Review Article

Mg-Li Hybrid Batteries: The Combination of Fast Kinetics and Reduced Overpotential

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It is imperative for the development of cost-effective and high-performance batteries. Currently, lithium-ion batteries still occupy most of the market. However, limited lithium (Li) resource and energy density retard their further development. The magnesium (Mg) metal has several significant advantages; those make it a viable alternative to Li as anode, including high volume specific capacity and dendrite-free plating during cycling and high abundance. The Mg-Li hybrid batteries can combine the advantages of Li ion and Mg metal to achieve fast electrode kinetics and smooth anode deposition morphology. This review summarizes recent progresses in cathode material design and anode interface modification for Mg-Li hybrid batteries. We aim to illustrate the contribution of Li⁺ to the electrochemical performance improvement at both cathode and anode sides and to provide inspiration for the future research in this field.

1. Introduction

The world energy structure is gradually shifting from fossil fuels to clean and renewable energy. Various countries also have corresponding programs, such as restricting the sales of traditional fuel vehicles and releasing green-car subsidy program to boost the application of new energy vehicles. These developments are inseparable from advanced energy storage and conversion devices. Lithium-ion batteries (LIBs) have dominated the market of portable electronic devices and electric vehicles due to the long life and stability since its launch. However, the limited Li resources and theoretical specific capacity (based on graphite anode) make LIBs unable to meet the future demand for energy storage systems. The utilization of lightweight metals (e.g., Li and Mg) as anodes is an inevitable trend for future energy storage systems to increase energy density. The high intrinsic

reactivity and instability of Li metal with air and moisture make processing and storage more difficult. The Li resources are not abundant in the earth's crust and unevenly geographically distributed, greatly leading to higher costs. In addition, there is a tendency of dendritic growth during the electrochemical deposition of Li, resulting in the dendrite penetration across separator and even a fatal short circuit of the cell. Although Mg exhibits higher redox potential (−2.37 V vs. standard hydrogen electrode, SHE) than Li (−3.04 V vs. SHE), the energy density of Mg metal batteries (MMBs) is compensated due to the doubled electron exchange per charge carrier. The gravimetric and volumetric capacities of Mg metal are as high as 2205 mA h g^{−1} and 3833 mA h cm^{−3}, respectively. Moreover, Mg-based technology also has received increasing attention due to the natural abundance and low cost of Mg metal. More specially, Mg is the fifth most abundant metal in the earth's crust (cost less

than 1/30 of Li) with excellent operation safety and smooth deposition morphology due to low self-diffusion barrier. Thus, MMBs are attractive candidates for large-scale energy storage systems.

It has been estimated that the volumetric energy density of Mg pouch cell (based on 50% excess Mg metal anode and Mo_6S_8 cathode) can reach 790 Wh L^{-1} , which can exceed that of LIBs (based on graphite anode and LiCoO_2 cathode), confirming the practical value of MMBs [1]. Although considering the potential advantages of MMBs in terms of cost and energy density, there are still several key factors that hinder the progress of MMBs towards application. The current challenge is twofold [2]: (1) Mg metal anode is incompatible with most electrolytes, and the electrolyte is reduced by Mg to form a passivation film on the anode surface that obstructs the migration of Mg^{2+} . (2) The divalent Mg^{2+} has a high charge density, and a strong binding force with anions and solvents, resulting in higher energy, is needed to desolvate and overcome the high diffusion barrier. Thus, the diffusion kinetics of Mg^{2+} in the electrode is relatively slow, and its high polarity easily damages the cathode structure, leading to poor electrochemical behavior.

To overcome the above obstacles, more electrolyte and cathode materials have been developed. For example, in 2000, Aurbach et al. reported a long-term cycling Mg full cell coupled with a Chevrel phase Mo_6S_8 cathode in a Grignard-based electrolyte [3]. However, the high Mg^{2+} migration barrier in solid state structures has not been solved. In order to design a multivalent metal battery system with a high energy density and high rate capability, in 2014, based on the classical Daniel battery model (Figure 1(a)), Yagi et al. proposed a dual-salt polyvalent-metal storage battery system (Figure 1(b)) [4]. Some candidates for anode and cathode materials in dual-salt system and the electromotive force (emf) values displayed by the corresponding combination are shown in Figure 1(c). The Mg-Li hybrid system delivers a suitable emf value and simultaneously combines the rapid diffusion of Li^+ in the cathode and the nondendritic deposition of Mg on the anode. The addition of Li^+ can activate the Mg-based battery system by improving the kinetics, broaden the choice of cathode materials, and also provide a new avenue for the future development of MMBs. After the proposal of a concept of Daniel-type hybrid batteries, Ichitsubo et al. then put forward a concept of “rocking-chair type” hybrid batteries [5]. They used a spinel oxide MgCo_2O_4 as cathode that allows the insertion of both Li^+ and Mg^{2+} . Based on a three-electrode beaker cell configuration, this concept was confirmed, though Mg anode is quickly passivated in the ionic liquid- (IL-) based electrolyte. Although this system is operated at 150°C , it also provides inspiration for the design of the Mg-Li hybrid batteries.

In the review, the promotion effects of Li^+ on the cathode and anode sides in Mg-Li hybrid batteries are discussed, such as improving high-rate cycling and low temperature performance and reducing the overpotential of Mg deposition/dissolution. Furthermore, the electrochemical performance of some examples in Mg-Li hybrid systems is

compared, and corresponding drawbacks and advantages are highlighted. We aim to illustrate the design and practicality of Mg-Li hybrid batteries and provide inspiration for further research in this field.

2. Mg-Li Hybrid Electrolyte

Mg-Li hybrid electrolytes are usually obtained by the addition of Li salt into Mg salt electrolyte. In this section, we will briefly introduce the formulation and corresponding electrochemical properties of several typical Mg-Li hybrid electrolytes.

As early as 2006, Gofer et al. confirmed that LiCl could improve the ionic conductivity of Mg electrolyte solutions [6]. In 2014, Yagi et al. introduced 0.2 M LiBF_4 into 0.5 M all-phenyl-complex (APC) and proposed the concept of dual-salt battery⁴. Unfortunately, BF_4^- may react with PhMgCl to form B(Ph)_4^- , which reduces the electrochemical window of the electrolyte to $\sim 2.5 \text{ V}$. So far, the most widely used Mg-Li hybrid electrolyte is still the combination of APC and LiCl. Cheng et al. added 1.0 M LiCl to 0.4 M APC in THF to obtain an Mg-Li hybrid electrolyte [7]. In the electrolytes containing LiCl, Li^+ intercalation is the main cathode reaction. Due to the excellent kinetics of Li^+ , the rate performance and cycle stability of the full cell with Mo_6S_8 cathode have been significantly improved. Cho et al. prepared a hybrid electrolyte by adding an appropriate amount of LiCl (0.1 M, 0.3 M and 0.5 M) in the diluted 0.2 M APC solution to precisely control the insertion chemistry [8]. For the electrolytes with LiCl content less than or equal to 0.3 M, the cointercalation of Mg^{2+} into the Mo_6S_8 cathode weakens the rate performance. When the LiCl concentration is increased to 0.5 M, the magnesiation can be completely suppressed and the full lithiation up to $\text{Li}_4\text{Mo}_6\text{S}_8$ can be reached. They also confirmed the relationship between the insertion chemistry at the cathode and the Li^+ activity in the electrolyte through calculations. As shown in Figure 1(d), by increasing the Li^+ activity, the Li^+ insertion potential can rise above the Mg^{2+} insertion potential to control the intercalation chemistry at the cathode side. And due to the decrease of Li^+ activity in the electrolyte during the discharge, the Li^+ activity must be increased to 1 in order to completely suppress Mg^{2+} insertion.

For $\text{Mg}(\text{BH}_4)_2$ -based electrolyte, it has been demonstrated that LiBH_4 addition can improve the coulombic efficiency (CE) [9]. Shao et al. further explored the influence of the concentration of LiBH_4 and different solvent on the performance in the case of 0.1 M $\text{Mg}(\text{BH}_4)_2$ electrolyte [10]. Taking the diglyme (DGM) solvent as an example, as the concentration of LiBH_4 increases, the kinetics of Mg plating/stripping is significantly enhanced due to the synergistic effect of chelating solvent and increased BH_4^- concentration. When the LiBH_4 concentration is 1.5 M, the current density reaches the maximum.

Cheng et al. investigated the regulation of Li salt on electrolyte chemistry [11]. They chose a series of Li salts of LiAlCl_4 , LiTFSI , LiCl , and LiPF_6 to add into 0.2 M $[\text{Mg}_2\text{Cl}_2(\text{DME})_4][\text{AlCl}_4]_2$ electrolyte to obtain dual-salt electrolytes with a targeted Li^+ concentration of 0.4 M. LiCl and

FIGURE 1: (a) Schematic illustration of classical Daniel battery. (b) Schematic illustration of septum-free dual-salt polyvalent-metal storage battery (PSB) model based on Daniel battery. (c) Examples of negative and positive electrode materials for the proposed PSBs [4]. (d) Lithiation and magnesiation potentials of Mo_6S_8 (vs. Mg/Mg^{2+}) at different Li^+ activities (a_{Li^+}) [8].

LiPF_6 cannot be completely dissolved, while LiTFSI exhibits superior solubility up to 2 M. Adopting 0.4 M LiAlCl_4 enhanced Mg electrolyte and LiFePO_4 or LiMn_2O_4 cathode loaded on Mo current collector enables the design of high voltage Mg-Li hybrid batteries.

In addition, LiTFSI was also often used as a Li source for other dual-salt electrolytes, especially in combination with nonnucleophilic Mg electrolytes, such as magnesium-bis(hexamethyldisilazide) (Mg-HMDS) [12]. There are also the combinations of $\text{MgCF}_3\text{SO}_3 + \text{LiCF}_3\text{SO}_3$ as well as

magnesium aluminate chloride complex (MACC) + LiCl for the Mg-S systems [13, 14].

3. Influence of Li^+ on Cathode in Mg-Li Hybrid Systems

Although the radii of Mg^{2+} and Li^+ are not much different, Mg ions are given slow kinetics of insertion into inorganic hosts due to the divalent character. Therefore, using Li^+ instead of Mg^{2+} to insert into the cathode host can increase the current density of battery operation and improve rate performance. In addition, the introduction of Li^+ can mitigate the size dependency of electrochemical kinetics, whereas a faster and more effective intercalation of Mg^{2+} was observed in the same material with nanosized particles than micron-sized particles. Next, we will introduce some examples of the improvement of cathode materials in the Mg-Li hybrid system, especially the reaction mechanism and the improvement of rate performance.

3.1. Enhanced Rate Performance and Cycle Stability. Similar to LIBs, the intercalation is also one of the important charge-storage mechanisms in the Mg-Li hybrid system. The research on intercalation-type materials in Mg-Li hybrid tends to embrace classical Chevrel phase Mo_6X_8 (X=S, Se, or their combination), layered structures like typical TiS_2 , TiO_2 , and V_2O_5 , and intercalation compounds which have been proven to be suitable electrode materials in Li battery systems, such as LiFePO_4 . There is almost no obvious structural change in the appropriate amount of Li^+ or Mg^{2+} intercalation/de-intercalation except inevitable volume expansion. The structural peculiarities of intercalation-type cathodes contribute to the highly reversible storage process and superior cycling stability.

Chevrel phase Mo_6S_8 as a classic cathode material for rechargeable Mg batteries has received widespread attention once it came out. For Mg-Li hybrid batteries, the intercalation mechanism of Mo_6S_8 has also been deeply investigated by several research groups. In the previous section, the influence of Li^+ concentration in the APC electrolyte on the selectivity of Mo_6S_8 to lithiation or magnesiation has been introduced. Cheng et al. combined the advantages of Mg anode and dual-salt electrolyte to obtain the outstanding rate performance of Mo_6S_8 (105 mA h g^{-1} at 15°C) [7]. For $\text{Mg}(\text{BH}_4)_2$ - LiBH_4 -DGM electrolyte, Shao et al. reported that an initial capacity of 99.5 mA h g^{-1} at C/10 rate with a 89.7% capacity retention for 300 cycles is governed by reversible Mg^{2+} insertion/deinsertion on Mo_6S_8 [10]. For the 0.1 M $\text{Mg}(\text{BH}_4)_2$ system with different solvents, the addition of LiBH_4 shows an increase in CE. And as the concentration of LiBH_4 increases, the CE value of the corresponding electrolyte also increases. The effect of LiBH_4 on electrochemical performance seems to be focused on changing Mg electrochemistry by BH_4^- rather than Li^+ to promote the Mg deposition/dissolution. The unique solvation structures endow the $\text{Mg}(\text{BH}_4)_2$ electrolyte with the differentiated CE values in different solvents. Compared with THF and DME solvents, DGM is both thermodynamically and kinetically favorable in the Mg stripping process. BH_4^- acts as the sec-

ond coordination, and the increased concentration of BH_4^- accelerates the Mg stripping by prompting the formation of coordination structures (e.g., $\text{Mg}(\text{BH}_4)_2\text{DGM}$, $\text{Mg}_2(\text{BH}_4)_4(\text{DME})_3$, and $\text{Mg}(\text{BH}_4)_2(\text{THF})_3$).

Layered MoS_2 is considered an attractive host for ion intercalation due to weak van der Waals' interaction between layers and the large interlayer distance. Hsu et al. demonstrated that commercial micron-scale MoS_2 could accommodate both Mg^{2+} and Li^+ after the phase transition induced by Li^+ -intercalation [15]. A plateau at 0.2 V in the first discharge is observed, corresponding to the phase transition from 2H-MoS_2 to 1T-MoS_2 [16]. In the subsequent cycles, a reversible capacity is 160 mA h g^{-1} at 25 mA g^{-1} . They also constructed an effective electronic conducting network by ball-milling MoS_2 with carbon nanotubes (CNT) or graphene nanosheets. Due to the improved charge transfer ability, the MoS_2/CNT and $\text{MoS}_2/\text{graphene}$ composite cathodes deliver the discharge capacities of $\sim 200 \text{ mA h g}^{-1}$ and $\sim 225 \text{ mA h g}^{-1}$, respectively. By constructing a sufficient electronic wiring network and hierarchical conductive structure, the performance of the cathode materials can be further improved. Hou et al. designed a hollow opening nanoflower (HONF) MoS_2 -CuS-EG electrode by a facile hydrothermal method [17], combining the high-conductivity CuS and expanded graphite (EG) with large pores. CuS facilitates electron transport and contributes to a small amount of capacity (9.46%). EG can alleviate volume expansion and improve cycle stability. And MoS_2 nanosheets with enlarged layer spacing make Li^+ intercalation easier.

Layered TiS_2 is also identified as a possible candidate for Mg-Li hybrid batteries because of its high capacity (240 mA h g^{-1}) and suitable voltage ($1.0\sim 1.6 \text{ V}$ vs. Mg/Mg^{2+}). Gao et al. studied the commercial micron-sized TiS_2 as cathode in Mg-Li hybrid batteries [18]. They found that there is only Li^+ intercalation into micron-sized TiS_2 in the dual-salt electrolyte. Owing to the superior reversibility of TiS_2 , a specific capacity of 161 mA h g^{-1} with a CE value as high as 99.5% is observed for at least 400 cycles with no capacity fade at C/3 rate. As shown in Figure 2(a), Yoo et al. also demonstrated that the performance of TiS_2 in Mg-Li hybrid batteries is better than that in Li metal batteries (LMBs) with high active material loading ($8.0 \pm 0.5 \text{ mg cm}^{-2}$) at 1 C ($=2 \text{ mA cm}^{-2}$) [19]. Due to the formation of Li dendrite, the reference Li battery suffers the fast capacity decay. The cross-sectional SEM image of Mg anode in Figure 2(b) shows the single-layer SEM image of Mg deposits with an average size of $\sim 100 \mu\text{m}$. Benefitting from the dendrite-free deposition of Mg anode, Mg-Li hybrid batteries have been confirmed to be new opportunities for their application in large-scale energy storage under practical high current and high areal capacity conditions.

Similarly, other layered sulfides can also be applied in the Mg-Li hybrid system. Sun et al. reported the performance of VS_2 nanosheet cathode in Mg-Li hybrid batteries [20]. VS_2 has a layered structure with a layer spacing of $5.76 \text{ \AA}$, composed of a metal vanadium layer between two sulfide layers to form a sandwich S-V-S structure. In a hybrid system, Li^+ intercalation/deintercalation is dominant at the cathode side during the electrochemical process. They also made

FIGURE 2: (a) Comparison of discharge capacities as a function of cycle number between Li-anode cell and Mg-metal hybrid cell. (b) Cross-sectional SEM image of Mg metal anode after plating [19]. (c) Rate performance comparison between VS₂-GO and VS₂. (1 C = 180 mA g⁻¹) [20]. (d) Comparison of rate capabilities of LTO electrodes in the electrolytes with and without LiCl [26]. (e) Cycle performance and (f) corresponding charge-discharge curves of LVP||APC-LiCl||Mg cells at room and lower temperatures (0, -10, -20, -30, and -40°C) at 100 mA g⁻¹ [42]. (g) Cyclic voltammogram curve of TiNb₂O₇ in hybrid Mg-Li batteries at room temperature at 0.1 mV s⁻¹; the colored area represents capacitive charge contribution [46]. (h) Discharge capacity of TNb₂O₇ in Li and hybrid Mg-Li batteries at 20°C (1550 mA g⁻¹) at 60°C, together with schematic diagram of Li⁺ intercalation [47].

the further improvement by wrapping VS₂ with graphene (VS₂-GO) to construct a conductive network. The VS₂-GO cathode exhibits an outstanding high-rate capacity of 129 mA h g⁻¹ at 80°C (1 C = 180 mA g⁻¹, Figure 2(c)) and long life (146 mA h g⁻¹ after 10000 cycles at 5 C). And it is estimated that the energy density of this hybrid system can reach up to 353 Wh kg⁻¹. The crystal structure of VS₄ con-

sists of V⁴⁺ ions coordinated to sulfur dimers (S₂²⁻) extending along the c axis, and the distance between atomic chains is 5.83 Å. And VS₄ has been demonstrated to have the ability to allow Mg²⁺ diffusion and storage due to linear open channels and sufficient S₂²⁻ active sites [21]. Wang et al. reported VS₄ nanodendrites as cathode for Mg-Li hybrid batteries [22]. Not only it is observed that Mg²⁺/Li⁺ cointercalation

occurs on the cathode side, but also the inductively coupled plasma optical emission spectrometer (ICP-OES) and electrochemical results indicate that the capacity contribution of Mg^{2+} storage is much higher than that of Li^+ , which is different from other $\text{Mg}^{2+}/\text{Li}^+$ coinsertion cathode materials. Although Li^+ contributes little to the capacity, Li^+ significantly accelerates the reaction kinetics; thus, the activation process is not observed during the initial cycles in the Mg-Li hybrid system. Benefitting from fast kinetics, the VS_4 cathode delivers a high reversible capacity of $\sim 300 \text{ mA h g}^{-1}$ at 100 mA g^{-1} and long-term cycling stability (110 mA h g^{-1} after 1500 cycles at 1000 mA g^{-1}).

Titanium-based materials have been reported as a class of alternative materials for anode of LIBs [23], such as TiO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO). Su et al. reported a Mg-Li hybrid battery with a Mg anode, a commercial anatase TiO_2 as cathode, and a $0.5 \text{ M Mg}(\text{BH}_4)_2$ - 1.5 M LiBH_4 /tetraglyme electrolyte [24]. They obtained an initial discharge capacity of $155.8 \text{ mA h g}^{-1}$, which decreases to $\sim 140 \text{ mA h g}^{-1}$ after 90 cycles at a rate of 0.2 C ($1 \text{ C} = 168 \text{ mA g}^{-1}$). Spinel LTO is considered a “zero-strain” material for Li and Mg insertion with only 0.2% and 0.8% change in the lattice constant, respectively [23, 25]. Wu et al. confirmed the coinsertion of Mg^{2+} and Li^+ into LTO through DFT calculations and experiments [26]. For the LTO nanoparticle ($>100 \text{ nm}$) electrode, there is the existence of a threshold Li^+ activity. Using the optimized 0.25 M APC - 0.25 M LiCl electrolyte, they obtained a reversible capacity of $\sim 175 \text{ mA h g}^{-1}$, where the intercalation of Mg^{2+} contributes more than 90 mA h g^{-1} . As shown in Figure 2(d), the introduction of Li^+ not only avoids the initial activation process but also improves the rate performance to 120 mA h g^{-1} at 300 mA g^{-1} . Miao et al. reported the Mg-Li hybrid batteries based on commercial LTO cathode with $0.5 \text{ M Mg}(\text{BH}_4)_2$ - 1.5 M LiBH_4 /tetraglyme and 0.4 M APC - 1.5 M LiBH_4 /THF electrolyte [27]. Due to lower overpotential and higher CE, the APC-based electrolyte system shows the better cycling performance. In addition, the Mg storage behavior of LTO cathode has a size dependence effect, resulting in negligible Mg^{2+} intercalation into commercial LTO used in this study. The conductivity of LTO can be further improved by doping at the Ti^{4+} sites with Fe^{3+} , Ni^{3+} , Al^{3+} , or Cr^{3+} . Yao et al. evaluated LiCrTiO_4 spinel as cathode for Mg-Li hybrid batteries [28]. Only Li^+ intercalation into the high-temperature synthesized LiCrTiO_4 is observed. LiCrTiO_4 exhibits a reversible capacity of $\sim 170 \text{ mA h g}^{-1}$ at 20 mA g^{-1} in 0.3 M APC - 1 M LiCl . Due to the lower operating voltage, titanium-based materials may not meet the demand for high-energy-density Mg-Li hybrid batteries.

Manganese oxides are reported as electrode materials with various structures, such as tunnel-type $\alpha\text{-MnO}_2$ (e.g., hollandite with a 2×2 tunnel and todorkite with a 3×3 tunnel), layered birnessite-type MnO_2 and spinel MnO_2 . For MMBs, MnO_2 cathode materials suffer poor capacity retention due to irreversible phase transition. Asif et al. prepared birnessite-type Ni-doped MnO_2 nanoflakes on CNT to improve electrochemical performance [29]. The optimized cathode delivers a maximum specific capacity of 175 mA h g^{-1} at 20 mA g^{-1} . Together with limited high-rate capacity ($\sim 60 \text{ mA h g}^{-1}$ at 1 A g^{-1}) and low voltage plateaus,

the prescribed cathodes are not a suitable choice for Mg-Li hybrid batteries. Then, Asif et al. prepared a ternary transition metal oxide $(\text{NiMnCo})_3\text{O}_4$ with the morphology of multishelled hollow spheres by a hydrothermal method and thermal treatment [30]. The $(\text{NiMnCo})_3\text{O}_4$ cathode exhibits an extraordinary reversible capacity of 550 mA h g^{-1} at 50 mA g^{-1} as well as a remarkable energy density (368 Wh kg^{-1}) and cycle life (277 mA h g^{-1} after 100 cycles) at 100 mA g^{-1} . Although the magnesiation/demagnesiation process is observed in APC electrolyte, the following Li^+ insertion reaction still dominates in the hybrid electrolyte: $x \text{ Li}^+ + x \text{ e}^- (\text{NiMnCo})_3\text{O}_4 \rightarrow \text{Li}_x(\text{NiMnCo})_3\text{O}_4$. Lithium manganese oxide with a high discharge voltage platform ($>2.0 \text{ V}$ vs. Mg/Mg^{2+}) is a family of promising cathode for high energy density Mg-Li hybrid batteries. Pan et al. investigated the electrochemical behavior of LiMn_2O_4 in two chloride-free hybrid electrolytes, namely, $\text{Mg}(\text{TFSI})_2$ - LiTFSI and $\text{Mg}(\text{CB11H}_{12})_2$ - LiTFSI [31]. LiMn_2O_4 exhibits an initial capacity of 106 mA h g^{-1} with a working voltage of $\sim 2.8 \text{ V}$, corresponding to Li^+ intercalation. However, the capacity fading in Mg-Li hybrid system is fast, and further optimization is needed. It is reported the Mn^{3+} suffers Jahn-Teller distortion and disproportionation reaction ($\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$), resulting in the structural collapse. Li-rich $\text{Li}_4\text{Mn}_5\text{O}_{12}$ with stable Mn^{4+} provides a theoretical capacity of 163 mA h g^{-1} . Cen et al. synthesized spinel $\text{Li}_4\text{Mn}_5\text{O}_{12}$ nano/microspheres via a hydrothermal and lower temperature sintering method and investigated its performance for Mg-Li hybrid batteries [32]. Due to the smaller lattice constant of $\text{Li}_4\text{Mn}_5\text{O}_{12}$, it is more difficult for Mg^{2+} or solvated MgCl^+ to diffuse in host, so only Li^+ intercalation occurs at the cathode side. Benefitting from nano/microhierarchical architecture and open 3D Li^+ channels, the $\text{Li}_4\text{Mn}_5\text{O}_{12}$ cathode exhibits a reversible capacity of 155 mA h g^{-1} at 0.1 C and the corresponding Mg-Li hybrid system has a high energy density of 326 Wh kg^{-1} .

Vanadium dioxide (VO_2) can offer a relatively high operating voltage ($\sim 2.5 \text{ V}$ vs. Li/Li^+ , $\sim 1.75 \text{ V}$ vs. Mg/Mg^{2+}) in the Mg-Li hybrid system to increase energy density. Pei et al. synthesized VO_2 nanoflakes through a hydrothermal method and investigated its performance in Mg-Li hybrid batteries [33]. It should be noted that since excessive Li^+ insertion damages the VO_2 structure, a suitable voltage window (0.5 – 2.0 V) could improve the cycle stability, and it corresponds to the discharge product of Li_xVO_2 ($x = 0.78$). The VO_2 nanoflakes exhibit a high discharge capacity of $206.8 \text{ mA h g}^{-1}$ and a capacity retention of 75% (after 100 cycles) at 100 mA g^{-1} . Vanadium pentoxide (V_2O_5) has abundant reserves and unique electrochemical storage properties. With different amounts of Li^+ inserted, V_2O_5 shows different capacity retentions due to the reversible or irreversible phase formation [34]. Yoo et al. observed one equivalent Li^+ insertion into V_2O_5 in 0.25 M APC - 0.25 M LiCl [35]. And it has been confirmed that V_2O_5 and MoO_3 allow a reversible Mg-ion intercalation. Based on this, Miao et al. reported layered vanadium-molybdenum-oxides V_2MoO_8 (VMO) with a high theoretical capacity of 493 mA h g^{-1} as cathode in Mg-Li hybrid batteries [36]. According to the result by ICP, after the first discharging, the cathode

becomes $\text{Mg}_{0.7}\text{Li}_{2.39}\text{V}_2\text{MoO}_8$, but the insertion of Li^+ and Mg^{2+} into the VMO structure is partially irreversible, resulting in a relatively low initial CE (87.15%). Although the initial discharge capacity is up to 312 mA h g^{-1} at 20 mA g^{-1} , the relatively poor retention is worrying. The Mg-Li hybrid electrolyte also can boost up the capacity of $\text{NaV}_3\text{O}_8 \cdot 1.69 \text{ H}_2\text{O}$ from 110 mA h g^{-1} (at 10 mA g^{-1} for pure Mg electrolyte system) to 446 mA h g^{-1} (at 20 mA g^{-1}) [37]. Pan et al. prepared a hollow MoO_2 microsphere and evaluated it as cathode for Mg-Li hybrid batteries [38]. Both Mg^{2+} and Li^+ intercalations occur on the cathode side, and Li^+ contributes more capacity. In view of limited capacity (an initial discharge capacity of $217.2 \text{ mA h g}^{-1}$ with the CE of 88% at 20 mA g^{-1}) and operating voltage ($\sim 0.8 \text{ V}$), compared with other batteries described in this review, batteries using MoO_2 as cathode do not have the value of continuing research.

The sodium superionic conductor (NASICON) $\text{N}_x\text{M}_2(\text{PO}_4)_3$ (M = transition metal and N = Li or Na) structure has been considered a promising electrode due to the existence of 3D large open framework that allows facile ion diffusion. $\text{LiTi}_2(\text{PO}_4)_3$ (LTP) has been investigated in aqueous LIBs. It has a high insertion voltage of 1.71 V (vs. Mg/Mg^{2+}) and can provide a relatively high theoretical energy density ($\sim 240 \text{ Wh kg}^{-1}$). Xu et al. prepared carbon-coated $\text{LiTi}_2(\text{PO}_4)_3$ microflowers (LTP-C) by a solvothermal method and subsequent annealing treatment [39]. The well-designed 3D hierarchical structure of LTP-C offers more efficient pathways for electron/ion transport, and especially, the 3D carbon skeleton significantly improves the charge-transfer kinetics. Thus, the LTP-C cathode delivers a reversible capacity of 136 mA h g^{-1} and a capacity retention of 94.0% after 400 cycles at 1 C , when assembled with Mg anode in APC-LiCl electrolyte. Moreover, the energy density of this hybrid system is estimated to be 220 Wh kg^{-1} . Sun et al. investigated the electrochemical performance of two iron Prussian blue analogue (PBA) cathodes with different hydration water contents ($\text{Fe}[\text{Fe}(\text{CN})_6]_{0.95} \cdot 2.3 \text{ H}_2\text{O}$ and $\text{Fe}[\text{Fe}(\text{CN})_6]_{0.95} \cdot 0.7 \text{ H}_2\text{O}$, denoted as 23-PBA and 07-PBA, respectively) coupled with an APC-LiCl dual-salt electrolyte and a Mg anode [40]. Due to strong π -backbonding, cyanoligands improve the chlorination resistance of PBA. PBA is a cubic structure with an open framework and large interstitial sizes to allow smooth ion intercalation. Both the PBA materials were performed in dual-salt electrolyte of 0.2 M APC and LiCl with different concentrations in three-electrode cell configuration at a current density of 10 mA g^{-1} . When the LiCl concentration increases up to 0.5 M , the highest discharge capacity attained is 125 mA h g^{-1} for both 23-PBA and 07-PBA. Unlike the case that Li^+ concentration affects the insertion mechanism of Mo_6S_8 , whether the presence or absence of Li^+ in the electrolyte, Mg^{2+} will not intercalate into the PBA structures from APC electrolyte. Long-term cycling of both materials was tested in coin cells at 200 mA g^{-1} , and 07-PBA exhibits the higher discharge capacity and better stability (65 mA h g^{-1} after 300 cycles). The release of more structural water into the electrolyte degrades the performance of 23-PBA. Despite the fact that the release of structural water may weaken electrochemical performance during cycling, it has a beneficial effect on the operating voltage.

3.2. Improvement of Low-Temperature Performance by Dual-Salt Electrolyte. In addition to the electrochemical performance in the conventional environment, the evaluation of low-temperature performance of battery is also of great significance. The low-temperature batteries can be used to design special energy storage devices for aerospace and deep-sea exploration and military missions. It is worth mentioning that THF with low viscosity and melting point makes THF-based dual-salt electrolyte have a natural advantage in extremely low temperature environment. In addition, LiCl also plays a significant role in resisting the freezing of solution, and as its concentration increases, the freezing point is lower. Thanks to the perfect combination of APC/THF and LiCl, Mg-Li hybrid batteries exhibit low-temperature performance that should be worthy of further development. But currently, there are only two reports about the low temperature performance on polyanion-compound cathode materials.

LiFePO_4 (LFP) as a classical cathode for LIBs is also investigated in Mg-Li hybrid system. When the prototype of the Mg-Li hybrid system was born, Yagi et al. tried to use LFP as cathode to confirm the concept of the dual-salt system [4]. Unfortunately, limited by the narrow electrochemical window ($\sim 2.5 \text{ V}$ vs. Mg), the charge capacity is only 60 mA g^{-1} . Subsequently, Zhang et al. adopted a pouch cell configuration based on LFP cathode, a flexible pyrolytic graphitic film as a current collector and APC-LiCl electrolyte to obtain an Mg-Li hybrid battery with a maximum energy density of 382.2 Wh kg^{-1} [41]. Notably, at 0°C , the LIB based on carbonate-based electrolyte still shows a slight advantage in capacity, and when the temperature is lower (from -10 to -40°C), the hybrid system outperforms its LIB counterpart. Rashad et al. tested $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) in $\text{Mg}(\text{BH}_4)_2$ - LiBH_4 /diglyme and APC-LiCl/THF electrolytes [42]. The performance of LVP at room temperature (with a reversible capacity of $147.8 \text{ mA h g}^{-1}$ at 50 mA g^{-1}) is not as good as other cathodes mentioned in this review; nevertheless, it can operate at lower temperature (from 0 to -40°C) and may be applied under extreme conditions. As shown in Figures 2(e) and 2(f), the low temperature performance of APC-LiCl/THF hybrid system (with reversible capacities of 117 , 93.4 , and 63.1 mA h g^{-1} at 0 , -20 , and -40°C , respectively) is better than that of the corresponding LIB systems. This advantage can be ascribed to the lower polarization of Mg-Li hybrid electrolytes. For $\text{Mg}(\text{BH}_4)_2$ - LiBH_4 /diglyme system, its performance at -20°C is still better than that of the corresponding LIBs. When the temperature decreases to -30°C , the diglyme-based electrolyte freezes, resulting in a negligible capacity. Therefore, the above experiments confirm that the APC-LiCl/THF electrolyte has a noteworthy advantage in low temperature performance.

3.3. Pseudocapacitance Behavior Dominated by Li^+ . Fast charging technology is an inevitable trend for future development of energy storage field, and pseudocapacitance effect has aroused widespread interest due to the possibility of achieving energy storage with simultaneous high power and high energy density [43]. For the Mg-Li hybrid system, there is also a considerable pseudocapacitance contribution dominated by Li^+ , which can further improve the rate performance.

Su et al. investigated the capacitive contribution of one-dimensional mesoporous monoclinic $\text{TiO}_2(\text{B})$ nanoflake cathode by hydrothermal synthesis in Mg-Li hybrid system [44]. In the pure $\text{Mg}(\text{BH}_4)_2$ electrolyte, Mg^{2+} neither inserts into $\text{TiO}_2(\text{B})$ nanoflakes nor participates in the pseudocapacitive reaction. After adding Li^+ , Mg may be activated and the intercalation of Li^+ and Mg^{2+} may contribute to the improved performance of the hybrid batteries. Compared with $\text{TiO}_2(\text{B})|\text{Li}$ cells, even the enhanced pseudocapacitive behavior is observed in Mg-Li cells with $\text{Mg}(\text{BH}_4)_2 + \text{LiB H}_4/\text{tetraglyme}$ electrolyte. In view of the contribution of pseudocapacitive reaction and fast ion transport promoted by mesoporous nanoflakes, the hybrid batteries deliver excellent rate performance with 130 mA h g^{-1} at 1 C up to 3000 cycles and 115 mA h g^{-1} at 2 C up to 6000 cycles.

MXene is a kind of transition-metal carbides/nitrides with a two-dimensional layered structure, which can be applied in electrode materials due to their unique physical and chemical properties. Liu et al. reported the prelithiated V_2C MXene in Mg-Li hybrid system [45]. First, V_2C MXene nanosheets are fabricated by selective etching, and then, Li foil is attached to V_2C to obtain the prelithiated V_2C via a self-discharge mechanism. By electrochemical lithiation, the interlayer spacing of V_2C is significantly expanded and the consumption of Li caused by the formation of the solid electrolyte interphase (SEI) film on the V_2C surface is compensated. The proposed reaction mechanism in the Mg-Li hybrid battery is shown in the following equations: $\text{V}_2\text{C} + 0.15 \text{ Li}^+ + 0.15 \text{ e}^- \longrightarrow \text{Li}_{0.15}\text{V}_2\text{C}$ and $\text{Li}_{0.15}\text{V}_2\text{C} + 0.44 \text{ Mg}^{2+} + 0.35 \text{ Li}^+ + 1.23 \text{ e}^- \rightleftharpoons \text{Mg}_{0.44}\text{Li}_{0.5}\text{V}_2\text{C}$ at the cathode side. Due to the structurally flexible interlayer, a charge storage mechanism with a combination of both electrostatic and faradaic natures is observed in MXene. The capacitive contribution to the total capacity for V_2C is $\sim 40.2\%$ at 0.5 mV s^{-1} . Li^+ in the dual-salt electrolyte can utilize the desirable pseudocapacitance contribution to achieve faster charge storage and more excellent rate performance.

Wadsley-Roth phase oxide electrode materials for LIBs, such as Nb_2O_5 , exhibit a larger pseudocapacitive contribution, thereby allowing rapid charging and discharging. Maletti et al. evaluated the ability of TiNb_2O_7 (TNO) and $\text{VNB}_9\text{O}_{25}$ (VNO) in Mg-Li hybrid batteries [46]. Both the materials have ReO_3 -like structure with shear planes. Compared with VNO, the migration of TNO on the (h0l) plane is more favored. For micro-sized TNO and VNO synthesized by high-temperature solid state reaction, Mg-Li hybrid batteries provide a comparable capacity to LIBs at room temperature (220 mA h g^{-1} for TNO and 150 mA h g^{-1} for VNO both at 0.1 C) and exhibit even better capacity retention than LIBs. Notably, 78% and 70% of the total capacities come from the capacitive contribution at 0.1 mV s^{-1} for TNO (Figure 2(g)) and VNO, respectively. These capacitive storage values are very close to that observed in Li batteries, which indicates the Mg-Li hybrid batteries can achieve fast charging technology comparable to Li batteries. Subsequently, Maletti et al. further investigated the structural evolution and cycling behavior of TNO electrodes in Mg-Li hybrid batteries [47]. Some initial Li insertion into TNO to expand the interlayers can facilitate Mg^{2+} coinsertion start-

ing from the composition $\text{Li}_{0.2}\text{TiNb}_2\text{O}_7$. However, due to the much slower Mg^{2+} diffusion kinetics, the Mg insertion into TNO may only be observed at a low current density. Compared with LMBs, Mg-Li hybrid batteries with nano-scale TNO have no advantage in capacity and capacity retention at room temperature. When operated at 60°C , as seen in Figure 2(h), Mg-Li hybrid batteries exhibit an extraordinary stable high-rate cycling capability (with a capacity retention of 86% after 500 cycles at 20 C rate), while the capacity retention of corresponding LMBs is only 16% likely due to the disintegration of SEI on Li anode at $\sim 60^\circ\text{C}$. Although the operating voltage is not high and the capacity is limited, the high-rate performance exhibited by TNO seems to have commercial prospects. However, its performance in Mg-Li hybrid battery is excessively dependent on temperature, and more modification is needed to make it appropriate for commercial use.

Organic materials are also a class of promising candidate for cathodes because of their low cost and structural designability. Due to the existence of high-density carbonyl groups ($\text{C}=\text{O}$) as redox sites, sodium rhodizonate ($\text{Na}_2\text{C}_6\text{O}_6$) and lithium rhodizonate ($\text{Li}_2\text{C}_6\text{O}_6$) with theoretical capacities of 501 and 580 mA h g^{-1} , respectively, have been reported as cathodes for Li-ion and Na-ion batteries. The crystal structure of $\text{Na}_2\text{C}_6\text{O}_6$ which is composed of layers of $\text{C}_6\text{O}_6^{2-}$ and Na^+ is located between the anion layers. $\text{Na}_2\text{C}_6\text{O}_6$ has higher conductivity and lower solubility than $\text{Li}_2\text{C}_6\text{O}_6$ due to larger-sized cation substitution. Tian et al. prepared the nanosized $\text{Na}_2\text{C}_6\text{O}_6$ by the antisolvent crystallization method to further improve its charge transport capacity [48]. Due to the sluggish Mg^{2+} in host lattices, $\text{Na}_2\text{C}_6\text{O}_6$ only delivers a negligible capacity in the APC electrolyte system. In the APC-LiCl system, since Li^+ with less steric hindrance dominantly inserts into cathode, instead of high-polarity Mg^{2+} , the capacity of $\text{Na}_2\text{C}_6\text{O}_6$ is significantly improved. The Mg-O-C and Li-O-C peaks detected by X-ray photoelectron spectroscopy (XPS) indicate a coinsertion of Mg^{2+} and Li^+ into $\text{Na}_2\text{C}_6\text{O}_6$. Irreversible trapping of a small amount of Mg^{2+} could alleviate the structure destruction and exfoliation of the C_6O_6 layers during charging and improve cycle stability. The reaction mechanism of $\text{Na}_2\text{C}_6\text{O}_6$ is shown in Figure 3(a). Mg-Li hybrid batteries with $\text{Na}_2\text{C}_6\text{O}_6$ cathode show a high discharge capacity of $\sim 450 \text{ mA h g}^{-1}$ based on four-electron transfer in the first cycle. A reversible three-electron transfer reaction based on $\text{Na}_2\text{Li}_4\text{C}_6\text{O}_6/\text{Na}_2\text{LiC}_6\text{O}_6$ occurs in the subsequent cycles, providing a discharge capacity of $\sim 350 \text{ mA h g}^{-1}$ at 50 mA g^{-1} . In addition, as seen in Figure 3(b), $\text{Na}_2\text{C}_6\text{O}_6$ delivers an outstanding high-rate performance with 200 and 175 mA h g^{-1} at 2.5 A g^{-1} (5 C) and 5 A g^{-1} (10 C), respectively, which also benefits from the reduced graphene oxide (rGO) network with quick charge transfer ability and the capacitive contribution of 60%–65% at various scan rates from 0.4 to 1 mV s^{-1} (Figure 3(c)). The application of rhodizonate salt cathodes has the potential to obtain high energy-density and power-density Mg-Li hybrid batteries. A less soluble and more conductive rhodizonate salt can be obtained by replacing pillar ions. Tian et al. also synthesized $\text{K}_2\text{C}_6\text{O}_6$ with ultra-large micro-sized grains (up to $30 \mu\text{m}$, Figure 3(d)) [49]. Compared

FIGURE 3: (a) Scheme of proposed redox mechanism and structure change of $\text{Na}_2\text{C}_6\text{O}_6$ during cycling. (b) Rate performance comparison of $\text{Na}_2\text{C}_6\text{O}_6$ wired by Super P and rGO. Inset: schematic illustration of cointercalation of Li and Mg into $\text{Na}_2\text{C}_6\text{O}_6$ molecules hybridized with rGO network. (c) Column graphs of rate-dependent charge storage contributions from both capacitive and intercalated processes for $\text{Na}_2\text{C}_6\text{O}_6$ [48]. (d) SEM image of $\text{K}_2\text{C}_6\text{O}_6$ powder. (e) Charge-discharge capacity and CE of Mg-Li hybrid battery based on $\text{K}_2\text{C}_6\text{O}_6$ cathode at 1 C [49].

with $\text{Na}_2\text{C}_6\text{O}_6$, the semiconductivity of $\text{K}_2\text{C}_6\text{O}_6$ endows it with the less use of conductive carbon to compensate for conductivity insufficiency. After charging, K^+ with larger volume and lower charge density is extruded from $\text{C}_6\text{O}_6^{2-}$ by the injection of Mg^{2+} and Li^+ , and no serious grain cracking and pulverization is observed during this process. The reaction mechanism of $\text{K}_2\text{C}_6\text{O}_6$ in Mg-Li hybrid batteries is similar to that of $\text{Na}_2\text{C}_6\text{O}_6$. $\text{K}_2\text{C}_6\text{O}_6$ exhibits a reversible capacity more than 300 mA h g^{-1} (based on a three-electron transfer reaction) at 0.1 C and an excellent cycling performance (at least 500 cycles at 1 C, Figure 3(e)). And the capacitive contribution of 40%–50% compensates for faradaic intercalation capacity at higher voltage region, thus, $\text{K}_2\text{C}_6\text{O}_6$ has a good rate performance with the capacities of 200, 130, and 60 mA h g^{-1} at 2 C, 5 C, and 10 C, respectively.

3.4. Boost of Conversion Reaction from Li^+ . Compared with intercalation-type cathodes, the research on conversion-type cathodes started later, but they have attracted widespread attention as potential high-energy-density alternatives to traditional intercalation-type cathodes for rechargeable batteries. For a typical conversion reaction, metal ions first diffuse into the host material, and then structural rearrangement and chemical bond rupture occur, accompanied by the release of a high capacity. These phase transitions are generally electrochemically reversible. Typical conversion-type cathode materials include metal chalcogenides and metal fluorides, etc. However, MMBs face the problem of kinetically sluggish Mg^{2+} diffusion into host material. Mg-Li hybrid electrolyte opens up a new avenue for the application of conversion-type cathodes in Mg-based batteries.

As resource-abundant FeS_2 and FeS have very high theoretical capacities of 894 and 609 mA h g^{-1} , respectively, it is attractive to apply them in energy storage batteries. Zhang et al. reported the Mg-Li hybrid batteries based on conversion type FeS_2 and FeS cathodes [50]. Due to the presence of electrophilic polysulfides, when the addition of Li salt is sufficient, nonnucleophilic $\text{Mg}(\text{BH}_4)_2$ -based electrolyte exhibits better rate and reversibility performance than that in the nucleophilic APC-based electrolyte. Under the optimized concentration and cutoff voltage conditions, the hybrid batteries perform better than Li/ FeS_x ones (Figure 4(a)), benefitting from dendrite-free Mg anode with potential SEI decoration, which can shield the corrosion of polysulfides. Although it is thermodynamically preferential for Mg to drive the conversion reaction, the process is actually controlled by kinetics. Therefore, the hybrid batteries perform according to the following reactions (Figure 4(b)): $\text{FeS}_2 + 2 \text{ Mg} + 4 \text{ Li}^+ \longrightarrow \text{Fe}^0 + 2 \text{ Li}_2\text{S} + 2 \text{ Mg}^{2+}$; $\text{FeS} + \text{Mg} + 2 \text{ Li}^+ \longrightarrow \text{Fe}^0 + \text{Li}_2\text{S} + \text{Mg}^{2+}$. Although the S-deficient Fe_7S_8 and Li_2FeS_2 are formed during the charging process, resulting in irreversible capacity loss, the combination of FeS_2 and Mg can achieve a high energy density close to 400 Wh kg^{-1} .

Chen et al. improved the electrochemical performance of FeS by designing a free-standing membrane electrode with FeS nanoparticles embedded in carbon nanofibers (CNFs) via a facile electrospinning method [51]. Benefitting from sufficient electron transport channels and the accommoda-

tion for large volumetric change during cycling, the FeS-CNF cathode exhibits an outstanding long-term cycling performance (with a stable capacity of $\sim 200 \text{ mA h g}^{-1}$ after 800 cycles) at a current density of 257 mA g^{-1} in the 0.4 M APC-0.4 M LiCl electrolyte. Together with the absence of the current collector and binder, the energy density of this system can reach up $\sim 300 \text{ Wh kg}^{-1}$, and it is a promising candidate for the application in flexible devices.

Cu-based chalcogenides have attracted great attention due to their desirable theoretical capacities, such as 560 mA h g^{-1} for CuS and 337 mA h g^{-1} for Cu_2S , but they are troubled by poor kinetic performance and need to be operated at an elevated temperature or extremely low current density. Li et al. used a hyperbranched polymer template to synthesize microflowlers Cu_9S_5 with a reversible capacity of 300 mA h g^{-1} at 50 mA g^{-1} [52]. Due to the electrochemical irreversibility of Li_2S after the first discharge process, Cu_9S_5 converts to $\text{Cu}_{1.96}\text{S}$ and the subsequent cycles follow the equation: $1.96 \text{ Cu} + \text{Li}_2\text{S} \leftrightarrow \text{Cu}_{1.96}\text{S} + 2 \text{ Li}^+ + 2 \text{ e}^-$. Wu et al. combined dual-salt electrolyte (0.25 M APC + 1.0 M LiCl) and well-designed cathodes ($\text{Cu}_{1.96}\text{S}$ - MoS_2 - MoO_2 and Cu_2Se - MoO_2) with nanowiring and hierarchical structure to obtain the maximum reversible capacities more than 200 mA h g^{-1} [53]. They selected the Cu-based metal-organic framework (MOF) HKUST-1 ($[\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_x]_n$) with large specific surface area and rich pores as precursor and infiltrated the Keggin-type polyoxometalate anion ($[\text{P}(\text{Mo}_{12}\text{O}_{40})]^{3-}$) into the voids of HKUST-1 to form POM @ MOF ($[\text{Cu}_2(\text{BTC})_{4/3}(\text{H}_2\text{O})_{21}[\text{H}_3\text{P}(\text{Mo}_{12}\text{O}_{40})]]$), denoted as NENU-5 as a composite template. Then, S-NENU ($\text{Cu}_{1.96}\text{S}$ - MoS_2 - MoO_2) and Se-NENU (Cu_2Se - MoO_2) were synthesized by thermal sulfuration and selenylation, respectively. The Cu_{2-y}X ($\text{X}=\text{S}, \text{Se}$) nanosheets of S-NENU and Se-NENU are modulated by C-coated MoO_2 pompons as conductive stakes, which can prevent the adherence (or aggregation) of surrounding Cu_{2-y}X nanosheets. In addition, a dominant Li-driven insertion-conversion behavior in dual-salt electrolyte further improves the reaction kinetics. Therefore, both the composite cathodes exhibit good long-term cycling performance with a CE value close to 100% at room temperature. Wang et al. also prepared carbon-encapsulated cuprous sulfide ($\text{Cu}_2\text{S}@C$) composite cathode via a MOF-derived sulfurization method [54]. Combining with the nonnucleophilic HMDS-based hybrid electrolyte, $\text{Cu}_2\text{S}@C$ shows the enhanced performance due to the alleviation of sulfide dissolution.

Cobalt sulfide (CoS_2) has also become a candidate of conversion cathode materials in the Mg-Li hybrid system in view of its theoretical capacity as high as 870 mA h g^{-1} . To alleviate the volume expansion of CoS_2 and avoid electrode pulverization during cycle, Asif et al. designed porous Ni/Zn codoped $\text{CoS}_2@C$ spheres [55]. In APC-LiCl hybrid electrolyte, Li^+ reacts with CoS_2 instead of Mg^{2+} , avoiding the formation of undissolved MgS and enhancing the conversion reversibility and cycle stability. The MOF-derived sulfurization method also was applied to fabricate CoS_2/C composite nanotube array electrode [56]. For Li batteries, discharge depth can affect the capacity retention. Thus, together with an appropriate working voltage range in Mg-Li hybrid batteries (0.01–2.0 V vs. Mg^{2+}/Mg corresponding

FIGURE 4: (a) Cycling performance comparison of Mg/Mg(BH₄)₂-LiBH₄/FeS₂, Li/Mg(BH₄)₂-LiBH₄/FeS₂, and Li/LiPF₆/FeS₂ batteries at 0.1 C; inset: corresponding rate performance of Mg/FeS₂ battery from 0.1 C to 2 C. (b) Scheme of Li-driven conversion reaction at the FeS_x cathode coupled with Mg metal plating/stripping at the anode [50]. (c) Reaction mechanism of Mg/S battery with LiTFSI additive [12]. (d) Schematic illustration to prepare ZIF-C host and ZIF-C-S composition electrode [60]. (e) Capacity stability comparison between Mg and S batteries with separator coated by rGO and without separator modification at 0.1 C. (f) Galvanostatic discharge/charge curves of Mg-S batteries with and without LiCl addition at different cycle stages [14].

to 0.7–2.7 V vs. Li⁺/Li), the CoS₂/C cathode exhibits a remarkable cycling performance (225.4 mA h g⁻¹ after 2000 cycles at 1 A g⁻¹).

Zhu et al. studied the performance of NiSe₂/Ti₃C₂ in Mg-Li hybrid batteries [57]. 2D MXene Ti₃C₂ as a conductive matrix supports NiSe₂, leading to the improved rate capability (a reversible capacity of 150 mA h g⁻¹ at 5 A g⁻¹). And the conversion reaction is expressed as follows: 3 NiSe₂ + 2 Mg + 4 Li⁺ → Ni₃Se₄ + 2 Li₂Se + 2 Mg²⁺. However, the authors did not provide the long-term performance of NiSe₂. Compared with other metal chalcogenides, NiSe₂ does not offer significant breakthrough in the battery-relevant metrics.

Sulfur (S) cathode has very high theoretical gravimetric and volumetric capacities of 1672 mA h g⁻¹ and 3459 mA h cm⁻³, respectively. And it is expected to achieve an energy density up to 1722 Wh kg⁻¹ when coupled with Mg metal anode. However, the development of magnesium-sulfur (Mg-S) batteries also faces considerable obstacles, including incompatibility with nucleophilic electrolytes, severe overcharge behavior of the cathode, low sulfur utilization, the formation of less dissoluble magnesium

polysulfide (Mg-PS), and the slow diffusion of Mg²⁺. Therefore, the tailor-made electrolyte systems, cathode hosts, and separators for Mg-S batteries are highly required.

According to the literatures, a Mg-S system based on Mg foil anode, sulfur cathode, and (Mg(HMDS)₂)-AlCl₃/THF electrolyte was first reported by Muldoon and coworkers in 2011 [58], though the capacity decay in the second cycle has exceeded 75%. Later, Mg(TFSI)₂ dissolved in glyme/di-glyme was also considered a promising electrolyte for Mg-S batteries. Zhao-Karger et al. used TFSI-based ionic liquid (N-methyl-N-butylpiperidinium bis(trifluoromethanesulfonyl)imide (PP₁₄TFSI)) as an additive and further improved the performance of Mg(HMDS)₂-based electrolyte for Mg-S batteries [59]. Until 2015, Gao et al. proposed the positive effect of Li⁺ on activating MgS_x species [12] and enhanced the cycle stability of Mg-S batteries by adding LiTFSI into Mg-HMDS electrolyte. As shown in Figure 4(c), Li⁺ enables the reactivation of the short chain Mg-PS through an ion exchange reaction or coordination with S²⁻ and S₂²⁻ on the Mg-PS surface to form readily soluble and rechargeable Li polysulfide (Li-PS) or hybrid Mg/Li polysulfide (MgLi-

PS). Although the loading of sulfur cathode in this work is low (15 wt%) and the cycling ability is insufficient (only 30 cycles), it illustrates the activation effect of the dual-salt electrolyte on the Mg-S system.

In addition to exploring nonnucleophilic electrolytes that are compatible with sulfur cathodes, the design of cathode structures that alleviate sulfur dissolution and increase sulfur loading is also one of the effective ways to enhance the cycle stability of Mg-S batteries. Zhou et al. reported a high rate Mg-S battery based on a Mg foil anode, a S/MOF derivative cathode, and a glass fiber separator coated by reduced graphene oxide (rGO) and Mg(HMDS)₂-AlCl₃-LiTFSI electrolyte [60]. Figure 4(d) shows a schematic process to prepare S cathode. The authors synthesized ZIF-67 derivative carbon host (ZIF-C) by a thermal pyrolysis of ZIF-67 and acid leaching, followed by sulfur infiltration to obtain an S cathode with a mass loading of 47%. The Co and N codoped ZIF-C with hierarchical porous morphology can trap soluble polysulfides and potentially catalyze the polysulfide conversion with better kinetics. During the discharging, S₈ is reduced to MgS_x ($x > 2$), Li₂S_y, Mg-Li-S species, and small amount of MgS/MgS₂, which are detected by XPS. It is confirmed that the conversion process is driven by Li⁺ and Mg²⁺, and the accumulation of MgS_x ($x \leq 2$) causes the capacity fading during long-term cycling. Since Mg-S batteries suffer more severe shuttle effect than Li-S batteries, the rGO-modified separator is used to alleviate the shuttle effect of polysulfides (Figure 4(e)). By combining with the optimized charging protocol (with cut-off charge capacity), the synergy of multiple strategies makes better cycling stability in Mg-S batteries. At 0.1 C rate, the full cell based on the modified separator exhibits a slowed capacity decay trend, and the reversible capacity is 450 mA h g⁻¹ after 250 cycles. At 1 C rate, the first discharge capacity is as high as 600 mA h g⁻¹, and the reversible capacity is still 400 mA h g⁻¹ after 200 cycles. Yang et al. reported a complex Mg(CF₃SO₃)₂-based electrolyte for Mg-S batteries [13]. The authors added LiCl or LiCF₃SO₃ into the solution of 0.125 M Mg(CF₃SO₃)₂ + 0.25 M AlCl₃ + 0.25 M MgCl₂ + 0.025 M anthracene/THF + tetraglyme (1:1 in volume ratio). Coupled with sulfur@microporous carbon cathode, the results show that Li⁺ promotes the dissociation of Mg-ions in the electrolyte and activates MgS/MgS₂ in the S cathode, resulting in the enhancement of specific capacity, reaction reversibility, and capacity retention. In addition, the addition of LiCF₃SO₃ enables the better performance than LiCl, in view that CF₃SO₃⁻ ions promote the Mg deposition/dissolution. Fan et al. achieved the reduction of overpotential and extension of cycle life of Mg-S batteries in MgCl₂-AlCl₃ complex electrolyte by using LiCl additive [14]. LiCl not only activates the S cathode but also facilitates the Mg deposition/dissolution on anode side to reduce voltage polarization of full cell (Figure 4(f)). Thus, the Mg-S batteries exhibit a remarkably stable cycling performance at 0.4 C (with a capacity of 300 mA h g⁻¹ after 500 cycles). In addition to sulfur cathode, sulfur-rich metal polysulfides are also good candidates for high-energy-density hybrid systems. Wang et al. developed amorphous MoS_x ($x = 5.7$, a-MoS_{5.7}) polysulfide as cathode in Mg-Li hybrid batteries with the dis-

charge mechanism of $a\text{-MoS}_{5.7} + x\text{Li}^+ + xe^- \longrightarrow \text{MoS}_{5.7-0.5x} + 0.5x\text{Li}_2\text{S}$ ($x \leq 8.4$) [61]. In the electrolytes without LiCl, the large charge-transfer resistance prevents Mg²⁺ from diffusion in $\alpha\text{-MoS}_{5.7}$; thus, Mg²⁺ hardly contributes to the capacity. Thanks to the fast Li⁺ diffusion, the MoS_{5.7} cathode delivers a high capacity of 812 mA h g⁻¹ with an average plateau of 1.02 V at 50 mA g⁻¹ and a high energy density of 761 Wh kg⁻¹ is realized.

Selenium (Se) has a notable theoretical capacity (a gravimetric capacity of 678 mA h g⁻¹ and a volumetric capacity of 3268 mA h cm⁻³) and a high electronic conductivity (10⁻³ S m⁻¹). Thus, Se is expected to build a system with high volumetric energy density similar to S. Similarly, the dissolution issue of high-order magnesium polysele-nides still plagues the Mg-Se system. Yuan et al. prepared a selenized polyacrylonitrile (Se/PAN) cathode with a Se content of 45.37 wt%, which was tested in APC-LiCl electrolyte [62]. In this system, only one plateau is observed in the discharge curve, indicating a direct interconversion between Se and Li₂Se without the formation of intermediate polyselenides. Although the capacity decay is slower (0.021% per cycle), considering the limited capacity at a higher current density (118.3 mA h g⁻¹ after 800 cycles at 400 mA g⁻¹), the Se cathode materials need further modification.

4. Influence of Li⁺ on Anode in Mg-Li Hybrid Systems

As known, a major advantage of Mg-Li hybrid batteries is the adoption of Mg metal anode with smooth deposition morphology. Especially at a rate up to 20 C (Figure 5(a)), compared with Li metal batteries, although the Mg anode suffers a higher overpotential in APC-LiCl electrolyte, it can prevent the local concentration of current and the growth of dendrites [47]. In addition to the characteristic advantages of Mg anode, Li⁺ will also have magical effects on the Mg anode side in the Mg-Li hybrid system, including tailoring SEI and reducing the overpotential. Li salt plays a vital role in regulating the composition of SEI on the Mg anode side. The Mg metal anode spontaneously reacts with the conventional electrolyte (salt and solvent) to form a passivation film, which is ionically and electronically insulating, on the surface of Mg anode. For example, a Mg electrolyte based on tetrakis(hexa-fluoroisopropoxy)borate anion (B(hfip)₄⁻), Mg[B(hfip)₄]₂/DME (denoted as MBhfip/DME), is partially decomposed on the surface of Mg metal anode with the formation of a fragile SEI, which cannot support stable and long-term cycles. Tang et al. introduced Mg²⁺ into the Li electrolyte Li[B(hfip)₄]/DME (denoted as LBhfip/DME) through the initial electrochemical cycles [63], and the in situ formed Mg-Li hybrid electrolyte can allow the highly reversible Mg plating/stripping. As shown in Figure 5(b), after a short activation period, the CE value reaches 99.0% and remains stable for 500 cycles. The stable and efficient plating/stripping behavior benefits from the formation of Li-containing SEI, by partial decomposition of LBhfip/DME electrolyte on the

FIGURE 5: (a) Cycling performance comparison of symmetric Li/Li cells and Mg/Mg cells in dual-salt electrolyte at 20 C [47]. (b) CE of Mg/Cu cell in LBhfp/DME electrolyte cycled at 0.5 mA cm^{-2} . (c) Li 1s XPS spectrum for cycled Mg anode surface from Mg/Cu cell in LBhfp/DME electrolyte after 100 charge-discharge cycles [63]. (d) Cycling behavior of Mg/Mg symmetrical cells in pristine $[\text{Mg-6THF}][\text{AlCl}_4]_2$ (blue) and LiCl-added (red) electrolytes at the current densities from 10 to $500 \mu\text{A cm}^{-2}$ [14]. (e) Configuration of quasi-solid-state Li-Mg dual-salt battery and the relationship between salt concentration and charge carrier mobility and density [64].

surface of Mg anode. Inorganic Li salts including Li_2CO_3 , Li_2O , and LiF species are detected on the cycled Mg electrode surface (Figure 5(c)). The SEI formed in LBhfp/DME electrolyte is more uniform and denser than that in MBhfp/DME. It is one of the potential reasons that Li-containing SEI can resist the passivation of Mg metal electrode in conventional electrolytes.

Adding an appropriate amount of LiTFSI to the $\text{Mg}(\text{TFSI})_2/\text{diglyme}$ electrolyte can enhance the Mg plating/stripping performance with improved CE and significantly decreased overpotential [31]. Recently, the LiCl additive was also found to enable the reduction of overpotential of Mg deposition/dissolution in the MACC electrolyte. Fan et al. activated the Mg anode/electrolyte interface through the solubilization effect of LiCl on MgCl_2 , thereby obtaining an Mg/S battery with an extended cycle life [14]. The low-solubility MgCl_2 on the Mg surface may cause high-voltage polarization. By adding 1 M LiCl, the solubility of MgCl_2 in THF can be increased to 0.6 M. As seen in Figure 5(d), the Mg/Mg symmetrical cell using LiCl-added electrolyte shows the almost constant overpotential, while the overpotential in pristine MACC electrolyte increases sharply as the current density increases from 10 to $500 \mu\text{A cm}^{-2}$. Notably, the decrease of overpotential is the synergistic effect of Li^+ and Cl^- , as well as the possible formation of soluble intermediate $[\text{Mg}_2(\mu\text{-Cl})_3\cdot 6\text{THF}]$ [$\text{LiCl}_2\cdot 2\text{THF}$], while neither Li^+ (from LiTFSI) nor Cl^- (from NaCl) alone can achieve a similar effect as LiCl.

Since many Mg-Li hybrid electrolytes contain Cl^- , the corrosion issue in liquid electrolytes cannot be avoided. Therefore, the fabrication of solid electrolyte free of Cl is a good strategy to remove this obstacle. Recently, Herzog-Arbeitman et al. first proposed the concept of quasi-solid-state Mg-Li hybrid battery (Figure 5(e)) with a high initial capacity of $141.5 \text{ mA h g}^{-1}$ (based on LiFePO_4 cathode) and CE over 90% in a Swagelok cell configuration [64]. The novel hybrid gel polymer electrolyte was prepared by swelling a poly(vinylidene difluoride-co-hexafluoropropylene) polymer matrix in 1-ethyl-2-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) ionic liquid containing the salts LiTFSI and $\text{Mg}(\text{TFSI})_2$. With the salt concentration increasing, the ionic mobility increases but the carrier number density decreases; thus, there are the optimum salt concentrations of 0.7 M LiTFSI and 0.7 M $\text{Mg}(\text{TFSI})_2$ with an ionic conductivity of 3.2 mS cm^{-1} . Although there is a fatal decay of this quasi-solid-state battery in the later cycles (<100 cycles), the first step has been taken in the development of a noncorrosive and processable electrolyte for Mg-Li hybrid solid-state batteries.

5. Conclusion

This review has summarized the recent progresses in Mg-Li hybrid batteries as a promising, high-energy-density, and cost-efficient alternative to Li-based systems. Among the

FIGURE 6: (a) Comparison of energy density and power density of some dual-salt systems mentioned in this review. (b) Electrochemical impedance spectra of VS₄ nanodendrites in Mg battery configurations without and with Li salt additive [22]. (c) Left: energy difference between the intercalation of x Li atoms and the corresponding intercalation of $x/2$ Mg atoms; right: the voltage plots as a function of cation insertion amount of x Li or $x/2$ Mg into TNO [47]. Cyclic voltammogram curves of (d) 0.5 M Mg(TFSI)₂ in diglyme (G2) and (e) Mg(TFSI)₂-Li(TFSI)₂/G2 with different salt concentrations at 100 mV s⁻¹ (platinum as working electrode and polished magnesium ribbons as counter and reference electrodes) [31]. (f) Schematic diagram of Li⁺ mediation in activating MgS_x species [12].

alternatives to LIBs, most multivalent metal batteries still suffer sluggish kinetics. Mg-Li hybrid batteries combine the advantages of both Li ion and Mg metal, including fast ion transport kinetics and smooth anode deposition. Research into Mg-Li hybrid batteries has been more widespread in the last several years, and especially recently, it has a trend of revival. We select some typical examples mentioned in this review and compared their energy density and power density in Figure 6. It is found that the conversion-type and multi-electron transfer cathodes (e.g., sulfur, sulfides,

organics, and NaV₃O₈) have the higher energy density (>400 Wh kg⁻¹) than that of insertion-type or single-electron transfer cathodes. The Mg-Li hybrid systems have shown promise to become a new energy storage system in the post-lithium-ion batteries era, though the above data ignores the weight of battery components. Compared with pure Mg electrolyte, the advantages of Mg-Li dual-salt electrolyte are also summarized in Figure 6. The presence of Li⁺ with excellent kinetics is beneficial to reduce the interface resistance. From the energy point of view, Li⁺ is preferably

inserted into cathode host. And the improvement of overpotential and CE by Li salts is also worth noting. In addition, Li^+ can reactivate the conversion reaction products (e.g., MgS_x) to improve the electrochemical reversibility of conversion type Mg-based batteries. Some other highlights are listed below.

- (1) In the majority of the hybrid battery systems mentioned in this review, the used electrolyte is a combination of APC and LiCl. And the concentration of LiCl has an effect on the conductivity and viscosity of the electrolyte, as well as the capacity [28, 32, 39]. At present, the combination of 0.25 M APC and 1 M LiCl is more applied in the investigation of Mg-Li hybrid system. In addition, the side reaction between APC and the current collector will narrow the actual electrochemical window [41]
- (2) Another important factor to influence the overall battery performance is the morphology and size of cathode grains. Hollow and porous structures can facilitate electrolyte infiltration and accommodate volume expansion during cycling [17, 30, 38]. Several research results discussed in this review confirmed that the nanosized cathode materials deliver a higher capacity than the corresponding micro-sized ones [26, 27]. This may be due to the large surface area and the enhanced mass transfer between electrolyte and active material
- (3) For the systems containing APC, it is necessary to use Mo current collector (or stainless steel with coating) to design the high voltage Mg-Li hybrid batteries [11, 28]. Considering the possible commercialization of Mg-Li hybrid batteries in the future, cathode fabrication process and selection of current collector should be taken seriously. The cost factor cannot be ignored; thus, cheap and earth-abundant elements (e.g., Fe, S, and organics) are preferred
- (4) For the intercalation-type cathodes, there are two intercalation mechanisms, including exclusive Li^+ intercalation and $\text{Mg}^{2+}/\text{Li}^+$ coinsertion. For the cathodes with $\text{Mg}^{2+}/\text{Li}^+$ coinsertion, only VS_4 and prelithiated V_2C show that Mg^{2+} contributes more capacity than Li^+ and nanosized LTO shows an almost equal contribution of Mg^{2+} to that of Li^+ [22, 26, 45]. The insertion of Mg^{2+} is more likely to cause irreversible phase transition and even structural collapse, leading to rapid capacity fading [48]. Therefore, whether to design a cathode that allows sufficient Mg^{2+} insertion still needs to be carefully considered
- (5) For Mg metal anode, the addition of Li salts significantly reduces the overpotential of Mg plating/stripping and constructs a reinforced SEI in noncorrosive electrolyte (e.g., LBHfP/DME) [14, 31, 63]. The improvement of electrochemical performance at Mg anode side may attribute to the reduced interfacial resistance and the enhanced interfacial compatibility

6. Prospect

In theory, Mg-Li hybrid battery is a good candidate for high-performance batteries, but in terms of practical energy densities, LIBs are still better. LIBs have achieved commercialization for several decades. And after a considerable amount of research, their energy density is almost close to the bottleneck. Even with the intensified efforts since 2014, the research into Mg-Li hybrid batteries is in its infancy. The significant investigations are still required to realize their practical applications.

To achieve high theoretical values in Mg-Li hybrid battery configuration, electrolyte must have high ion conductivity and wide electrochemical window. Although some Mg electrolytes have been developed over the years, they cannot replace APC in terms of cost, synthesis process, and compatibility with Mg metal anode. Thus, developing stable and practical electrolyte and Mg metal anode are necessary. The cathode must be well designed, such as constructing hierarchical porous structure to make electrolyte permeate cathode material, alleviate its volume expansion, and improve the diffusion kinetics. To enhance the electrical conductivity of cathode, sufficient electronic conductive network or wiring is also essential. As a research hotspot, fast charging is also a future trend. Therefore, it is also necessary to improve the rate performance of the Mg-Li hybrid system to reach practical level. In addition, for S cathode, there is also a severe shuttle effect, and more modification strategies are required, such as separator decoration and charging mode optimization. The research on the influence of dual-salt electrolyte on the anode is far from enough, including but not limited to the composition of SEI and the effect of Li salt on the solvation structure, which need more in-depth analysis. In terms of practicality, some issues about electrolyte must be investigated in depth. Most the reports of Mg-Li hybrid batteries adopted glass fiber as the separator based on a coin cell configuration. It is inevitable that more amount of electrolyte is required to wet the inner separator compared with the case of commercial polymer Celgard as the separator. Combining with the active material mass loading, the volume of electrolyte with extra Li salt consumption used in Mg-Li hybrid systems is still far from the lean electrolyte standard of MMBs. Thus, more investigations under practical conditions (e.g., high mass loading, high-concentration salt, and pouch cell configuration) are urgently needed.

Data Availability

All data related to the analysis in this study are present in the paper.

Conflicts of Interest

The authors declare no conflict of interest.

Authors' Contributions

YJL and CLL analyzed the data and wrote and revised the manuscript. YJL and YJZ prepared the figures. CLL, KG, and JTZ supervised the project.

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