

# Development of cathode materials for rechargeable magnesium batteries: From intercalation to enolization

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## Abstract

In the past decade, magnesium batteries have been pursued as potentially low-cost, high-energy, and safe alternatives to Li-ion batteries due to the use of earth-abundant, high-capacity, and dendrite-free Mg anodes. However, strong interactions of Mg<sup>2+</sup> with electrolyte solutions and cathode materials lead to sluggish ion dissociation and diffusion in cathode materials, resulting in low capacity and sluggish kinetics in intercalation cathode materials. In this article, we review the development of cathode materials for Mg batteries, guided by a better understanding of electrolyte-electrode interactions and the strong influence of electrolyte solutions on cathode storage mechanisms. We first examine the challenges of Mg<sup>2+</sup>-storage cathodes based on intercalation chemistry. We then discuss cathode materials that store complex ions due to complications arising from electrolyte solutions. We further review conversion-type and enolization-type cathode materials, which bypass cation dissociation and solid-state ion diffusion altogether. The goal of this work is to provide readers with an overview of cathode material design strategies that have enabled genuine Mg<sup>2+</sup> storage with competitive performance.

## Key Points

- The origin of the sluggish kinetics and low capacity of Mg<sup>2+</sup>-storage
- Cathode storage with complex ions
- Conversion-type and enolization-type cathode materials

## Introduction

Growing global energy needs and climate change demand a paradigm shift from fossil fuels to sustainable energy resources such as wind, solar, tidal, biomass, and geothermal (Armand and Tarascon, 2008; Dunn *et al.*, 2011). These resources are inherently intermittent and generally disconnected from the electric grids that currently supply the vast majority of electricity. Unfortunately, we currently only have the capacity to store around 1% of the worldwide energy consumption and 98% of such storage comes through pumped hydro with an energy density of only 1 Wh m<sup>-3</sup> (Lewis, 2007). When comparing energy storage technologies, key parameters to consider include capital cost per cycle, battery safety, and cost of maintenance (Scrosati *et al.*, 2011).

While the lithium-ion battery price has fallen 88% over the last decade, demand for - lithium is expected to surge due to the rapid growth of lithium-ion battery-powered electric vehicles. Alternative battery technologies that use more abundant elements may offer higher energy density and better safety features. Mg is among the top ten most abundant elements in the Earth's crust (Yoo *et al.*, 2013). In rechargeable Mg batteries, Mg<sup>2+</sup> cations shuttle back and forth between the cathode and anode without causing a drastic change in the composition of electrolyte solutions. This operating principle is similar to that of lithium-ion batteries, suggesting the possibility to transfer the fundamental knowledge and manufacturing experiences from lithium-ion battery industry for a swift adoption of Mg batteries. Interestingly, electroplating of Mg shows a dendrite-free manner in high-performance Mg electrolytes (Yoo *et al.*, 2013; Liang *et al.*, 2020), in sharp contrast to the typical dendritic/mossy morphologies of lithium metal. This homogeneous, densely packed Mg crystals show promise for better safety as a metal anode.

The first rechargeable Mg battery was reported by Aurbach *et al.*, in which Chevrel phase  $\text{Mo}_6\text{S}_8$  (1.15 V versus  $\text{Mg}^{2+}/\text{Mg}$ , 75 mAh  $\text{g}^{-1}$ ) cathode, Mg metal anode, and dichloro complex (DCC) electrolyte were used (Aurbach *et al.*, 2000). This landmark work set the foundation for rechargeable Mg battery development. The progress of Mg electrolytes has recently been reviewed by Mohtadi *et al.* (2021). To provide the context for the discussion of cathode materials, we only provide a brief discussion of Mg electrolytes here. Historically, Mg was unable to reversibly plate from an electrolyte solution consisting of simple Mg salts due to the formation of a dense passivation layer on the Mg surface (Gregory *et al.*, 1990). Therefore, Mg electrolyte solutions, such as dichloro complex (DCC) (Aurbach *et al.*, 2000; Aurbach *et al.*, 2002), all-phenyl complex (APC) (Mizrahi *et al.*, 2008), and magnesium aluminum chloride complex (MACC) (Doe *et al.*, 2014), were developed relying on the presence of chloride to increase salt solubility and improve the reversibility of Mg plating/stripping. However, the presence of chlorides leads to serious challenges such as corrosion of current collectors and high dissociation energy of the Mg-Cl bond. It is therefore considered a critical step to develop single salt chloride-free electrolytes. Chloride-free boron cluster-based electrolyte ( $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$ ), pioneered by Mohtadi *et al.*, is recognized as a breakthrough in Mg electrolytes, featuring highly reversible Mg plating/stripping efficiency, high anodic stability and excellent water stability (Tutusaus *et al.*, 2015). Follow-up modifications of the  $\text{CB}_{11}\text{H}_{12}^-$  anion through fluorination of the C-H bond further increased anodic stability by  $\sim 0.3$  V (Hahn *et al.*, 2018).

In this article, we provide an overview of the development of cathode materials in rechargeable Mg batteries. We analyze the performance-limiting factors in classical chloride-based complex electrolytes and novel singlesalt chloride-free electrolytes. We present approaches to overcome such challenges, ranging from intercalation cathodes with  $\text{Mg}^{2+}$  storage to intercalation cathodes with complex-cation storage and hybrid ion storage. Finally, we discuss conversion-type and enolization-type materials that bypass cation dissociation and enable authentic Mg storage.

## $\text{Mg}^{2+}$ -Storage Cathodes Based on Intercalation Chemistry

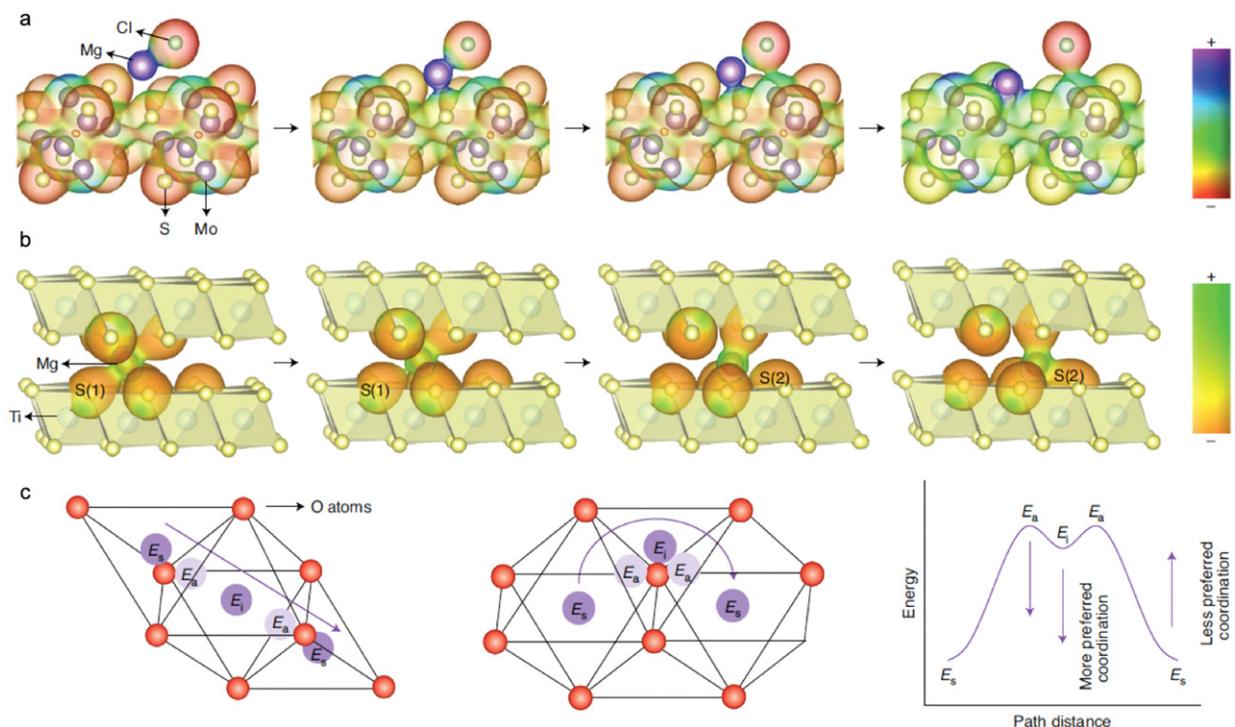
Cathode materials based on intercalation chemistry have been extensively investigated for Mg batteries (Canepa *et al.*, 2017). In addition to Chevrel phase  $\text{Mo}_6\text{S}_8$ , spinel  $\text{Ti}_2\text{S}_4$  is reported to show higher capacity at a slightly higher voltage (1.2 V versus  $\text{Mg}^{2+}/\text{Mg}$ , 192 mAh  $\text{g}^{-1}$ ). Compared to monovalent lithium ions,  $\text{Mg}^{2+}$  holds twice the amount of charge while having a similar ionic radius. As a result,  $\text{Mg}^{2+}$  is highly polarizing as the polarization strength is determined by  $q/r^2$ , where  $q$  is the charge number of the cations and  $r$  is the radius. The high polarizing nature of  $\text{Mg}^{2+}$  results in strong Coulombic interaction with the intercalation host, leading to sluggish solid-state ion diffusion at room temperature (Liang *et al.*, 2020).

Furthermore,  $\text{Mg}^{2+}$  cations have strong interactions with electrolyte solution species, which is further complicated by the complex composition of electrolyte solutions. In chloride-containing electrolytes, the dissociation energy to break the Mg-Cl bond could exceed 3 eV (Wan *et al.*, 2015). It is therefore evident that the ion dissociation from electrolyte complexes and solid-state diffusion, two essential processes in classical intercalation chemistry, should be strategically addressed in the rational design of  $\text{Mg}^{2+}$ -storage intercalation cathodes.

The first challenge is that  $\text{Mg}^{2+}$  in the electrolyte solutions needs to be freed from the strongly bound anions and solvent molecules before entering a host. As mentioned above, the energy cost for breaking the Mg-Cl bond is calculated to be  $\sim 3$  eV (Wan *et al.*, 2015). The success of the Chevrel phase  $\text{Mo}_6\text{S}_8$  has been attributed to its unique surface catalysis capability (Wan *et al.*, 2015). The density functional theory (DFT) calculation shows that the surface atoms of  $\text{Mo}_6\text{S}_8$  could catalyze dissociation of the Mg-Cl bond through two concerted interactions by coordinating electron-rich S anions to  $\text{Mg}^{2+}$  and electron-deficient Mo to  $\text{Cl}^-$  anions (Fig. 1(a)), resulting in the reduced cleavage barrier of the Mg-Cl bond from 3.0 to 0.2–0.8 eV. Although the surface catalysis capability has been only reported for the Chevrel phase, spinel  $\text{Ti}_2\text{S}_4$  may also share similar capability. Compared to Mg-Cl bond, Mg-solvent interaction is much weaker, such as 0.8 eV for Mg-THF (Wan *et al.*, 2015), hence the solvent molecules most likely have been desolvated at the surface of  $\text{Mo}_6\text{S}_8$ .

The second challenge is that  $\text{Mg}^{2+}$  has sluggish solid-state diffusion in intercalation cathode materials. Both chemical and structural angles could provide certain insights. The chemical factor is the chemical hardness of the cations and the host anions. Reasonable diffusivity of  $\text{Mg}^{2+}$  is achieved in soft chalcogenide-based host lattices but not in oxide hosts since the anionic framework based on  $\text{S}^{2-}$  or  $\text{Se}^{2-}$  is much softer than  $\text{O}^{2-}$ -based framework. The anions  $\text{S}^{2-}$  and  $\text{Se}^{2-}$  are highly polarizable and form relatively covalent bonds with  $\text{Mg}^{2+}$  (Liang *et al.*, 2020). The high polarizability of chalcogenide anions helps to stabilize the intermediate states during  $\text{Mg}^{2+}$  diffusion between coordination sites. Fig. 1(b) shows an example where migration of  $\text{Mg}^{2+}$  in a framework made of soft anions is always partially coordinated by anions that are not immediately adjacent, which contributes to many temporarily stabilized configurations. Both of the state-of-the-art intercalation-type materials, Chevrel phase  $\text{Mo}_6\text{S}_8$  and spinel  $\text{Ti}_2\text{S}_4$ , rely on the construction of frameworks with soft anions. However, the kinetics still requires improvement (Aurbach *et al.*, 2000; Sun *et al.*, 2016a).

Structure factors such as crystal systems, cavity size, framework flexibility, etc., come together to define the coordination environment of  $\text{Mg}^{2+}$ . Computational modeling of hypothetical systems has been conducted to investigate the relationship between  $\text{Mg}^{2+}$  diffusion barrier, preferred coordination number, and their coordination environment in hosts. Fig. 1(c) shows an example of the migration of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$  in spinel  $\text{Mn}_2\text{O}_4$  from a stable tetrahedral site (with energy  $E_s$ ) through a 3-O plane ( $E_a$ ) to an intermediate octahedral site ( $E_i$ ). Two structural features could favor  $\text{Mg}^{2+}$  migration. First, structures with intercalation sites where  $\text{Mg}^{2+}$  ions have an unfavorable coordination number energy (thus high  $E_s$ ) and intermediate sites where  $\text{Mg}^{2+}$  ions have preferred coordination numbers (thus lower  $E_a$  and  $E_i$ ) will provide a low migration barrier. Second, structures that provide migration paths where the coordination number of  $\text{Mg}^{2+}$  ions changes as little as possible could also enable low migration barriers.



**Fig. 1** Schematic illustration of the intercalation of Mg<sup>2+</sup> in cathode materials. (a) Mechanism of catalytic dissociation of MgCl<sup>+</sup> on the surface of Mo<sub>6</sub>S<sub>8</sub>. (b) Polarizable anion-assisted Mg<sup>2+</sup> diffusion in layered TiS<sub>2</sub>. (c) Coordination environment in spinel Mn<sub>2</sub>O<sub>4</sub> and olivine FePO<sub>4</sub> affecting the diffusion of Mg<sup>2+</sup>. Reprinted with permission from Liang, Y., Dong, H., Aurbach, D., Yao, Y., 2020. Current status and future directions of multivalent metal-ion batteries. *Nat. Energy* 5, 646–656.

In addition to approaches from chemical and structural factors, reducing the particle size of the cathode materials to shorten the ion diffusion lengths has also been found effective in enhancing the electrode/electrolyte interaction. Aurbach *et al.* studied the effect of particle size on the electrochemical performances (Aurbach *et al.*, 2007). The cyclic voltammograms of Mg<sub>x</sub>Mo<sub>6</sub>S<sub>8-n</sub>Se<sub>n</sub> nanomaterials showed more reversible and faster kinetics than their micron-sized counterparts, demonstrating superior rate performances and higher specific capacities of electrodes comprising Mg<sub>x</sub>Mo<sub>6</sub>S<sub>8-n</sub>Se<sub>n</sub>. Nazar *et al.* systematically investigated the effect of particle size on the electrochemical performance of layered TiS<sub>2</sub> and spinel Ti<sub>2</sub>S<sub>4</sub> (Blanc *et al.*, 2020). The nano-sized layered TiS<sub>2</sub> synthesized using a liquid synthetic route exhibited greatly improved electrochemical performance in comparison to the micro-sized material. Low coulombic efficiency (CE) of micron-sized TiS<sub>2</sub> (current density: 12 mA g<sup>-1</sup>; temperature: 60°C) led to 47% irreversible capacity, low initial discharge capacity, and poor cycling stability have been reported, in contrast to the high initial discharge capacity, high initial CE, and enhanced cycling stability when nano-sized TiS<sub>2</sub> was used. Nano-sized spinel Ti<sub>2</sub>S<sub>4</sub> prepared using ball milling also showed significantly improved cycling behavior (capacity decay rate: 0.13% for nano versus 0.7% for micro per cycle). However, a lower initial discharge capacity was observed, resulting from the surface degradation during the high energy milling process. Nazar *et al.* reported that nano-sized CuCo<sub>2</sub>S<sub>4</sub> prepared by mechanical milling showed a high capacity of 180 mAh g<sup>-1</sup> at 60°C (Blanc *et al.*, 2020). Furthermore, nano-sized CuCo<sub>2</sub>S<sub>4</sub> with a highly porous network synthesized by a low temperature melt approach enabled an enhanced capacity of 350 mAh g<sup>-1</sup> at 60°C, nearly double that of mechanical milled CuCo<sub>2</sub>S<sub>4</sub>. These results show reducing particle size is an effective approach to improve the electrochemical performances.

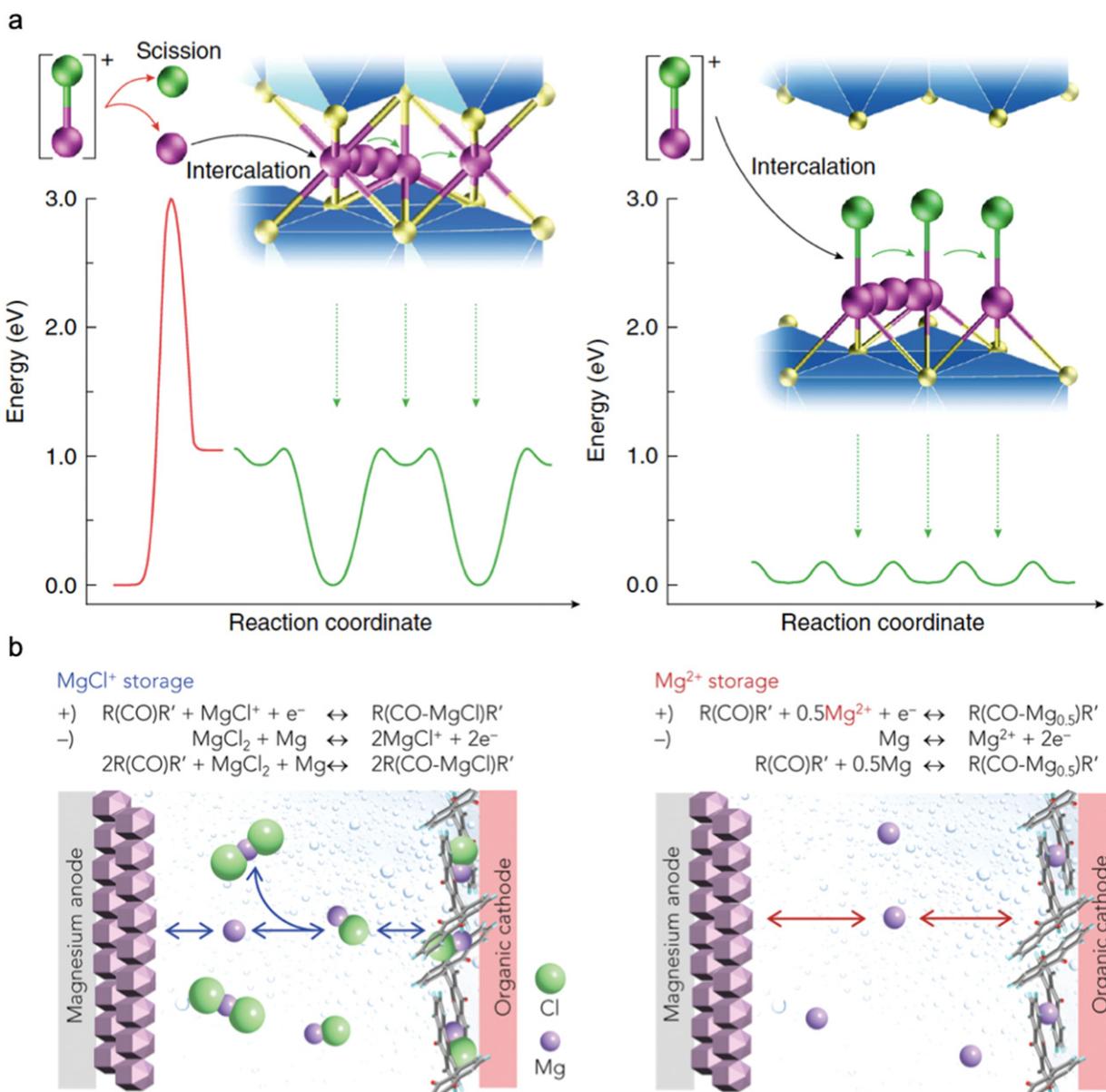
High-voltage materials such as V<sub>2</sub>O<sub>5</sub> have been pursued. Recent studies revealed that proton intercalation instead traditionally believed Mg<sup>2+</sup> intercalation was the dominant reaction in V<sub>2</sub>O<sub>5</sub> even in dry non-aqueous electrolytes (Verrelli *et al.*, 2018). Cabana *et al.* reported that α-V<sub>2</sub>O<sub>5</sub> is able to store Mg<sup>2+</sup> at 110°C with an anodically stable ionic liquid electrolyte (Yoo *et al.*, 2019). However, Mg metal anode is still not compatible with this ionic liquid electrolyte.

### Cathodes Storing Complex Cations

The storage mechanism of Mg cathodes is often complicated by the complex composition of Mg electrolyte solutions. For cells with chloride-containing electrolyte solutions, intercalation of Mg<sup>2+</sup> would require freeing the cation from the strong Mg-Cl bonds. This step is sometimes bypassed through direct storage of the complex ions (MgCl<sup>+</sup>, AlCl<sub>2</sub><sup>+</sup>, AlCl<sub>4</sub><sup>-</sup> etc.) instead of the bare Mg<sup>2+</sup>. In some cases, solvated ions are stored without stripping off the solvent molecules. Cathodes storing complex cations, including solvated ions, have been shown in intercalation compounds with large interstitial spaces as well as in redox-active polymers. To unambiguously identify the reaction mechanism, it is required to quantify the elemental composition of discharged products and their spatial distribution.

## Two-Dimensional Layered Cathodes Storing Complex Cations

Moving from  $\text{Mg}^{2+}$  to  $\text{MgCl}^+$  storage circumvents the high dissociation energy of the Mg-Cl bond ( $\sim 3$  eV) and reduces the polarization strength of the ion, leading to a lower diffusion energy barrier. Our group first demonstrated a cathode with  $\text{MgCl}^+$  storage using an interlayer-expanded  $\text{TiS}_2$  cathode (Fig. 2(a)) (Yoo *et al.*, 2017). DFT modeling shows the migration barrier is reduced from 1.06 to 0.51 eV when interlayer spacing increases from 0.57 to 1.09 nm, and further decreases to 0.18 eV if  $\text{MgCl}^+$  is considered as the active species. The fast kinetics of  $\text{MgCl}^+$  in interlayer-expanded  $\text{TiS}_2$  enabled the large specific capacity ( $239 \text{ mAh g}^{-1}$ ), corresponding to 1  $\text{MgCl}^+$  intercalation per formula of  $\text{TiS}_2$ , and excellent rate capability (70% of the capacity retention at a current density of  $240 \text{ mAh g}^{-1}$ ). Following this first demonstration, many groups followed the interlayer expansion approach in other host materials (Zhou *et al.*, 2018; Xue *et al.*, 2019). For example, interlayer-expanded  $\text{VOPO}_4$  nanosheets with an interlayer distance of 1.42 nm were synthesized by Mai *et al.* using a facile ultrasonication exfoliation and self-assembly route, which also enabled the efficient storage of  $\text{MgCl}^+$  (Zhou *et al.*, 2018). As a result, a high specific discharge capacity of  $310 \text{ mAh g}^{-1}$ , remarkable rate capability ( $109 \text{ mAh g}^{-1}$  at  $2000 \text{ mA g}^{-1}$ ) and long cycle life ( $192 \text{ mAh g}^{-1}$  after 500 cycles) were obtained.



**Fig. 2** Challenges of  $\text{Mg}^{2+}$  storage in cathode materials. (a) Energy diagrams for the intercalation and diffusion of  $\text{Mg}^{2+}$  and  $\text{MgCl}^+$ . Intercalation of  $\text{MgCl}^+$  in interlayer expanded  $\text{TiS}_2$  bypasses the breakage of the Mg-Cl bond. Mg and Cl atoms are shown as purple and green spheres, respectively. (b) Schematic illustration of the  $\text{MgCl}^+$ - and  $\text{Mg}$ -storage mechanism in organic polymers. Reprinted with permission from (a) Yoo, H.D., *et al.*, 2017. Fast kinetics of magnesium monochloride cations in interlayer-expanded titanium disulfide for magnesium rechargeable batteries. *Nat. Commun.* 8, 339. (b) Dong, H., *et al.*, 2019. Directing Mg-storage chemistry in organic polymers toward high-energy Mg batteries. *Joule* 3, 782–793.

Jin *et al.* reported that expanded VS<sub>2</sub> nanoflowers based on MgCl<sup>+</sup> and Mg<sup>2+</sup> co-storage mechanisms also delivered high reversible capacity of 245 mAh g<sup>-1</sup> at 100 mA g<sup>-1</sup> and great rate performance (103 mAh g<sup>-1</sup> at 2000 mA g<sup>-1</sup>) (Xue *et al.*, 2019).

In chloride-free electrolytes, Zhao-Karger *et al.* discovered solvated Mg<sup>2+</sup> species ([Mg(DME)<sub>x</sub>]<sup>2+</sup>) were stored in nanostructured 1T-MoS<sub>2</sub> without stripping off the solvent molecules (Li *et al.*, 2018a). With the solvated Mg<sup>2+</sup> intercalation, the polarization strength of Mg<sup>2+</sup> is greatly reduced, resulting in a high reversible capacity of 120 mAh g<sup>-1</sup> and long-term cycling stability (200 cycles).

### Redox-Active Polymers

In addition to layered sulfides, redox-active quinone-based polymers have also been reported to demonstrate promising electrochemical performance. Unlike intercalation compounds, quinone polymers store ions via an enolization reaction, where the active species existing in the electrolytes coordinate with the negatively charged oxygen atoms during the reduction of the carbonyl groups, and un-coordinate during the oxidation process. Dominko *et al.* first investigated a quinone polymer poly(anthraquinoyl) sulfide (PAQS) in various chloride-containing Mg electrolytes (Bitenc *et al.*, 2015). A high reversible capacity of ~200 mAh g<sup>-1</sup> was obtained. However, this battery suffered from limited cycling stability owing to dissolution of PAQS. 1,4-polyanthraquinone (P14AQ) was later investigated by Liao *et al.* in Cl-containing Mg electrolytes, which showed limited solubility in THF based electrolytes and thus long-term cycle life has been demonstrated (Pan *et al.*, 2016a). Our group showed that, in chloride-containing electrolytes, organic polymers store MgCl<sup>+</sup>, at least partially, instead of the previously assumed genuine Mg<sup>2+</sup> (Dong *et al.*, 2019). (Fig. 2(b)). EDS of discharged cathodes shows clear evidence of MgCl<sup>+</sup> storage. During the discharge of a MgCl-storage cell, a Mg atom in the Mg metal anode loses two electrons and enters the electrolyte as Mg<sup>2+</sup>. Mg<sup>2+</sup> then accepts a Cl<sup>-</sup> from the MgCl<sub>2</sub> in the electrolyte and forms MgCl<sup>+</sup>, which enters the cathode as monovalent cations. Since the cathode stores both Mg<sup>2+</sup> and Cl<sup>-</sup> but the anode stores only Mg, the electrolyte has to double as a Cl<sup>-</sup> reservoir (in addition to ion conduction), and the amount of Cl<sup>-</sup> in the electrolyte must at least match the capacity of the cathode. Mg<sup>2+</sup> storage in organic polymer cathodes was demonstrated by using chloride-free Mg metal-compatible electrolytes. As shown in Fig. 2(b), the Mg-storage scenario is a simple rocking chair mechanism where the flux of Mg<sup>2+</sup> goes from the anode to the cathode during discharge and vice versa.

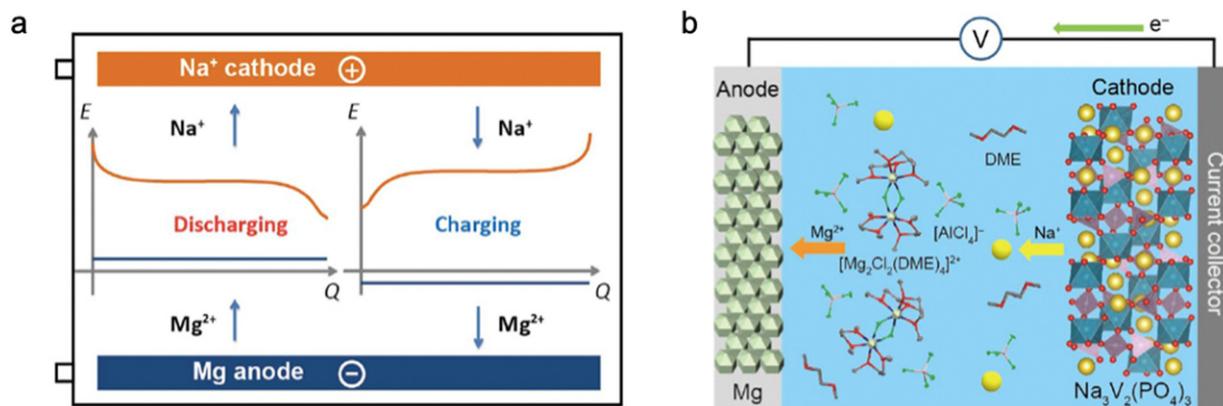
MgCl<sup>+</sup> and solvated Mg<sup>2+</sup> storage chemistry bypass the problematic ion pair dissociation or dissolution step, but it is essential to recognize that the cell-level specific energy will be dramatically limited by the weight of the electrolytes because the charge carrier ions at the cathode and anode electrodes are different, so the electrolytes have to contain enough necessary ions (e.g., Cl<sup>-</sup>) to sustain the cathode reaction (Dong *et al.*, 2019). The appropriate evaluation of cathodes requires unequivocal identification of the reaction mechanisms. Quantification of the elemental composition of discharged products is of extreme importance. Inductively coupled plasma spectroscopy, X-ray absorption spectroscopy, solid-state nuclear magnetic resonance, and so on, all provide such insights into the bulk composition of cathodes.

The storage of complex species complicates the cell configuration compared to lithium-ion batteries. In the latter systems, bare lithium ions move between the electrodes while the solution concentration remains invariant, enabling the use of a very small amount of electrolyte solution that serves solely as an ion-transfer medium. In contrast, rechargeable batteries based on the storage of complex species at the cathode and pure metal at the anode would suffer from material imbalance during charging and discharging which alters the concentration, ion species, and so on in the electrolyte solutions. In a practical cell where the amount of electrolyte solution is limited, these changes could impact the electrodes' reaction mechanisms, cell stability, and energy density. In fact, these batteries may not qualify as authentic Mg batteries, even though they may still be referred to as Mg metal batteries as long as a Mg metal anode is involved. The characterization of discharged cathodes is important for identifying cathode materials capable of genuine Mg-ion storage.

### Hybrid Ion Batteries

An alternative battery concept that fully exploits the cost and safety benefits of the Mg anode but bypasses the sluggish intercalation of Mg<sup>2+</sup> is a hybrid magnesium-lithium-ion battery (MLIB) or magnesium-sodium-ion battery (MNIB), which combines a Mg anode with a cathode that can store cations with excellent solid-state diffusion (e.g., Li<sup>+</sup> or Na<sup>+</sup>) in a mixed Mg-Li or Mg-Na dual-salt electrolyte (Cheng *et al.*, 2016; Li *et al.*, 2017). The working principle of a MNIB is illustrated in Figs. 3(a) and (b). Because the redox potential of Mg<sup>2+</sup>/Mg is 0.67 V and 0.24 V higher than that of Li<sup>+</sup>/Li and Na<sup>+</sup>/Na, reversible Mg deposition/stripping should occur at the anode side before Li and Na deposition/stripping can take place. On the cathode side, the Li<sup>+</sup> (or Na<sup>+</sup>) ion dominates intercalation because Mg<sup>2+</sup> diffuses several orders of magnitude slower compared to Li<sup>+</sup> (or Na<sup>+</sup>) in the same cathode materials. Due to the asymmetric use of Mg<sup>2+</sup> and Li<sup>+</sup> (or Na<sup>+</sup>) on each side of the electrodes, the hybrid electrolyte has to function as an ion reservoir to supply enough Li<sup>+</sup> (or Na<sup>+</sup>) and receive Mg<sup>2+</sup> during discharge, and vice versa during charge. Therefore, the selection of a suitable hybrid electrolyte is important for obtaining high energy density and stable cycling.

In 2006, Aurbach and coworkers reported the first MLIB by adding LiCl to the DCC solution for higher ionic conductivity and using Chevrel phase as a Li-intercalation cathode (Gofer *et al.*, 2006). Yagi and coworkers revisited the MLIB concept using LiFePO<sub>4</sub> as the cathode in 2014, however, the prototype cells show low Coulombic efficiency and short cycle life (Yagi *et al.*, 2014). Since then, many reports have investigated novel cathode materials and dual-salt electrolytes, attracting a great deal of scientific and technological interest. The hybrid ion electrolyte is the key component that plays an important role in this chemistry. Especially for high-voltage cathode materials, electrolytes with higher anodic stability are required. Li *et al.* identified a new dimagnesium-dichloro dimer [DMDC, Mg<sub>2</sub>(μ-Cl)<sub>2</sub>(DME)<sub>4</sub>] cation complex in dimethoxyethane (DME) (Cheng *et al.*, 2015). This type of



**Fig. 3** (a) Illustration of the operating principle of a Mg–Na hybrid battery. During battery discharging,  $\text{Na}^+$  ions intercalate into the cathode and  $\text{Mg}^{2+}$  ions dissolve from a Mg anode. The corresponding voltage profiles of the positive and negative electrodes are shown in orange and blue lines, respectively. (b) Electro-active species involved during charging a hybrid battery made of a  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  cathode, a Mg anode, and an electrolyte of 0.2 M  $[\text{Mg}_2\text{Cl}_2][\text{AlCl}_4]_2$  and 0.4 M  $\text{NaAlCl}_4$  in DME. Reprinted with permission from Li, Y., *et al.*, 2017. A high-voltage rechargeable magnesium-sodium hybrid battery. *Nano Energy* 34, 188–194.

electrolyte (e.g.,  $\text{MgCl}_2\text{-AlCl}_3$ ,  $\text{MgCl}_2\text{-Mg}(\text{TFSI})_2$ ) shows wide anodic stability ( $> 3.4$  V versus  $\text{Mg}^{2+}/\text{Mg}$ ). Dual-salt electrolytes based on DMDC cation complex can be prepared through dissolving Li or Na salts. However, chloride in the electrolytes causes serious corrosion issues for current collectors such as stainless steel and aluminum. Liao *et al.* reported two chloride-free dual-salt electrolytes, namely  $\text{Mg}(\text{TFSI})_2\text{-LiTFSI}$  and  $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2\text{-LiTFSI}$ , anodically stable up to 3.8 V versus  $\text{Mg}^{2+}/\text{Mg}$  even with aluminum current collectors (Pan *et al.*, 2016b). Many  $\text{Li}^+$  (or  $\text{Na}^+$ )-based cathode materials are compatible with dual-salt electrolytes as long as their operating voltage window does not exceed the anodic stability of the electrolytes (Cheng *et al.*, 2016).

To fully exploit the rate capability, various nano-sized compounds were investigated, such as  $\text{FeS}_2$  nanocrystals (Walter *et al.*, 2015), Prussian blue nanoparticles (Sun *et al.*, 2016b),  $\text{MoS}_2$  nanosheets (Truong *et al.*, 2017), and  $\text{TiO}_2$  nanoflakes (Su *et al.*, 2016). Nevertheless, the value of this technology remains controversial due to the low cell-level energy density (Cheng *et al.*, 2016). As discussed in the section “Redox-Active Polymers”, the specific energy of hybrid ion batteries is limited by the salt concentration. Concentrated electrolytes are able to alleviate the reduced energy density. However, concentrated electrolytes exhibit high cost and decreased ionic conductivity (Yoo *et al.*, 2015).

## Conversion-Type Materials

Moving from intercalation to conversion reactions may tackle the dissociation challenge and solid-state ion diffusion problems. Conversion-type materials such as chalcogens, chalcogenides, and halogens undergo two-phase solid-liquid reactions, which do not involve solid-state ion diffusion. Muldoon *et al.* reported the first proof-of-concept magnesium-sulfur (Mg-S) battery using a non-nucleophilic hexamethyldisilazide magnesium chloride (HMDSMgCl) based electrolyte (Kim *et al.*, 2011). Significant progress has been achieved since this demonstration. To date, Mg-S batteries have delivered reversible specific capacities of up to 1200  $\text{mAh g}^{-1}$  at 1.1–1.4 V (Du *et al.*, 2017). Similar to the issue of Li-S batteries, fast capacity decay owing to the dissolution of polysulfide is one of the major challenges. Moreover, Aurbach *et al.* reported that the polysulfides in the electrolytes lead to the formation of a passivation layer on the Mg metal anode, resulting from the precipitation of insoluble Mg-S species (Salama *et al.*, 2018). This passivation layer dramatically impacts the reversibility of Mg anode. In sharp contrast, dissolved iodine was shown to reduce the Mg plating-stripping overpotential, however, the coulombic efficiency has not been reported for this system (Li *et al.*, 2018b). Nazar *et al.* reported that micron-sized CuS delivered a discharge capacity of 550  $\text{mAh g}^{-1}$  at 150°C, corresponding to 98% of its theoretical capacity (Duffort *et al.*, 2016). However, the high operating temperature increases the parasitic reactions. Therefore, nanosizing CuS particles was required to achieve reasonable capacities at lower temperatures. The same group later showed that nano-sized CuS via a liquid synthetic route dramatically improved electrochemical performance at room temperature (Blanc *et al.*, 2020). All these materials have shown performance that rivals or surpasses intercalation compounds and may represent the long-sought-after solution.

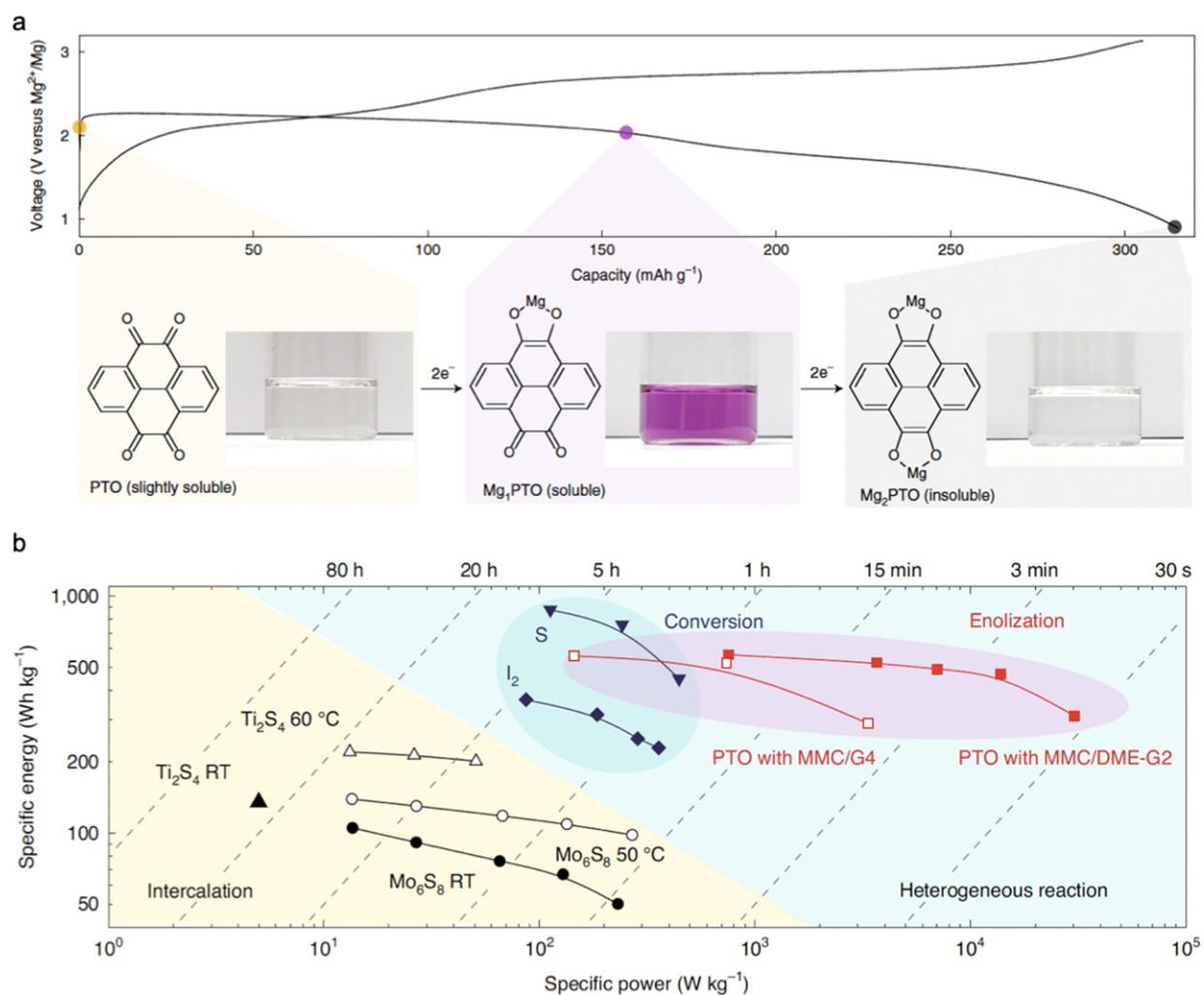
## Enolization-Type Materials

Molecular crystals can efficiently store  $\text{Mg}^{2+}$  through a solid-liquid heterogeneous enolization ( $\text{C}=\text{O} \rightleftharpoons \text{C}-\text{O}^-$ ) redox chemistry (Dong *et al.*, 2020). Our group recently illustrated this enolization chemistry utilizing a pyrene-4,5,9,10-tetraone (PTO) cathode (Dong *et al.*, 2020). The heterogeneous enolization process is shown in Fig. 4(a). During discharge, the PTO cathode materials are reduced to

a soluble  $\text{Mg}_1\text{PTO}$  intermediate, then to an insoluble  $\text{Mg}_2\text{PTO}$  as the final product. The two two-electron reactions involving the solid-liquid two-phase reactions bypass the sluggish solid-state  $\text{Mg}^{2+}$  diffusion in conventional intercalation compounds.

Compared to organic polymers, molecular crystals are able to store  $\text{Mg}^+$  without involving solvent molecules. Such a difference could be explained by different solvent-organic material interactions: for redox polymers, the electrolyte swells polymer chains, and there is no driving force for desolvation to take place; for molecular crystals, the solid-liquid-solid reaction enables the final discharged product to be free-of-solvent. It is noted that chloride-free electrolytes have to be applied in this case, otherwise  $\text{MgCl}^+$  active species are still possibly stored in molecular crystals instead of  $\text{Mg}^{2+}$ .

The key difference between the heterogeneous enolization redox chemistry and the conversion reaction is the absence of covalent bond cleavage/re-formation in the enolization redox mechanism ( $\text{C}=\text{O} \rightleftharpoons \text{C}-\text{O}^-$ ), which results in the significant improvement of the redox kinetics and reversibility. Cathode material loss resulting from the dissolution of  $\text{Mg}_1\text{PTO}$  intermediate can be effectively controlled through the insertion of a thin and lightweight graphene oxide film between the cathode and the separator to block the intermediate. Fig. 4(b) compares the Ragone plot of state-of-the-art Mg metal batteries storing  $\text{Mg}^{2+}$  cations, excluding batteries storing complex ions, such as previously reported organic compounds, which have been shown to store either  $\text{MgCl}^+$  (in  $\text{MgCl}$ -based electrolytes) or solvated  $\text{Mg}^{2+}$  ions. Both intercalation-type cathodes ( $\text{Mo}_6\text{S}_8$ ,  $\text{Ti}_2\text{S}_4$ ) and conversion-type cathodes (S and  $\text{I}_2$ ) display slow kinetics (up to 2 C). In contrast, cathode material relying on an enolization redox mechanism demonstrates a specific power of  $30.4 \text{ kW kg}^{-1}$ , while still providing a high material-level specific energy of  $313 \text{ Wh kg}^{-1}$ . The new concepts for Mg-organic batteries should have a role in guiding the design of the next generation of materials guided by the vast possibilities of organic substitution, modifications, and solubility control.



**Fig. 4** (a) Voltage profile of a Mg-PTO cell with  $\text{Mg}(\text{CB}_{11}\text{H}_{12})_2/\text{tetraglyme}$  and reductive enolization of PTO to  $\text{Mg}_1\text{PTO}$  and  $\text{Mg}_2\text{PTO}$ . (b) Ragone plot of state-of-the-art Mg metal batteries that store  $\text{Mg}^{2+}$  ions. Reprinted with permission from Dong, H., *et al.*, 2020. High-power Mg batteries enabled by heterogeneous enolization redox chemistry and weakly coordinating electrolytes. *Nat. Energy* 5, 1043–1050.

## Conclusion

State-of-the-art Mg batteries are still far from reaching their full potential, particularly resulting from the high dissociation energy of solvated ions and high activation energy for ion transport in electrode materials. Overcoming these barriers is inevitable for a Mg battery to become successful. Cells based on  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{MgCl}^+$ , or solvated  $\text{Mg}^{2+}$  storage chemistries may not qualify as authentic Mg batteries. These systems have to require a large amount of the electrolytes, limiting their practical energy density and stability. Cathodes based on intercalation chemistry are the most widely studied. Current successful intercalation compounds are all based on soft anions. The design of the intercalation compounds with surface catalysis capability is necessary for fast interfacial reaction kinetics. Nano-sized intercalation compounds are an effective way to alleviate sluggish  $\text{Mg}^{2+}$  diffusion so that promising candidates will not be overlooked. Conversion-type cathode materials are good candidates for Mg batteries. The theoretical volumetric energy density of Mg-S batteries is even higher than that of Li-S batteries. Nevertheless, the migration of polysulfides from the sulfur cathode to the Mg anode has to be completely avoided. The heterogeneous enolization redox chemistry utilizing molecular crystals sets a new direction for developing high-power Mg batteries. Dedicated cell-level engineering efforts are required to achieve high cell-level energy density and fast charging capability.

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