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$_6$S$_8$ 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 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$_6$S$_8$ 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$_2$O$_4$ 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 liquid 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 battery [4]. Unfortunately, BF$_4^-$ may react with PhMgCl to form B(Ph)$_2$Cl, which reduces the electrochemical window of the electrolyte to ~2.5 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$_6$S$_8$ 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$_6$S$_8$ 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 Li$_x$Mo$_6$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 Mg(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 Mg(BH$_4$)$_2$ electrolyte [10]. Taking the diglyme (DGM) solvent as an example, 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 [Mg$_2$Cl$_2$(DME)$_4$][AlCl$_4$]$_2$ electrolyte to obtain dual-salt electrolytes with a targeted Li$^+$ concentration of 0.4 M. LiCl and...
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$_2$O$_4$ 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 MgCF$_3$SO$_3$ + LiCF$_3$SO$_3$ as well as

![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$_6$S$_8$ (vs. Mg/Mg$^{2+}$) at different Li$^+$ activities ($a_{Li^+}$) [8].](image-url)
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$_x$X$_8$ (X=S, Se, or their combination), layered structures like typical TiS$_2$, TiO$_2$, and V$_2$O$_5$, 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$_x$S$_8$ 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$_x$S$_8$ has also been deeply investigated by several research groups. In the previous section, the influence of Li$^+$ concentration in the APC electrolyte on the performance of Mo$_x$S$_8$ is focused on changing Mg electrochemistry by BH$_4^-$ rather than Li$^+$ to promote the Mg deposition/dissolution. The unique solvation structures endow the Mg(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 second coordination, and the increased concentration of BH$_4^-$ accelerates the Mg stripping by prompting the formation of coordination structures (e.g., Mg(BH$_4$)$_2$DGM, Mg$_2$(BH$_4$)$_3$(DME)$_2$, and Mg(BH$_4$)$_2$(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) and graphene nanosheets. Due to the improved charge transfer ability, the MoS$_2$/CNT and MoS$_2$/graphene composite cathodes deliver the discharge capacities of ~200 mA h g$^{-1}$ and ~225 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 (1.0–1.6 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 ± 0.5 mg cm$^{-2}$) at 1 C (=2 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 polyhedral Mg deposits with an average size of ~100 μm. Benefiting 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 Å, 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
the further improvement by wrapping VS$_2$ with graphene (VS$_2$-GO) to construct a conductive network. The VS$_2$-GO cathode exhibits an outstanding high-rate capacity of 129 mA h g$^{-1}$ at 80 C (1 C = 180 mA g$^{-1}$) [20]. And it is estimated that the energy density of this hybrid system can reach up to 353 Wh kg$^{-1}$. The crystal structure of VS$_4$ consists of V$^{4+}$ ions coordinated to sulfur dimers (S$_2^{2-}$) extending along the c axis, and the distance between atomic chains is 5.83 Å. And VS$_4$ has been demonstrated to have the ability to allow Mg$^{2+}$ diffusion and storage due to linear open channels and sufficient S$_2^{2-}$ active sites [21]. Wang et al. reported VS$_4$ nanodendrites as cathode for Mg-Li hybrid batteries [22]. Not only it is observed that Mg$^{2+}$/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 Mg$^{2+}$/Li$^+$ cointercalation 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 V$_2$O$_3$ cathode delivers a high reversible capacity of ~300 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 Li$_2$Ti$_3$O$_7$ (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 M Mg(BH$_4$)$_2$-1.5 M LiBH$_4$/tetraglyme electrolyte [24]. They obtained an initial discharge capacity of 155.8 mA h g$^{-1}$, which decreases to ~140 mA h g$^{-1}$ after 90 cycles at a rate of 0.2 C (1 C = 168 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 cointercalation of Mg$^{2+}$ and Li$^+$ into LTO through DFT calculations and experiments [26]. For the LTO nanoparticle (>100 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 ~175 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 M Mg(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 ~170 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 α-MnO$_2$ (e.g., hollandite with a 2 ⨉ 2 tunnel and todorokite 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 (~60 mA h g$^{-1}$ at 1 A g$^{-1}$) and low voltage plateaus, the prediscribed cathodes are not a suitable choice for Mg-Li hybrid batteries. Then, Asif et al. prepared a ternary transition metal oxide (NiMnCo)$_2$O$_4$ with the morphology of multishelled hollow spheres by a hydrothermal method and thermal treatment [30]. The (NiMnCo)$_2$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: $\text{xLi}^+ + \text{x}e^- (\text{NiMnCo})_2\text{O}_4 \rightarrow \text{Li}_x(\text{NiMnCo})_2\text{O}_4$. Lithium manganese oxide with a high discharge voltage platform (>2.0 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$_2$O$_4$ in two chloride-free hybrid electrolytes, namely, Mg(TFSI)$_2$-LiTFSI and Mg(CB11H12)2-LiTFSI [31]. LiMn$_2$O$_4$ exhibits an initial capacity of 106 mA h g$^{-1}$ with a working voltage of ~2.8 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 (Mn$^{3+}$ → Mn$^{2+}$ + Mn$^{4+}$), resulting in the structural collapse. Li-rich Li$_{0.5}$Mn$_{0.5}$O$_2$ with stable Mn$^{3+}$ provides a theoretical capacity of 163 mA h g$^{-1}$. Cen et al. synthesized spinel Li$_{0.5}$Mn$_{0.5}$O$_2$ 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 Li$_{0.5}$Mn$_{0.5}$O$_2$, it is more difficult for Mg$^{2+}$ or solvated MgCl$^+$ to diffuse into host, so only Li$^+$ intercalation occurs at the cathode side. Benefitting from nano/microhierarchical architecture and open 3D Li$^+$ channels, the Li$_{0.5}$Mn$_{0.5}$O$_2$ 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 (~2.5 V vs. Li/Li$^+$, ~1.75 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$_x$VO$_2$ (x = 0.78). The VO$_2$ nanoflakes exhibit a high discharge capacity of 206.8 mA h g$^{-1}$ and a capacity retention of 75% (after 100 cycles) at 100 mA g$^{-1}$. Vanadium pentoxide (V$_2$O$_5$) has abundant reserves and unique electrochemical storage properties. With different amounts of Li$^+$ inserted, V$_2$O$_5$ shows different capacity retentions due to the reversible or irreversible phase formation [34]. Yoo et al. observed one equivalent Li$^+$ insertion into V$_2$O$_5$ in 0.25 M APC-0.25 M LiCl [35]. And it has been confirmed that V$_2$O$_5$ and MoO$_3$ allow a reversible Mg-ion intercalation. Based on this, Miao et al. reported layered vanadium-molybdenum-oxides V$_2$MoO$_8$ (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 Mg_{0.7}Li_{0.39}V_{2}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 mAh 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 NaV\(_2\)O\(_4\).1.69 H\(_2\)O from 110 mAh g\(^{-1}\) (at 10 mA g\(^{-1}\) for pure Mg electrolyte system) to 446 mAh 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 mAh g\(^{-1}\) with the CE of 88% at 20 mA g\(^{-1}\)) and operating voltage (~0.8 V), compared with other batteries described in this review, batteries using MoO\(_2\) as cathode do not have the value of continuing research.

The lithium superionic conductor (NASICON) N\(_{x}\)M\(_2\)(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. LiTi\(_{1}\)(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 (~240 Wh kg\(^{-1}\)). Xu et al. prepared carbon-coated LiTi\(_{3}\)(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 mAh 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 (Fe[Fe(CN)]\(_{11}\)·3H\(_2\)O and Fe[Fe(CN)]\(_{12}\)·0.7H\(_2\)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 mAh g\(^{-1}\) for both 23-PBA and 07-PBA. Unlike the case that Li\(^+\) concentration affects the insertion mechanism of Mo\(_{3}\)S\(_{8}\) 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 (55 mAh 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 (~2.5 V vs. Mg), the charge capacity is only 60 mAh g\(^{-1}\). Subsequently, Zhang et al. adopted a pouch cell configuration based on LFP cathode, a flexible pyrolytic graphic film as a current collector and APC-LiCl electrolyte to obtain an Mg-Li hybrid battery with a maximum energy density of 382.2 W h 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 Li\(_{x}\)V\(_{2}\)(PO\(_4\))\(_{3}\) (LVP) in Mg(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 mAh 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 mAh 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 Mg(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 TiO$_2$(B) nanoflake cathode by hydrothermal synthesis in Mg-Li hybrid system [44]. In the pure Mg(BH$_4$)$_2$ electrolyte, Mg$^{2+}$ neither inserts into TiO$_2$(B) nanoflakes nor participates in the pseudocapacitive reaction. After adding Li$^+$, Mg may be activated and the cointercalation of Li$^+$ and Mg$^{2+}$ may contribute to the improved performance of the hybrid batteries. Compared with TiO$_2$(B)/Li cells, even the enhanced pseudocapacitive improved performance of the hybrid batteries. Compared with 3000 cycles and 115 mA h g$^{-1}$, even the enhanced pseudocapacitive behavior is observed in Mg-Li cells with Mg(BH$_4$)$_2$ + LiB H$_4$/tetrachloromethane 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 $V_2$C MXene in Mg-Li hybrid system [45]. First, $V_2$C MXene nanosheets are fabricated by selective etching, and then, Li foil is attached to $V_2$C to obtain the prelithiated $V_2$C via a self-discharge mechanism. By electrochemical lithiumiation, the interlayer spacing of $V_2$C is significantly expanded and the consumption of Li caused by the formation of the solid electrolyte interphase (SEI) film on the $V_2$C surface is compensated. The proposed reaction mechanism in the Mg-Li hybrid battery is shown in the following equations: $V_2$C + 0.15 Li$^+$ + 0.15 e$^-$ $\rightarrow$ Li$_{0.15}$V$_2$C and Li$_{0.15}$V$_2$C + 0.44 Mg$^{2+}$ + 0.35 Li$^+$ + 1.23 e$^-$ $\rightarrow$ Mg$_{0.44}$Li$_{0.5}$V$_2$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 $V_2$C is around 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.

Wadsworth-Roth phase oxide electrode materials for LIBs, such as Nb$_2$O$_5$, exhibit a larger pseudocapacitive contribution, thereby allowing rapid charging and discharging. Malletti et al. evaluated the ability of TiNb$_5$O$_{17}$ (TNO) and VNb$_2$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 microporized 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, Malletti 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$^{2+}$ coinserter starting from the composition Li$_{0.2}$TiNb$_2$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 nanoscale 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 ~60°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 (C=O) as redox sites, sodium rhodizonate (Na$_2$C$_6$O$_6$) and lithium rhodizonate (Li$_2$C$_6$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 Na$_2$C$_6$O$_6$ which is composed of layers of C$_6$O$_6$$^{2-}$ and Na$^+$ is located between the anion layers. Na$_2$C$_6$O$_6$ has higher conductivity and lower solubility than Li$_2$C$_6$O$_6$ due to larger-sized cation substitution. Tian et al. prepared the nanosized Na$_2$C$_6$O$_6$ by the antisolvent crystallization method to further improve its charge transport capacity [48]. Due to the sluggish Mg$^{2+}$ in host lattices, Na$_2$C$_6$O$_6$ only delivers a negligible capacity in the APC electrolyte system. In the APC-LiCl system, since Mg$^+$ with less steric hindrance dominantly inserts into cathode, instead of high-polarity Mg$^{2+}$, the capacity of Na$_2$C$_6$O$_6$ is significantly improved. The Mg-O-C and Li-O-C peaks detected by X-ray photoelectron spectroscopy (XPS) indicate a cointercalation of Mg$^{2+}$ and Li$^+$ into Na$_2$C$_6$O$_6$. Irreversible trapping of a small amount of Mg$^{2+}$ could alleviate the structure destruction and exfoliation of the C$_6$O$_6$ layers during charging and improving cycle stability. The reaction mechanism of Na$_2$C$_6$O$_6$ is shown in Figure 3(a). Mg-Li hybrid batteries with Na$_2$C$_6$O$_6$ cathode show a high discharge capacity of ~450 mA h g$^{-1}$ based on four-electron transfer in the first cycle. A reversible three-electron transfer reaction based on Na$_2$Li$_2$C$_6$O$_6$/Na$_2$LiC$_6$O$_6$ occurs in the subsequent cycles, providing a discharge capacity of ~350 mA h g$^{-1}$ at 50 mA g$^{-1}$. In addition, as seen in Figure 3(b), Na$_2$C$_6$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 K$_2$C$_6$O$_6$ with ultra-large microrosized grains (up to 30 μm, Figure 3(d)) [49]. Compared
Specific capacity (mAh/g)

Figure 3: (a) Scheme of proposed redox mechanism and structure change of Na$_2$C$_6$O$_6$ during cycling. (b) Rate performance comparison of Na$_2$C$_6$O$_6$ wired by Super P and rGO. Inset: schematic illustration of cointercalation of Li and Mg into Na$_2$C$_6$O$_6$ molecules hybridized with rGO network. (c) Column graphs of rate-dependent charge storage contributions from both capacitive and intercalated processes for Na$_2$C$_6$O$_6$ [48]. (d) SEM image of K$_2$C$_6$O$_6$ powder. (e) Charge-discharge capacity and CE of Mg-Li hybrid battery based on K$_2$C$_6$O$_6$ cathode at 1 C [49].
with Na2C2O4, the semiconductivity of K2C2O4 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 C2O4−2 by the injection of Mg2+ and Li+, and no serious grain cracking and pulverization is observed during this process. The reaction mechanism of K2C2O4 in Mg-Li hybrid batteries is similar to that of Na2C2O4. K2C2O4 exhibits a reversible capacity more than 300 mAh 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, K2C2O4 has a good rate performance with the capacities of 200, 130, and 60 mAh 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 Mg2+ 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 FeS2 and FeS have very high theoretical capacities of 894 and 609 mAh 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 FeS2 and FeS cathodes [50]. Due to the presence of electrophilic polysulfides, when the addition of Li salt is sufficient, nonnucleophilic Mg(BH4)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/FeS2 ones (Figure 4(a)), benefiting from dendrite-free Mg anode with potential SEI decoration, which can shield the corrosion of polysulfides. Although it is thermodynamically preferable 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)): FeS2 + 2 Mg + 4Li7− → Fe0 + 2Li2S + 2 Mg2+; FeS + Mg + 2Li7− → Fe0 + Li2S + Mg2+. Although the S-deficient Fe-S and Li2FeS are formed during the charging process, resulting in irreversible capacity loss, the combination of FeS2 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]. Benefiting from sufficient electron transport channels and the accommodation for large volumetric change during cycling, the FeS-CNFe cathode exhibits an outstanding long-term cycling performance (with a stable capacity of ≈200 mAh 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 to 300 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 mAh g−1 for CuS and 337 mAh g−1 for Cu2S, 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 microflowers Cu9S5 with a reversible capacity of 300 mAh g−1 at 50 mA g−1 [52]. Due to the electrochemical irreversibility of Li2S after the first discharge process, Cu9S5 converts to Cu19S6 and the subsequent cycles follow the equation: 1.96 Cu + Li2S ↔ Cu19S6 + 2Li+ + 2e−. Wu et al. combined dual-salt electrolyte (0.25 M APC + 1.0 M LiCl) and well-designed cathodes (Cu9S5-MoS2-MoO2 and CuSe-SeO2) with nanowiring and hierarchical structure to obtain the maximum reversible capacities more than 200 mAh g−1 [53]. They selected the Cu-based metal-organic framework (MOF) HKUST−1 ([Cu1(BTC)2(H2O)x]n) with large specific surface area and rich pores as precursor and infiltrated the Keggin-type polyoxometalate anion ([P(Mo9O20)])3− into the voids of HKUST−1 to form POM<sub>⊂</sub>MOF ([Cu1(BTC)2(H2O)x]n[P(Mo9O20)]), denoted as NENU−5) as a composite template. Then, S-NENU (Cu19S5-MoS2-MoO2) and Se-NENU (CuSe-SeO2) were synthesized by thermal sulfuration and selenylation, respectively. The Cu2−xX (X=S, Se) nanosheets of S-NENU and Se-NENU are modulated by C-coated MoO2 popmons as conductive stakes, which can prevent the adherence (or aggregation) of surrounding Cu2−xX 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 (Cu2S@C) composite cathode via a MOF-derived sulfuration method [54]. Combining with the nonnucleophilic HMDS-based hybrid electrolyte, Cu2S@C shows the enhanced performance due to the alleviation of sulfide dissolution.

Cobalt sulfide (CoS2) 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 mAh g−1. To alleviate the volume expansion of CoS2 and avoid electrode pulverization during cycle, Asif et al. designed porous Ni/Zn codoped CoS2@C spheres [55]. In APC-LiCl hybrid electrolyte, Li+ reacts with CoS2 instead of Mg2+, avoiding the formation of undissolved MgS and enhancing the conversion reversibility and cycle stability. The MOF-derived sulfuration method also was applied to fabricate CoS2/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. Mg2+/Mg corresponding...
to 0.7–2.7 V vs. Li+/Li), the CoS₂/C cathode exhibits a remarkable cycling performance (225.4 mAh 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 mAh g⁻¹ and 3459 mAh 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-ethylether 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 (PP₄₄TFSI)) 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 MgSₓ 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 S₄²⁻ 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, Sx is reduced to MgSx (x > 2), Li2Sx, Mg-Li-S species, and small amount of Mg/SmS2, which are detected by XPS. It is confirmed that the conversion process is driven by Li+ and Mg2+, and the accumulation of MgSx (x ≤ 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 860 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/macroporous 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 reduced 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 MoSx (x = 5.7, a-MoS5.7) polysulfide as cathode in Mg-Li hybrid batteries with the discharge mechanism of a-MoS5.7 + x Li⁺ + xe⁻ → MoS5.7−x + 0.5x Li2S (x ≤ 8.4) [61]. In the electrolytes without LiCl, the large charge-transfer resistance prevents Mg5+ from diffusion in a-MoS5.7; thus, Mg5+ hardly contributes to the capacity. Thanks to the fast Li⁺ diffusion, the MoS5.7 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 polyselenides 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(hexafluorosopropylxoy)borate anion (B(hfpp)₄−), Mg[B(hfpp)₄]ₓ/DME (denoted as MBhfp/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 Mg5⁺ into the Li electrolyte Li[B(hfpp)₄]ₓ/DME (denoted as LBhfp/DME) through the initial electrochemical cycles [63], and the in situ formed Mg-Li hybrid electrolyte can allow the highly reversible Mg plating/striping. 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/striping behavior benefits from the formation of Li-containing SEI, by partial decomposition of LBhfp/DME electrolyte on the
surface of Mg anode. Inorganic Li salts including Li₂CO₃, Li₂O, and LiF species are detected on the cycled Mg electrode surface (Figure 5(c)). The SEI formed in LBhfip/DME electrolyte is more uniform and denser than that in MBhfip/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 Mg(TFSI)₂/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 MgCl₂, thereby obtaining an Mg/S battery with an extended cycle life [14]. The low-solubility MgCl₂ on the Mg surface may cause high-voltage polarization. By adding 1 M LiCl, the solubility of MgCl₂ in THF can be increased to 0.6 M. As seen in Figure 5(d), the Mg/Mg symmetric 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 μA cm⁻². Notably, the decrease of overpotential is the synergistic effect of Li⁺ and Cl⁻, as well as the possible formation of soluble intermediate [Mg₂(μ-Cl)₆THF] [LiCl₂·2THF], 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 mAh g⁻¹ (based on LiFePO₄ 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 Mg(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 Mg(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
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 NaV$_2$O$_4$) 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\textsuperscript{+} can reactivate the conversion reaction products (e.g., MgS\textsubscript{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 microsized 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\textsuperscript{+} intercalation and Mg\textsuperscript{2+}/Li\textsuperscript{+} cointercalation. For the cathodes with Mg\textsuperscript{2+}/Li\textsuperscript{+} cointercalation, only VS\textsubscript{4} and prelithiated V\textsubscript{2}C show that Mg\textsuperscript{2+} contributes more capacity than Li\textsuperscript{+} and nanosized LTO shows an almost equal contribution of Mg\textsuperscript{2+} to that of Li\textsuperscript{+} [22, 26, 45]. The insertion of Mg\textsuperscript{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\textsuperscript{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., LBHF/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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