 M Mg(ClO₄)₂ \cdot 6H₂O/ PC electrolyte, much better than previously reported results.

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Subsequently, extensive investigations about the effect of water in electrolyte on the reversible insertion of Mg²⁺ was conducted by Aurbach et al.^[167] The authors initially galvanostatically cycled the spinel-Mn₃O₄ in aqueous electrolyte dissolved 1 м MgSO₄ by using the reverse process of layered-to-spinel transition to obtain the MnO2 with crystal water (being important on the stability of MnO₂ layered structure). The chemical formula of sample after 50 cycles is $MnO_2 \cdot 0.94H_2O$. The electrochemical performance was measured by the three-electrode system in Mg(ClO₄)₂/ACN electrolytes containing different amount of water. With the increase of water content from 0.5 to 10 m, the discharge capacity has a continuous increase from 56.8 to 227.6 mAh g⁻¹. With high concentration of water (10 м) in the electrolyte, layered MnO₂ exhibits a high discharge capacity (about 230 mAh g⁻¹) and high working voltage (2.8 V vs Mg²⁺/Mg) at 0.1 A g⁻¹. It also displays outstanding rate performance (48.6% capacity retention at 2 A g⁻¹) and long-cycling stability (37.5% capacity loss after 10 000 cycles). Furthermore, XRD, ABF-STEM, and fast-Fourier-transform (FFT) images give the details about the insertion of hydrated Mg²⁺ and water position rearrangement during cycling. However, it should be excluded that the higher capacity and improved Mg-storage performance are caused by proton intercalation. Lee et al. presented a complicated process about the water-stimulated Mg²⁺ insertion mechanism with the H₂O to Mg ratio of 6:1 based on the amorphous MnO₂.^[168] They conducted ex situ XPS and angle-resolved XPS (AR-XPS) experiments to study the surface reactions and concluded the insertion/conversion mechanism at the surface of MnO_2 . There is the formation of $Mg(OH)_2$ at the MnO₂ surface along with the cointercalation of Mg²⁺ and H₂O. However, further experiments (as the authors suggested) are needed to confirm the results. The extent and reversibility of H₂O/Mg coinsertion into manganese based cathodes such as $Mn_2O_4,^{[169,170]}\ MgMn_2O_4,^{[98]}$ and $Mg_{0.15}MnO_2\cdot 0.9H_2O^{[139]}$ were also studied and similar results were also obtained.

2.3.3. Other Conditions

Wang et al. demonstrated that the capacity of VOPO4 can be activated through introducing water both in the structure and electrolytes.^[171] The water contained in structure or electrolyte (larger than 10⁻²) can not only lubricate the kinetics of Mg²⁺ but also reduce the charge transfer process, leading to much higher capacity. $Mg(V_3O_8)_2 \cdot nH_2O$ is one of the premier materials which demonstrate reversible Mg insertion properties.^[172] With the enhancement of crystal water, it delivers the discharge capacity of about 150 mAh g^{-1} at the first cycle and >80 mAh g^{-1} after 60 cycles. Mai et al. reported on the preintercalation of Mg^{2+} or Mn^{2+} ions into xerogel- V_2O_5 and used as positive electrode versus AC cloth in 0.3 м Mg(TFSI)₂/AC electrolyte.^[173,174] The Mg²⁺ or Mn²⁺ ions have an effect on the structural stability and electronic conductivity. Combined with the shielding effect of H_2O in the crystal structure, the obtained $Mg_{0.3}V_2O_5 \cdot 1.1H_2O$ and Mn_{0.04}V₂O₅·1.17H₂O demonstrate excellent cycling performance (little capacity decay after 10 000 cycles at 2 A g⁻¹). However, vanadium based cathodes are not compatible with full Mg cell electrolytes, they can only be used in conventional electrolyte solutions (ACN, PC, and so on) which are not compatible with Mg anode. So, there is the question that whether the water content (a very small amount) influences the Mg²⁺ deposition in the Grignard reagent dissolved THF electrolyte (compatible with Mg anode). Ichikawa et al. investigated the Mg²⁺ deposition with different water in Grignard reagent based electrolyte through the CV measurements and concluded that the concentration of water will destroy the electrolyte, which is known to all.^[175] The excessive content of water will increase the overpotential of Mg deposition which leading to the change of deposition morphology. Therefore, the water content should be as low as possible and it would be best to leave the electrolyte several hours or use the activated molecular (3 Å) to absorb some water.

However, every coin has two sides. Accompanied with the positive effect, there are some undesirable or harmful effects such as the incompatible of polar molecules with Mg metal anode, electrolytes, and so on. So, researchers should focus on the investigation of highly stable molecules (contained in electrolytes or host lattice) which can not only promote Mg²⁺ mobility but also avoid the serious side reactions.

2.4. Organic Molecules Preintercalation

Organic molecules also have the similar role with the water in the host structures, and offer better electrochemical performance. Compared with the crystal water, the preintercalated organic molecules are more stable and inactive, which just worked as a pillar to expand the layers accompanied by enhanced Mg²⁺ diffusion kinetics and improved Mg-storage performance. However, up to now, only several organic molecules have been reported as effective intercalants to improve the Mg-storage performance. In this section, we will review the experimental and computational investigations on preintercalation organic species and effects.

2.4.1. Preintercalation During the Synthesis

Yao et al. synthesized the interlayer-expanded MoS₂ by inserting a specific amount of PEO ($[CH_2-CH_2-O]_n$) through the modified chemical delamination-reassembly method.^[176] First, they performed the DFT calculations to identify the possibility of interlayer expansion and gave a direction on material synthesis. The results indicate that the Mg diffusion barrier decreases (from 1.12 to 0.38 and then to 0.22 eV) with the increase of interlayer spacing (from 0.65 to 0.8 and 0.9 nm) (Figure 14a,b). At the same time, the chemical bond between Mg and S atoms is stretched and then broken to one side (Figure 14c-e). In order to achieve a low Mg diffusion barrier which is comparable with that of Li⁺ (about 0.49 eV, d = 0.618 nm), the interlayer distance should be as large as 0.772 nm (about 25% increase).^[177] On the other hand, PEO is highly stable and ionically conductive when introduced into the MoS₂ layers. More importantly, the inserted PEO just functions as a pillar without side effect and the properties of MoS₂ can be reserved. Based on the theoretical analysis, the authors conducted various amount of PEO intercalated into the MoS₂ lattice to expand the interlayer spacing. Figure 15







Figure 14. a) The calculated Mg diffusion energy barrier along with the decrease of interlayer spacing. b) Potential energy diagram and c–e) bonding interaction conditions between Mg and S atoms when the interlayer distance is 0.65, 0.8, and 0.9 nm. Reproduced with permission.^[176] Copyright 2015, American Chemical Society.



Figure 15. a) The synthesis process of interlayer expanded MoS_2 with the different molar ration of MoS_2 to PEO (original, 1:0, 1:0.5, and 1:1) and b) the corresponding TEM images. Reproduced with permission.^[176] Copyright 2015, American Chemical Society.



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shows the synthesizing processes and the obtained interlayer expanded MoS₂ structure.^[178] The XRD, TEM measurements were used to give a specific value of interlayer distance (0.62, 1.22, and 1.40 nm) with different molar ratios of MoS₂ to PEO (1:0, 1:0.5, and 1:1) and infrared spectroscopy was performed to identify the insertion of PEO. The Mg-storage performance was investigated with Mg metal anode in APC electrolyte. As expected, the specific capacity continuously increases with the expansion of interlayer (from 0.61 to 1.40) at various current densities. The interlayer expanded MoS₂ demonstrates much higher discharge capacity and improved rate capability. The GITT results gave further evidence about the improved Mg diffusivity in expanded MoS₂ which is at the same level with that of Mo_6S_8 .^[38,176,179] Similarly, Rhodes et al. introduced PEO during the synthesizing process of V₂O₅ sol-gel to increase the V₂O₅ interlayer spaces and reduce the interaction barrier of divalent Mg ions.^[180] As a result of the V₂O₅-PEO structure, the composite demonstrated about fivefold increasing of Mgstorage capacity, enhanced rate performance and improved cycling stability compared with V₂O₅ xerogels. Both of the two works point out a new direction for RMBs and even other multivalent-ion batteries.

Inspired by the work described above, Mai et al. synthesized interlayer expanded VOPO₄ by the ultrasonicated exfoliation and self-assembly method.^[181] First, they synthesized bulk VOPO₄·2H₂O by a hydrothermal method (denoted as OH-VOPO₄), and then through displacement reaction with PA (C₆H₇N) molecules to realize the interlayer expanding (labeled as PA-VOPO₄). The presented XRD patterns (**Figure 16**a) show that the (001) plane shifted to a lower angle, confirming the interlayer distance is expanded from 0.74 (OH-VOPO₄) to 1.42 nm (PA-VOPO₄). With Mg metal anode in APC electrolyte (Figure 16c.d), the PA-VOPO₄ demonstrates relatively lower polarization and superior specific capacity compared with OH-VOPO₄ at various current densities. Even at the high rate of 2 A g⁻¹, the expanded VOPO₄ exhibits high specific capacity of 109 mAh g⁻¹ which is quite remarkable among the reported cathodes.^[181] The fabricated PA-VOPO₄ exhibits a high specific capacity of 192 mAh g⁻¹ after 500 cycles at 0.1 A g⁻¹, demonstrating outstanding long-term cycling performance. Moreover, the ex situ XRD results at different charge/discharge conditions illustrate the reversibility of PA-VOPO₄ structure. Take the complexity of APC electrolyte into consideration, the authors conducted XPS (Figure 16b), EDS and ICP tests to give more investigation to further identify the intercalated species. After careful analysis of these results, the reversible intercalation of MgCl⁺ into PA-VOPO₄ (large interlayer distance of 1.42 nm) instead of Mg²⁺ was confirmed. While, only Mg²⁺ ions intercalated into OH-VOPO4 due to the limited interlayer lattice of 0.74 nm. Theoretical analysis of Mg²⁺ and MgCl⁺ diffusion behaviors was also provided with the first-principles computations based on DFT calculations (Figure 16e,f). There are two possible pathways (P1 and P2) for the diffusion of intercalated ions (Mg²⁺ and MgCl⁺). However, the MgCl⁺ diffusion possesses a much lower energy barrier along with the P1 pathway and the calculated diffusivity is about 1.5×10^{13} faster than that of Mg²⁺. As a result, reversible intercalation of MgCl⁺ with fast kinetics is preferable in the expanded VOPO₄ host, which is in agreement with experimental investigations. The reversible intercalation of MgCl⁺ in the expanded VOPO₄ structure possesses lower



Figure 16. a) XRD patterns. b) XPS spectra of Mg 1s and Cl 2p for PA-VOPO₄ at fully charged/discharged states. c) Charge/discharge profiles of PA-VOPO₄ and OH-VOPO₄ at 50th cycle. d) Rate performance of PA-VOPO₄ and OH-VOPO₄. e) The possible diffusion routines for Mg²⁺ and MgCl⁺ in VOPO₄. f) The diffusion barrier curves of Mg²⁺ and MgCl⁺ transport through different pathways. Reproduced with permission.^[181] Copyright 2018, Wiley.

migration barrier and faster diffusion kinetics. In another piece of work, 2-ethylhexylamine was introduced as a pillar to expand the interlayer spacing of VS₂ during the process of synthesis.^[182] The interlayer distance of (001) lattice plane is expanded from 0.573 to 0.993 nm. XPS and EDS analyses indicate the intercalation of MgCl⁺ and desolvated Mg²⁺ ions, which is different from that of PA pillared VOPO4 (only MgCl⁺ ions intercalation). With enhanced Mg-ion diffusion, expanded VS₂ displays high discharge capacity (245 mAh g⁻¹ at 0.1 A g⁻¹), outstanding rate performance (103 mAh at 2 A g⁻¹) and outstanding longcycling performance (90 mAh g⁻¹ after 600 cycles). However, the reaction mechanism is intercalation pseudocapacitance with little contribution of conversion reaction, and pseudocapacitive contribution is about 64% at 1 mV s⁻¹. Instead of Mg²⁺ storage chemistry, the intercalation of MgCl⁺ will lead to the larger consumption of electrolyte and lower specific energy of the battery.^[94]

On the other hand, the intercalated organic ions may have an effect on the host surface. 2D Ti₃C₂ MXene has been successfully used as the electrode in LIBs, NIBs, and supercapacitors owing to the advantages of outstanding electrical conductivity and high volumetric capacity.^[183,184] However, it demonstrated a negligible capacity when introduced in RMBs in the previous study.^[185] Yan et al. used the cetyltrimethylammonium (CTAB) as a cationic surfactant to preintercalate it into the $Ti_3C_2T_r$ $(T_r represents the surface functional groups)$ and make it possible to improve the Mg-storage performance.^[75] The intercalated CTA⁺ has an effect on inducing the charge transfer from CTA⁺ to $Ti_3C_2T_x$, in this way, reducing the Mg²⁺ diffusion barrier on $Ti_3C_2T_x$ surface. It also expanded the interlayer spacing, however, this is not the main reason for the enhanced performance in this system. When coupled with Mg anode in APC electrolyte, CTA^+ preintercalated $Ti_3C_2T_x$ displays high specific capacity of 100 mAh g⁻¹ at 0.05 A g⁻¹, excellent longterm cycling stability (above 30 mAh g^{-1} at 0.2 A g^{-1} even after 250 cycles) and outstanding rate capability (45 mAh g^{-1} at 2 A g^{-1}).

In summary, these works really give a new modification method on Mg-storage electrode materials; however, the selection of organic molecules and corresponding specific layered materials is full of difficulties. The extension of this approach is still a problem for the compatibility of selected organic pillar with cathode, anode and electrolyte.

2.4.2. In Situ Preintercalation in the First Discharge Process

Recently, Yao and co-workers performed the preintercalation of $Py_{1,4}^+$ (1-butyl-1-methylpyrrolidinium chloride, denoted as $Py_{1,4}$ Cl) into TiS₂ structure and obtained improved electrochemical performance.^[186] Due to the moisture-sensitive property of TiS₂, they introduced the $Py_{1,4}^+$ as an organic pillar to expand the layers during discharge process (in situ method). The structural evolution of TiS₂ in the first two cycles and the insertion of $Py_{1,4}^+$ were investigated through the in operando XRD, high-energy XRD and ex situ STEM measurements (**Figure 17**a,b). In the initial activation process (first discharging to 1.0 and 0.2 V), the (001) plane with *c* = 5.69 Å is expanded to 10.87 and 18.63 Å. With further discharging to 0 V, the interlayer distance is not expanded anymore. Combining a series of techniques including EDS, ICP optical emission spectrometry

(ICP-OES), XPS, and EELS, the intercalating species of Py14+ and MgCl⁺ were confirmed (Figure 17c). The specific value of Pv_{14}^+ (0.2 M) for per formula of TiS₂ when discharged to 0 V is calculated through TGA. Through further analysis of the obtained results, they concluded the preintercalation of Py14⁺ and its irreversible intercalation after the activation process, while MgCl⁺ intercalation is reversible in the following cycles. The electrochemical performance is shown in Figure 17d-f. The expanded TiS₂ shows a high specific capacity of about 240 mAh g⁻¹, indicating the intercalation of 1 mol MgCl⁺ for per formula of TiS₂ (based on the mass of TiS₂). The obtained cathode also demonstrates outstanding long-term cycling performance (80% capacity retention after 400 cycles at 1 C) and outstanding temperature adaptability (from -45 to 60 °C). As the authors mentioned at the beginning, the lower polarity of MgCl⁺ possesses faster diffusion kinetics than Mg²⁺ and quantitative evidence was provided by computational calculations.^[187] The expanded interlayer distances further reduced the migration barrier and lead to faster kinetics. For these two reasons, with the preintercalation of Py_{14}^+ , the expanded TiS₂ displays excellent electrochemical performance. The structural evolution during initial discharge is shown in Figure 17g. The first inserted Py14⁺ worked as pillars to expand the interlayer distance and make it ready for the intercalation of MgCl⁺. The intercalated MgCl⁺ further expanded the distance and made it possible for the reversible intercalation of MgCl⁺. During the cycling, Py1,4+ stays inside the structure, whereas the highly reversible of MgCl⁺ is achieved. Similarly, the Mg²⁺ desolvation energy in VS₂ is reduced from 3.0 to 0.67 eV with the addition of 1-butyl-1-methylpiperidinium chloride (denoted as PP14Cl) into 0.4 м APC electrolyte.^[188] Furthermore, PP₁₄⁺ intercalates into VS2 during the initial discharge process to expand the interlayer distance, in this way, Mg²⁺ diffusion coefficient is increased by three orders of magnitude. Both the two aspects contribute greatly to the Mg-storage performance of VS₂. The similar experiments were also performed to expand the interchain distance of chain-like structure VS4 and the Mg-storage performance is significantly improved when compared with the unexpanded VS₄ structure.^[189]

In summary, expanding the layers through preintercalation of organic molecules is a feasible strategy to enhance the electrochemical performance for layered materials. Choi et al. have given an extensive description about the reported works of which introducing water or organic molecules as intercalated components into materials and the enhanced performance when they are employed as electrodes of LIBs and post-LIBs.^[190] However, just as the authors presented, the studies about the use of water intercalated materials in RMBs are mostly focused on vanadium oxide based and manganese oxide based compounds. In terms of intercalated organic molecules, only several related works (PEO into MoS₂ and V₂O₅, Py_{1,4}⁺ into TiS₂, PA into VOPO₄, and CTAB into $Ti_3C_2T_x$) are reported. Although the intercalation process and resulted effects of organic molecules on materials are experimentally and theoretically analyzed in the literature, the extension of this strategy is still full of challenges because it is difficult to select a specific organic pillar and the corresponding layered structures. In this respect, the extensive investigation is needed to guide the direction in developing this strategy.



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b а С d spacing (A) 20 10 5 2 (110) (014) (016) (107) (002) (004) (013) (111) Mg CI (001) Ti Normalized intensities (a.u.) 4 (005) (012) / (015 1001 Mg (002) (004) 3 (100) CI (008) Counts (a.u.) (110) /(111) (012) (013) C (003) -(014) Ti 2 (001) 2 (100) (011) (011) (110)Ma CI (012) (013) (100) (111) (110) (103) (001) (100) (002 (012)0 S (111) 0.5 1.0 1.5 2.0 2.5 3.0 3.5 2 3 Image Ti С Ti+C 20 (°, 2 = 0.10798 Å) Energy (keV) f d x in (MgCl), exTiS₂ е 0.0 0.2 0.4 0.6 0.8 1.0 2.0 2.0 Coulombic efficiency (%) Voltage (V vs Mg/Mg2+) Voltage (V vs Mg/Mg2+) 240 mA g Capacity (mAh g_{TIS2}⁻¹) 150 1.5 1.5 g an 10 0.0 0.5 1.0 100 24 mA g 1.0 80 MILLION DE LA COMPANY 0.5 240 mA g 0.5 Charge 50 70 Transient Discharge Open circuit 0.0 0.0 60 0 0 100 200 300 0 100 200 400 0 100 200 300 500 Capacity (mAh g_{TIS2}⁻¹) Capacity (mAh g_{TIS2}⁻¹) Cycle number g Initial expansion Further expansion Structural distortion by Pristine TiS₂ by Py14⁺ intercalation by MgCl⁺ and Py14⁺ MgCl⁺ intercalation TiS₂ MaCl⁺ Pv14+ THF c = 18.63 Å c = 5.69 Å c = 10.86 Å c = 18.63 Å

Figure 17. a) High energy XRD patterns of TiS₂ at different stages (stages 0–3 corresponding to the pristine TiS₂, discharged to 1, 0.2, and 0 V, respectively). b) STEM images when recharged to 2 V (stage 4). c) EDS spectra for stages 1–4. d) Charge/discharge profiles of expanded TiS₂ at 24 and 240 mAh g^{-1} . e) Cycling performance at 240 mAh g^{-1} . f) GITT curve and MgCl⁺ diffusivity (inset). g) The schematic of structural evolution about the interlayer expanding process with the discharge went on. Reproduced with permission.^[186] Copyright 2017, Springer.

2.5. Nanostructure Construction

Much time and effort has been dedicated to the research and development of Mg battery in the last few decades.^[191] As mentioned earlier, one of the biggest challenge in developing Mg battery cathodes is how to overcome the negative effect caused by the divalent Mg²⁺ in the diffusion pathway. Benefited from the devoted efforts, there are three well-known representative approaches have been proposed to improve the Mg diffusivity or decrease the diffusion pathway. The first is by introducing a small amount of strong dipoles to shield the divalent Mg²⁺ ions.

With the charge shielding effect of highly polar molecules, the Mg²⁺ is converted into much less polarizing ion accompanied with improved diffusivity. The second is through the expansion of interlayer distance to improve the Mg²⁺ diffusion kinetics or even change the intercalation species. The details are discussed in the charge shielding section and preintercalation section, respectively. The third is drastically decreasing the particle size of the electrodes.^[192–195] As reported in LIBs and NIBs, the nanostructured materials have several important advantages compared with the bulk ones, such as increased contact interface of electrolyte and electrode, and shorter diffusion lengths

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for electrons and ions.^[196–199] In RMBs, using nanostructured composites is also an effective way to obtain a decreased route for Mg^{2+} diffusion with better performance. In this section, the advances of nanostructure construction method for cathodes and anodes of RMBs that have been recently reported are presented.

2.5.1. Nanostructured Cathodes

Among the various cathode materials, Mo₆S₈ is often amenable to excellent Mg-storage performance. However, it suffers from some intrinsic limitations, resulting in Mg trapped in its host at room temperature. In order to reduce the diffusion distance, Aurbach et al. decreased the particle size by milling the pristine Mo₆S₈.^[200] They conducted the experiment both in air and Ar atmosphere with different milling time (from 1 to 15 min). The SEM and nitrogen isothermal adsorption results indicate that the sample milled in pure Ar has a smaller particle size and higher surface area, and hence, higher rate capability and specific capacity. Similarly, Kim et al. synthesized various mean particle sizes of Mo₆S₈ through the molten salt method and examined their electrochemical performance.^[201] When the particle size is decreased from 750 to 570 nm, the higher discharge capacity and better rate performance are achieved owing to the shorter diffusion length. However, further decrease from 570 to 240 nm will lead to unwanted side reaction. The results indicate that the sample with 570 nm demonstrates the best electrochemical properties although it is not the smallest size. As described earlier, the commonly strategy of minimizing the particle size to nanoscale is not necessary for Mo₆S₈ due to its unique structure. The mobility of Mg in the Mo₆S₈ is highly related to the temperature and Mg trapping happens at room temperature. By increasing the temperature or reducing the particle size, part of the trapped Mg can be released.

Layered oxides. Aurbach et al. explored the electrochemical and structural changes of thin film cathode materials of layered V₂O₅ and MoO₃.^[60] V₂O₅ and MoO₃ film with nanoscale thickness and particles size were fabricated via vacuum deposition and electrodeposition approach, respectively. The CV curves of thin film V2O5 cathode indicate highly reversible electrochemical insertion and deinsertion of Mg2+ ions (efficiency of about 100%). The high capacity of 150 mAh g⁻¹, corresponding to about 0.5 Mg^{2+} for per formula of V_2O_5 is displayed in the typical galvanostatic titration measurement at 0.5 μ A cm⁻². They used the same approach to study the insertion mechanism of Mg²⁺ into MoO₃. After the necessary conditioning process,^[59,202] the thin film MoO₃ shows the specific capacity of 220 mAh g⁻¹ in galvanostatic titration test (0.3 μ A cm⁻²). Both the thin film samples can be cycled with high coulombic efficiency (about 100%) and demonstrate highly stable specific capacity during cycling.

Layered diselenides. WSe₂ has attracted much attention for its extraordinary properties of low thermal conductivity, efficient p-type field effect performance and high hydrophobic sticky surface.^[203–205] However, the application of WSe₂ in energy storage systems is rarely reported. Shen et al. synthesized a novel nanostructured WSe₂ via chemical vapor deposition approach and used as the potential cathode material for RMBs.^[74] The SEM, TEM and selected-area electron diffraction (SAED) measurements (Figure 18a,b) indicate that the synthesized WSe₂ nanowires have a diameter of about 100 nm with high crystallinity. The electrochemical performance of WSe2 nanowire-assembled film cathode was performed in Mg(AlCl₂BuEt)₂/THF electrolyte with Mg as the anode in the voltage range of 0.3 and 3 V (Figure 18c-f). It exhibits a high platform at about 1.6 V with the capacity of 220 mAh g⁻¹ at 0.05 A g⁻¹, and excellent cycling performance of about 203 mAh g⁻¹ after 160 cycles. However, WSe₂ bulk sample shows poor cycling stability with a high capacity loss of 90% after 100 cycles. Furthermore, the WSe2 nanowire cathode delivers enhanced rate performance with the discharge capacity of 142 mAh g⁻¹ at 0.8 A g⁻¹. It also shows superior cycling performance without obvious decay in capacity for 50 cycles at high rate (120 and 103 mAh g⁻¹ at 1.5 and 3 A g⁻¹). The authors conducted first-principles DFT to give the theoretical analysis, together with experimental results, extensively investigated the reason for excellent Mg-storage behavior of WSe₂ nanowire. It should be pointed out that the employed voltage window (0.3-3 V) was beyond the anodic limit of electrolyte (about 2.5 V), thus promoted the undesired side reactions of electrolyte.

Tunnel structures. Compared with layered structures, MnO₂ with the tunnel structures is attractive due to its high theoretical voltage (2.8 V vs Mg²⁺/Mg) and specific capacity (\approx 310 mAh g⁻¹). In order to achieve better Mg-storage capacity, Matsui et al. synthesized the nanosized MnO2 cathode. The electrochemical performance is tested with Mg foil as counter and reference electrode in hexamethyldisilazide magnesium chloride electrolyte.^[142] α -MnO₂ nanoparticles has an average size of 20 nm and displays high capacity of 280 mAh g⁻¹, much higher compared with that of 100 nm particles (170 mAh g⁻¹). Doo et al. synthesized nanostructured λ -MnO₂ and α -MnO₂ by using acid treatment of spinel MgMn₂O₄.^[206] The electrochemical performance is tested with Ag/AgNO3 as reference electrode in Mg(ClO₄)₂ electrolyte. The nanostructured λ -MnO₂ shows higher capacity (330 mAh g^{-1}) and cyclability due to the facile interfacial reaction. However, why the capacity is higher than that of theoretical is not mentioned. Yin et al. synthesized the MgMn₂O₄ nanoparticles through the modified Pechini method with different annealing temperatures to change the crystalline size.^[98] With smaller crystallite size and higher surface area, the sample annealed at 400 °C (12 nm) delivers much higher capacity of 220 mAh g $^{-1}$ than that of annealed at 550 °C (42 nm) of 70 mAh g⁻¹ in Mg(TFSI)₂/ACN electrolyte.

Other structures. Vullum-Bruer et al. fabricated the spongelike porous Mn_3O_4 nanoparticles with a small size of 10 nm and a high surface area of 102 m² g^{-1,[207]} When assembled with Mg anode in APC electrolyte, the Mn_3O_4 cathode delivers a high specific capacity of 190 mAh g⁻¹ at 0.1 C, and a stable capacity around 60–70 mAh g⁻¹ lasted for 1000 cycles at 1 C. Wu et al. reported the flower-like CoS with nanostructure which prepared through solvothermal method.^[208] The CoS cathode displays a plateau at 1.1 V with high discharge capacity of 120 mAh g⁻¹ at 0.05 A g⁻¹ in the Mg(AlCl₂BuEt)₂/THF electrolyte against the Mg metal anode. It also displays an enhanced cycling stability with the capacity of 120.6 and 105.9 mAh g⁻¹ after 40 and 60 cycles, respectively. Luo et al. synthesized VO₂ nanorods and nanosheets through the facile hydrothermal







Figure 18. a) SEM images of the synthesized WSe₂ nanowires. b) TEM image and SAED pattern. c) Schematic illustration of the assembled cell. d) The discharge/charge profiles of WSe₂ nanowire-assembled film at the current density of 0.05 A g⁻¹. e) The cycling performance and f) corresponding Coulombic efficiency of WSe₂ nanowire-assembled film and WSe₂ bulk. Reproduced with permission.^[74] Copyright 2013, American Chemical Society.

method.^[209] The nanorods structure has the effect on reducing the diffusion pathway and improving the Mg²⁺ diffusion rate, as a result, VO₂ nanorods deliver higher capacity of 391 mAh g⁻¹ than nanosheets of 356 mAh g⁻¹, as well as better cycling stability of 94.7% than 42% after 10 cycles at 0.025 A g⁻¹ in Mg(ClO₄)₂/ACN electrolyte.

Designing specific structure with mesoporous morphology (no matter nanometer sized or micrometer sized) can also achieve the same effect of nanostructure. NuLi et al. synthesized a MgCoSiO₄ cathode with mesoporous structure through the mixed solvothermal approach.^[210] In comparison, they also prepared the MgCoSiO₄ bulk (a few micrometers in size) and the well-defined crystalline particles (500–800 nm) through the high temperature reaction and molten salt method, respectively. The BET test confirmed the mesoporosity of MgCoSiO₄ and indicated the average mesoporous size of 3.7 nm and the high surface areas of 13.3 m² g⁻¹. The battery performance of

MgCoSiO₄ cathode was examined against a Mg metal anode in Mg(AlCl₂BuEt)₂/THF electrolyte. The mesoporous MgCoSiO₄ exhibits a higher plateau (1.65 V) and much higher discharge capacity (167 mAh g⁻¹) compared with the well-defined crystalline particles (1.55 V, 123.3 mAh g^{-1}) and bulk forms (1.55 V, 70.2 mAh g⁻¹). The mesoporous structure can effectively accelerate the ionic conductivity and alleviate the structural damage during charge/discharge cycling process.^[211,212] Meng et al. also investigated the morphology influence on the electrochemical performance of VS_4 .^[213] Three controllable morphologies (solid sphere, flower-like microsphere and ultrathin nanosheets surrounded solid sphere) are obtained through the simple hydrothermal method. Among the three samples, the flower-like microsphere VS₄ has great quantity of interspace between nanosheets, higher surface area and active sites. Therefore, flower-like VS₄ exhibits much better electrochemical performance (lower capacity decay of 10% after 400 cycles) than that of other samples.



2.5.2. Nanostructured Anodes

In primary and secondary batteries, Mg metal has been regarded as the ideal anode attributed to the low-cost, environmental friendliness, and low oxidation potential properties. For this reason, studies on the other anode materials have rarely been reported. In primary batteries, the low utilization of Mg metal anode and the formation of passivation film on Mg surface have impeded its widespread commercial application. Chen et al. employed a specific amount of NaNO₂ as an inhibitor in Mg(NO₃)₂ electrolyte and investigated the effect of Mg with different particle sizes on the Mg/MnO₂ primary battery performance.^[214] Through the vapor deposition process at different deposition temperatures of 240, 270, and 300 °C, the authors synthesized microspheres and micro/nanospheres mixed Mg products. The average diameters increased from 1.0-5.0 to 3.0-6.0 µm with the temperature increased from 240 to 270 °C, and a mixed diameter of 1.5–3.0 μm and 50-100 nm (abundance) was obtained when the deposition temperature further increased to 300 °C (Figure 19a). With smaller particle size and higher specific surface area (1.92 m² g⁻¹), the product prepared at 300 °C shows more negative property and higher current density in the linear sweep voltammograms (LSV) test (Figure 19b). The galvanostatic discharge profiles of four samples at 0.025 A g^{-1} are displayed in Figure 19c. The product prepared at 300 °C exhibits the highest discharge capacity of 768 mAh g⁻¹, it is worth to mention that all the samples synthesized in this work display much higher capacity than commercial Mg powder. For another example, through the ionic liquid-assisted chemical reduction method, they prepared the ultrasmall Mg particles with an average diameter of 2.5 nm and then fabricated the RMBs with grapheme-like MoS₂

cathode in Mg(AlCl₂BuEt)₂/THF electrolyte.^[68] In comparison, the battery with bulk Mg anode is also assembled. The battery with the ultrasmall Mg nanoparticles anode shows a one-fold capacity increase (170 mAh g⁻¹) than the battery with bulk Mg anode (about 85 mAh g⁻¹), and excellent cycling stability with 95% capacity retention after 50 cycles. However, the manufacturing operation of the ultrasmall Mg particles is so complex that it restricts the practical application.

Up to now, some cathode materials have demonstrated excellent Mg-storage performance, however, most of the electrochemical performance are performed in conventional electrolytes which are not compatible with Mg anode. In order to make practical use of these cathodes, it is necessary to investigate other anode systems. Liu et al. developed the nanostructured Bi anode for RMBs.^[215] The Bi nanotubes with the diameter of around 8 nm were synthesized through a hydrothermal method. For comparison, the Bi microparticles (about 100 µm) and Bi nanoparticles (30-50 nm) were also prepared. The electrochemical performance was tested in Mg(BH₄)₂ and LiBH₄ dissolved diglyme electrolyte against the Mg cathode. As expected, the Bi nanotubes demonstrate much better cycling performance of 92.3% capacity retention (303 mAh g⁻¹) after 200 cycles and the best rate performance of 350 and 216 mAh g⁻¹ at 0.05 and 5 C, respectively. The authors concluded that the Mg-storage performance is significantly influenced by the morphology and size of Bi.

2.6. Decoration with Carbon



Several optimization strategies have been described in the above sections and all these methods are focused on facilitating the

Figure 19. a) SEM images of the Mg products deposited at 240, 270, and 300 °C. b) The LSV of Mg anode with different particle sizes at 20 mV s⁻¹. c) The discharge profiles of Mg/MnO₂ batteries at the current density of 0.025 A g⁻¹. Reproduced with permission.^[214] Copyright 2009, Springer.

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diffusion kinetics of Mg²⁺ in the host materials. However, on the other hand, the improvement of electron conductivity of the electrodes is also an important aspect. At present, decorating the electrodes with highly conductive agents, such as carbon materials, is always a facile and effective approach to ensure the efficient and fast access of electrons. In this section, the latest advances in fabrication of carbon-based composites to improve the electrochemical performance are discussed.

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Carbon, as highly conductive agents, has various types and has been widely used in improving the conductivity of the materials. When preparing the electrodes, almost all of the materials need a specific amount (usually >10 wt%) of conductive agents (such as super-P carbon, acetylene black and so on). However, the effect is much inferior compared with that of fabricated with electrode in the synthesizing process.^[216] To enhance the conductivity of materials, researchers have prepared various carbon decorated composites and achieved better electrochemical performance. Imamura et al. used the acetylene black as a surfactant to prepare a homogeneous V₂O₅/ carbon composite and achieved an improved Mg-storage performance.^[158] With the weight ratio of 1:3 (V₂O₅ to carbon), spherical carbon particles were coated by the thin layer of V_2O_5 .^[217] In this way, the composite exhibits enhanced electronic conductivity and higher reaction areas through the combination with carbon. The electrochemical measurements were conducted via the three-electrode cell with Mg(ClO₄)₂/ACN electrolyte. The high discharge capacity of about 600 mAh g⁻¹ is obtained at 1 A g^{-1} based on the weight of V₂O₅, while it is far more higher than that of the commonly V_2O_5 displays (150 mAh g⁻¹) in the same conditions. Although ICP results are unable to support the high capacity, however, the reaction mechanism is still unclear and the authors attributed it to the side reactions. Liu et al. synthesized the composite of highly dispersed V₂O₅ supported by porous carbon frameworks through the ambient hydrolysis deposition (AHD) method, and it demonstrated good reaction kinetics when used as the electrode of RMBs. [32,218] The porous carbon was synthesized through the resorcinol and formaldehyde precursors (RFC). The weight ratio of V₂O₅ to porous carbon can be controlled with different numbers of AHD cycles, and the authors focused on the amount of V₂O₅ at about 45% (confirmed by TGA) to obtain the best Mg-storage performance.^[218] The authors conducted a series of measurements including XRD, Raman, TEM, EDS, STEM, NMR, and XPS to give enough information for the successful fabrication of V₂O₅ within the composite and the interaction between V₂O₅ and the carbon support. The AHD obtained V₂O₅ nanoclusters supported by RFC frameworks have various dimensional structures and can offer numerous reactive sites to react with Mg ions. This reaction is mostly surface oriented which leads to excellent capacitive behavior. When assembled with Mg anode in magnesium aluminum chloride complexes (MACC) electrolyte, the V₂O₅ nanoclusters deliver a high pseudocapacitive capacity of about 350 mAh g^{-1} (about 180 mAh g^{-1} base on the composite) at 0.04 A $g^{-1.[218-220]}$ In comparison, both the bulk V₂O₅ and RFC alone exhibits much lower capacities in the same conditions. The pseudocapacitive behavior of the composite offers outstanding rate performance of about 100 mAh g⁻¹ at high rate of 0.64 A g⁻¹. Nevertheless, inferior cycling stability is reflected by a low capacity of about 90 mAh g⁻¹ after 50 cycles at 0.32 A $g^{-1}\!.$ Jiao et al. reported on the sandwich-structured MoS_2/C with preferable electrochemical performance as the anode of RMBs.^[221] Through a hydrothermal method followed by calcinations, the sandwich-structured MoS₂/C microspheres (graphene-like nanosheets on the surfaces) was successfully synthesized. In the calcination process, the amount of glucose is of great importance for the formation of graphene-like structure, which has a high contact area with electrolyte and thereby accelerating the mobility of Mg²⁺ from electrolyte to the active surface of MoS₂. In addition, the existence of carbonaceous materials can effectively improve the conductivity of MoS₂, resulting in enhanced Mg-storage performance. The electrochemical performance of MoS₂/C was performed via the two-electrode cell against Mg metal anode in the APC electrolyte. At 0.05 A g^{-1} , the MoS₂/C electrode exhibits a high specific capacity of 213 mAh g⁻¹ (much closer to the theoretical capacity of 223.2 mAh g⁻¹) and the capacity of 118.8 mAh g⁻¹ is remained after 20 cycles.

Multiwalled carbon nanotubes (MWNTs) are effective conductivity agents to guarantee the mechanical integrity and convenient routes for the mobility of Mg²⁺ ions and electrons. Chen et al. synthesized the MWNT/C/Mg103Mn0.97SiO4 nanocomposite using the one step CVD method.^[222] Firstly, the authors prepared the Mg103Mn097SiO4 nanocomparticles with the average diameter of 80-100 nm and then added a carbon layer coating on the particles to form a Mg1.03Mn0.97SiO4@C core-shell structure. Finally, the MWNTs were deposited on Mg103Mn097SiO4@C nanoparticles as the network among Mg103Mn097SiO4 nanoparticles through the CVD approach. The coated carbon layer and hierarchical nanostructure of MWNTs can improve the conductivity, and provide larger electrode/electrolyte contact surface. When used as cathode in Mg(AlCl₂BuEt)₂/THF electrolyte against the Mg anode, MWNT/C/Mg103Mn097SiO4 nanocomposite demonthe strates a higher specific capacity of 300 mAh g⁻¹, better rate capability and outstanding cycling stability compared with the pure $Mg_{1.03}Mn_{0.97}SiO_4$ nanoparticles and carbon coated Mg_{1.03}Mn_{0.97}SiO₄ composite.

Graphene is another conductive agent which has been successfully used to improve the low electronic conductivity of materials benefited from its excellent electrical, thermal, and mechanical properties.^[223,224] Furthermore, graphene is prone to functionalize with other molecules and worked as a supporting matrix with the active materials distributed on the surface or between the nanosheets.^[225-227] The graphene decorating process is sometimes performed by a hydrothermal or solvothermal reaction. For example, Wang et al. synthesized the graphene wrapped V₂O₅ microparticles by solvothermal reaction.^[228] When used as cathode in Mg(AlCl₂BuEt)₂/THF electrolyte against the Mg foil counter and reference electrodes, the prepared composite delivers a high capacity of 178 mAh g⁻¹ in the initial discharge, and 140 mAh g⁻¹ even after 20 cycles. V₂O₅ cathode with the presence of graphene demonstrates remarkable enhanced performance as a full Mg cell cathode, whereas, most of the previous works are performed in the three-electrode system. In this work the graphene decorating effect was confirmed. Jiao et al. presented the MoS₂ microspheres supported by graphene by using the hydrothermal method and subsequent heat treatment.^[226] During the synthesizing process,



graphene nanosheets act as substrates which provide new sites for the nucleation and following growth of MoS_2 .^[226,229] With the stacking of graphene and the growth of MoS₂ layers, the distinct MoS₂/graphene sandwich structure was formed to offer more channels for the reversible intercalation of Mg²⁺. In order to confirm the enhanced conductivity, the electrochemical measurements of MoS₂ with different content of graphene (0, 3.21, 10.07, and 20.48 wt%, respectively) were performed in APC electrolyte against a Mg anode. All the graphene decorated samples exhibit higher discharge capacity and outstanding cycling performance compared with the pure MoS₂, and the composite with 10.07 wt% carbon shows the best performance (104.2 and 74.1 mAh g^{-1} after 30 and 50 cycles at 0.02 A g^{-1}). The results indicate that a proper amount of graphene can really improve the conductivity of MoS₂ and promote the transportation of Mg²⁺.

2.7. Electrode-Electrolyte Interface Optimization

The biggest advantage of Grignard reagents based electrolytes, such as Mg(AlCl₂BuEt)₂/THF and APC is their compatibility with Mg anode. In these electrolytes, the formation of blocking layers on Mg surface can be prevented, so that the reversible Mg deposition/stripping on the Mg anode side can be realized.^[39,230] However, these electrolytes are expensive, toxic and difficult to be synthesized. The most important limitation of these electrolytes is their low anodic stability (≤ 3.0 V vs Mg²⁺/ Mg), which restricts the energy density of assembled batteries. High-voltage electrolytes based on conventional solvents and simple Mg salts are not compatible with Mg anode due to the poorly conductive or even nonconductive blocking layers formed on Mg surface. To solve this problem, a new strategy through the modification of electrode-electrolyte surface is recently proposed, especially by controlling the formation of solid electrolyte interface (SEI).

For example, Wang et al. conducted the experiments through the addition of iodine into electrolyte to form a conductive magnesium iodide layer instead of passivation layer.^[231] XPS results indicate the formation of MgI₂ layers on the Mg electrode when the iodine concentrations in Mg(TFSI)₂/dimethoxyethane (DME) electrolyte is higher than 5×10^{-3} M. The EIS measurements of Mg anode show that the overall resistance (R_{ct} and R_{SEI}) drops by 3 orders of magnitude, which gives direct evidence of the reduced overpotential for Mg electrode. To give further information about the effect of iodine on cathode, the Mg/S full cell is fabricated. By the comparison of charge/discharge curves, the battery with iodine in the electrolyte displays a much lower voltage hysteresis of 0.67 V (1.69 V in the blank electrolyte), which can be ascribed to the lower Mg deposition/ stripping overpotential. This work demonstrates that the Mg anode performance as well as the overall battery performance is largely influenced by the surface chemistry and the composition of SEI. Luo et al. fabricated a Ge-based protection layer on Mg anode surface through the addition of GeCl₄ in ether electrolyte.^[232] This protection layer can effectively avoid the formation of passivation layer on Mg anode and the reversible Mg dissolution-deposition is realized. It is worth noting that the composition of the layer is stable during long charge/

discharge cycling. The authors also assembled the Mg/TiS2 and Mg/Ti₃C₂ full cell in Mg(TFSI)₂/DME electrolyte with GeCl₄ addition. A deeper investigation and more direct evidence on the importance of electrode-electrolyte surface have been presented by Ban and co-workers.^[233] They conducted an artificial Mg²⁺-conducting interface (originated from polyacrylonitrile and Mg trifluoromethanesulfonate) on the Mg anode surface, which was elastic and can accommodate the drastic volumetric change, therefore, leading to an enhanced reversibility of Mg deposition/stripping kinetics. The STEM, HAADF, and EDS mapping results indicate the successful coating of the artificial interphase and give a direct observation of the thin film with about 100 nm in thickness. In comparison, the reversibility of Mg deposition/stripping on bare Mg and coated Mg were performed in four different electrolytes (Figure 20). In APC electrolyte, both the coated Mg and uncoated Mg show reversibility of Mg deposition/stripping process (Figure 20a). However, in Mg(TFSI)₂/PC system, the bare Mg exhibits a high increased overpotential (>1.0 V) due to the formation of blocking layers (Figure 20b,c). The electrochemical performance of coated Mg was tested at very low current density (0.01 mA cm⁻²) and low specific capacity was obtained. The authors gave an analysis about the structure of artificial interphase by the time-of-flight secondary-ion mass spectrometry and TGA, however, the adequate structure or component is not given. The EIS analysis shows that the artificial interphase has a high ionic conductivity of about $1.19\times 10^{-6}~S~cm^{-1}$ which has not much difference with that of Li⁺-polymer electrolytes.^[234] The electrochemical performance was performed in Mg(TFSI)2/PC electrolyte (with and without water) against an orthorhombic V2O5 cathode. More importantly, the coated Mg/V2O5 full cell shows much better cycling stability, especially in Mg(TFSI)₂/PC + H₂O electrolyte (Figure 20d,e). The coated Mg demonstrates much higher capacity and superior cycling stability than that of pristine Mg anode. Specifically, more experiments should be conducted to exclude the reversible proton insertion rather than Mg²⁺ in such high water content electrolyte.^[133] The above works make it possible to use a Mg anode in conventional electrolytes with both fast kinetics and better reversibility of the divalent Mg²⁺ deposition/stripping. It is a big step for the development of high energy density and high power density RMBs. However, it is challenging to synthesize the desired SEI layer on Mg surface, which should guarantee the reversible Mg2+ deposition and stripping, prevent the reduction of electrolyte, and maintain the structure stability during cycling.

3. Summary and Perspectives

In summary, RMBs are a promising candidate owing to the high safety, low-cost, and high natural abundance of Mg metal. However, the development of RMBs is strongly impeded by the slow solid-state-diffusion of Mg^{2+} in cathodes, the lack of high-performance electrolytes and the difficulty of using Mg anodes. In this review, we have presented seven optimization strategies proposed in the literature, including the modification of cathodes and anodes. Generally, doping ions, nano-structure construction and composite fabrication are frequently effective modification methods to improve the electrochemical





Figure 20. a) The reversible of Mg deposition/stripping test of both coated Mg and pristine Mg in APC electrolyte and b) in Mg(TFSI)₂/PC electrolyte. c) The long cycling reversibility for 1000 h of Mg deposition/stripping in Mg(TFSI)₂/PC electrolyte. d) Full-cell cycling performance of Mg–V₂O₅ in different electrolytes, the content of H₂O is 3 M. e) Voltage profiles of coated/bare Mg–V₂O₅ in 0.5 M MgTFSI₂/PC + 3 M H₂O electrolyte. Reproduced with permission.^[23] Copyright 2018, Springer.

performance of RMBs. The approaches of changing the crystal form and charge shielding are widely adopted in V-, Ti-, and Mn-based cathodes, and rarely reported for other material systems. Although numerous of experimental and computational investigations have been conducted on organic molecule preintercalation, the selection of specific organic materials and the corresponding host structures are still full of challenges. The newly developed modification strategy of electrode–electrolyte interface optimization can realize the Mg plating/stripping on Mg anode in simple Mg salt electrolyte, but the construction of the ideal protection layer on Mg surface is rather difficult. It is challenging to select an adequate strategy to improve the overall performance of RMBs due to the complex interplay and incompatibility of unique cathode, anode and electrolyte. On the other hand, combining two or three of these strategies is another promising direction. The application of multiple strategies in oxides (V_2O_5 , MnO_2), sulfides (TiS_2 , CuS) has proved to be an effective method, more effort are still needed to improve the Mg-storage performance of organic materials, polyanions, Prussian blue analog and so forth. We suggest future emphasis should focus on the development of new innovative approaches toward the utilization of Mg metal anode and the extension of existed strategies to high voltage materials. Furthermore, the high energy density magnesium–sulfur battery is a promising direction due to the high capacity, acceptable operating voltage of S cathode. In addition, the investigation of novel electrolytes with noncorrosive properties is also critical, for which govern the select of electrode materials and current collectors. More experimental and theoretical efforts on the above mentioned aspects are still needed to realize high-energy RMBs.

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Conflict of Interest

The authors declare no conflict of interest.

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