Cathode Materials for Magnesium and Magnesium-ion based Batteries

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Abstract

Rechargeable magnesium-ion batteries are a promising candidate technology to address future electrical energy storage needs of large scale mobile and stationary devices, due to the high environmental abundance of magnesium metal and divalent character of magnesium ion. With the recent increase in reports discussing cathode materials for magnesium-ion batteries, it is instructive to assess recent research in order to provide inspiration for future research. This review is a summary of the different chemistries and structures of the materials developed for magnesium ion cathodes. The particular strategies which may lead to future research initiatives are amplified.

1. Introduction

The efficient management of energy sources, both renewable and non-renewable, on local and large bases, is critical to addressing important global issues such as energy demand, fossil fuels economies and limitations, and human induced climate change. Crucial to the efficient management of energy sources are batteries of various performance profiles which can store and release generated electrical energy at levels appropriate for a number of application power demands. For example, the development of electric vehicles, as well as the growing electrical energy storage needs of mobile and stationary devices demonstrate the need for rechargeable batteries with a variety of application-based performance capabilities, including sufficient energy density, appropriate voltage and current capabilities, and the safe management of heat. Another critical issue in battery development is cost. One of the most successful and broadly implemented rechargeable battery technologies developed to date is lithium ion. However, questions regarding the future of using lithium ion technology for large scale applications center on the sustainability and high cost of lithium, especially due to the projected increase in demand for lithium based electrodes used in hybrid and plug in electric vehicles and stationary (grid) storage [1-3]. It is projected that costs may continue to rise as these new

technologies gain a greater share of the market, and new lithium reserves will be needed to keep up with demand [3].

Of the possible alternatives to lithium-ion, rechargeable magnesium-ion batteries are a promising candidate, and research into the technology has accelerated in recent years (**Figure 1**).

Figure 1. Number of publications (A) and citations (B) for the topic “Magnesium battery cathode” over the past 20 years, based on Web of Science searches conducted in August 2014.

Magnesium-ion technology is promising for several reasons. First, due to the natural abundance of magnesium in the earth’s crust, approximately 10^4 times that of lithium, its incorporation into electrode materials is inexpensive (**Table 1**). Secondly, magnesium is more atmosphere stable and has a higher melting point than lithium, making it safer relative to lithium [4]. The divalent nature of magnesium ions also presents a potential advantage in terms of volumetric capacity (3833 mAh/cm^3 for Mg vs. 2046 mAh/cm^3 for Li).

Characteristics	Mg	Li	Reference
Pauling Ionic Radius	65	60	[3]
Voltage vs. S.H.E.	-2.37	-3.04	[2]
Elemental abundance (ppm in earth's crust)	2.33E+04	2.00E+01	[5]
volumetric capacity (mAh/cm^3)	3833	2046	[6]
gravimetric capacity (mAh/g)	2205	3862	[4]

Table 1. Comparison of characteristics of magnesium (Mg) and lithium (Li).

Despite these positive attributes, the development of magnesium-ion technology has not kept pace with that of lithium ion technology. One critical issue impeding progress has been development of a suitable electrolyte which will enable reversible release of Mg^{2+} ions from a magnesium metal anode [7]. Unlike Li^+ ion conducting surface films formed by polar aprotic electrolyte solutions on Li metal electrodes, surface films on magnesium metal often block the

transport of Mg^{2+} ions [8]. For example, the use of magnesium salts such as $\text{Mg}(\text{ClO}_4)_2$ and $\text{Mg}(\text{BF}_4)_2$ paired with organic solvents such as carbonates or nitriles results in the formation of surface films which passivate the magnesium metal electrode [8]. Thus, the use of magnesium based electrolytes which are analogous to those commonly used with Li^+ ion technology is not ideal. Notably, an advancement in this area was reported in 2000 with the development of electrolyte based on magnesium organo-haloaluminate complexes dissolved in tetrahydrofuran (THF) or glyme based solvents [9]. These electrolytes allow for electrochemical deposition-dissolution of magnesium and have a stable electrochemical window of 2.5 V, thereby allowing for the testing of practical cathode materials. However, the magnesium haloaluminate complexes are corrosive and reactive, particularly with water, causing additional constraints in terms of the necessary stabilities of the cell components.

A second ongoing challenge is the development of cathode materials which have high reversible capacity and adequate operating voltage under appropriate power output conditions. Due to the high valency of Mg^{2+} ions, the kinetics of solid state diffusion through inorganic cathode materials is slow, resulting in low reversible capacity and reduced power output. Recent work suggests that low Mg^{2+} mobility is caused by both strong ionic interactions as well as redistribution of the divalently charged cations in the host material [10]. To address these issues, several strategies have been reported. For example, mesoporous and nanostructured materials [11] which display large surface areas have been employed as electrode materials in order to decrease the diffusion length for Mg^{2+} ions into host cathode sites. Further, the use of materials with high divalent ion mobility [12, 13] have been used as electrode materials in order to increase current capabilities.

With the recent increase in reports involving cathode materials for magnesium-ion batteries, it is important to assess recent research in order to provide inspiration for future research. Specifically, there are many magnesium-ion studies involving numerous cathode compositions and various phases (**Table 2**). In the past five years there have been several reviews written about magnesium-ion batteries [4, 6, 13]. The goal of this review is to augment the previous literature in this field by focusing on structure-function relationships of various classes of cathode materials in the context of their coordination chemistry. By summarizing the electrochemical performance in magnesium based systems in light of the known structures which function most effectively as magnesium ion cathodes, we hope to reveal particular strategies which may facilitate future developments in this field.

Cathode Material Class	Types of Composition	Formula	Number of Publications
Vanadium Oxide	Vanadium Pentoxide	V_2O_5	17 [14-30]
	Vanadium Bronze	V_3O_8	3 [16, 31, 32]
	Magnesiated Vanadium Pentoxide	$Mg_xV_2O_5$	1 [33]
Prussian Blue	Nickel Hexacyanoferrate	$NiFe(CN)_6$	1 [34]
	Copper Hexacyanoferrate	$CuFe(CN)_6$	1 [35]
Molybdenum Sulfide	Chevrel Phase	Mo_6S_8	15 [9, 10, 36-48]
	Chevrel Phase	Mo_6T_8 (T=S or Se)	7 [12, 49-54]
	Molybdenum Disulfide	MoS_2	5 [55-59]
Molybdenum Oxide	Orthorhombic	MoO_3	5 [16-18, 60, 61]
Manganese Oxide	Hollandite	MnO_2	5 [62-66]
	Todorokite	MnO_2	1 [63]
	Birnessite	MnO_2	1 [65]
	Spinel	MnO_2	3 [67, 68]
	Post-spinel	MnO_2	1 [69]
Silicates	Manganese Silicate	$Mg_{1.03}Mn_{0.97}SiO_4$	6 [69-74]
	Iron Silicate	$MgFeSiO_4$	2 [75, 76]
	Cobalt Silicate	$MgCoSiO_4$	2 [77, 78]

Table 2. Cathode materials used in magnesium-ion batteries.

2. Cathode Materials

2.1. Vanadium Oxide

Figure 2. Crystallographic structure of crystalline V_2O_5 [79].

Crystalline V_2O_5 consists of layers of V_2O_5 – based polyhedra, which provides pathways for ion insertion and removal (**Figure 2**). A screening of metal-oxides and metal-sulfides to determine Mg^{2+} reversibility indicated that V_2O_5 had an open circuit voltage of 2.66 V, the second highest voltage of all the screened compounds when paired with magnesium foil in 1.0 M $Mg(ClO_4)_2$ in THF. Notably, the highest open-circuit voltage belonged to lead-oxide compounds; however the large density of lead results in low gravimetric energy density.

Intercalation of Mg^{2+} into V_2O_5 is a slow process, possibly due to chemical modification of the V_2O_5 crystal surface [7]. Further, V_2O_5 electric conductivity is low. To optimize the diffusional pathways of Mg^{2+} during the charging and discharging of V_2O_5 , reports have appeared involving the control of crystallite size [14, 22-24] and the use of conductive additives [19, 20]. Decreasing crystallite size decreases the diffusion path length within the V_2O_5 crystals, improving capacity at higher current rates. This strategy has been utilized in work which investigates nanocrystalline V_2O_5 [14] and V_2O_5 nanotubes [22-24], although more work needs to be completed to compare the electrochemistry of the nanocrystalline materials with microcrystalline V_2O_5 in order to accurately assess the effectiveness of this approach. The use of conductive materials has also been tested as a means of improving Mg^{2+} diffusion. When the electrochemical performance of a composite carbon – V_2O_5 xerogel consisting of aggregated acetylene black carbon particles covered with a thin layer (<100 nm) of V_2O_5 xerogel was compared to that of an electrode prepared via a conventional mixture of V_2O_5 , the composite exhibited higher capacity [19, 20]. This improvement was attributed to shorter diffusion length of Mg^{2+} through the thin V_2O_5 layer in the composite.

Vanadium oxide gels ($V_2O_5 \cdot nH_2O$) have crystal structures comprised of layered square-pyramidal VO_5 polyhedra in which V^{5+} is coordinated with five oxygen atoms. Water molecules are bound between the layers of V_2O_5 . The layered structure allows V_2O_5 to cleave along the layers, but also provides channels for ion insertion and deinsertion. A critical aspect in the research of V_2O_5 cathodes is water content, because water in the electrolyte can solvate and partially shield the divalent magnesium-ion charge, allowing for easier insertion and deinsertion into the crystal. Notably, desolvation energies for magnesium are two or more times greater than desolvation energies for lithium, due to the divalency of magnesium ions [80]. The effects of water bound to layered vanadium oxide xerogel crystals $V_2O_5 (H_2O)_y$ ($y \leq 2$ to 3) were studied in nonaqueous salt melt electrolytes [32]. The water content in the cathode was determined to be essential for shielding the 2^+ charge of magnesium ions to facilitate insertion and deinsertion. Hydrated vanadium oxides exhibited a capacity of 170 mAh/g in 1 M $Mg(ClO_4)_2$ in acetonitrile electrolyte upon the first discharge and pure V_2O_5 exhibited a capacity which was less than 50 mAh/g during its first discharge. However, some water molecules stayed bound to the magnesium and were removed from the lattice during charging. Removal of water molecules

ultimately led to structural failure of the crystal upon cycling and a diminished capacity after the first cycle (60 to 70 mAh/g in subsequent cycles). Reported water content in the V_2O_5 cathode crystal has ranged from no water [14] to 3 moles of water per mole of V_2O_5 [32], but the water content is usually about 1.6-1.8 moles of water per mole of V_2O_5 [15, 28, 33, 81].

In more recent studies, groups have continued to investigate hydrated V_2O_5 xerogels [15, 19, 20, 28, 33, 82] and aerogels [25, 29]. Gels not only have the enhanced capability to insert and expel magnesium ions due to water content, but gels are also porous structures with large surface areas which allow for more surface diffusion. Xerogels and aerogels differ in the solvent drying process in which solvent is removed from the nanosized pores and capillaries after the material is synthesized. Xerogels are dried at ambient conditions, leading to a more compact and denser material than aerogels. Aerogels are dried by filling the pores and capillaries with a supercritical fluid and then cooling such that the pores become filled with a gas. This process allows the pores to remain intact, increasing the surface area of the material. V_2O_5 aerogel has ~ 30 times larger surface area than V_2O_5 xerogel [83]. Intuitively, greater surface area should create more diffusional sites and more insertion/deinsertion of magnesium ions, thus increasing the material's ability to accommodate high rate charge and discharge. Additionally, increasing surface area and minimizing the amount of bulk material should increase the capacity because there is less isolated bulk material which the intercalating ions cannot reach. However, aerogels have only been observed to electrochemically insert 0.6 moles of Mg^{2+} per mole of V_2O_5 [25, 29] which is about the same as nanocrystalline V_2O_5 [7]. Interestingly, a composite carbon - V_2O_5 xerogel exhibited electrochemical insertion of up to 1.84 moles of Mg^{2+} per mole of V_2O_5 [20]. The cyclic voltammogram for the V_2O_5 xerogel/carbon composite using 1M $\text{Mg}(\text{ClO}_4)_2$ dissolved in acetonitrile with magnesium metal counter and Ag/Ag^+ reference is shown in **Figure 3** [19]. Two broad cathodic peaks associated with the Mg^{2+} insertion process were observed, pointing toward the existence of two Mg sites in the V_2O_5 xerogel. Previous work on lithium intercalation into V_2O_5 xerogels has also observed the existence of two distinct lithium insertion sites [84]. Similarities between the voltammograms for Mg^{2+} and Li^+ suggest that Mg^{2+} ions are inserted into the same sites as Li^+ ions [19]. Using ex-situ FTIR spectra, the peak at -0.15V vs. Ag/Ag^+ was proposed to be associated with Mg^{2+} insertion into an innerlayer site, while the peak at -0.65 V vs. Ag/Ag^+ was proposed to be due to insertion into an interlayer site [19].

Figure 3. Cyclic voltammogram for a composite $\text{V}_2\text{O}_5/\text{carbon}$ electrode. The electrolyte used was $1\text{M Mg}(\text{ClO}_4)_2$ in acetonitrile with magnesium metal counter and Ag/Ag^+ reference [19].

Figure 4. Cyclic voltammetry of the $\text{Mg}_x\text{V}_2\text{O}_5$ xerogel in a) acetonitrile and b) carbonate based magnesium-ion electrolytes [33].

A low temperature synthesis method has been developed to synthesize magnesiated V_2O_5 xerogels with the formula $\text{Mg}_{0.1}\text{V}_2\text{O}_5 \cdot 1.8\text{H}_2\text{O}$ [33]. The low temperature $\text{Mg}_x\text{V}_2\text{O}_5$ xerogel was prepared by dissolving magnesium vanadate (MgV_2O_6) in water, followed by treatment with an ion exchange resin to form a magnesium deficient $\text{Mg}_x\text{V}_2\text{O}_5$ sol. The xerogel product was recovered after gelation and drying. Electrochemical tests in acetonitrile based electrolytes indicated that the material had an initial discharge capacity of 300 mAh/g upon the first discharge. A capacity of ~ 250 mAh/g was maintained over 8 cycles. **Figure 4** shows cyclic voltammetry of the $\text{Mg}_x\text{V}_2\text{O}_5$ xerogel in acetonitrile vs. carbonate based electrolytes. The projected operating voltage with a magnesium anode was estimated to be 3.2 V vs. Mg/Mg^{2+} , with an energy density of 800 mWh per gram of active cathode material. The high operating voltage and limited, yet successful cycling performance suggest that this material is worthy of further investigation. Previously, significant capacity degradation was observed at approximately 30 cycles for a V_2O_5 gel/carbon composite cathode [19, 20]. The magnesiated $\text{Mg}_{0.1}\text{V}_2\text{O}_5 \cdot 1.8\text{H}_2\text{O}$ xerogel may have long-lasting cycle life because of the initial amount of magnesium ions in the cathode that were inserted during the ion exchange step in the synthesis

process. The added ions could provide structural stability to the cathode so that it will not deteriorate upon cycling.

The xerogel form of V_2O_5 with 1.6-2 moles of water per mole of V_2O_5 provides the best high rate performance and capacity of any V_2O_5 reported [14, 19, 20, 25, 32, 33]. The difficulty is understanding whether the enhanced performance is caused by 1) the presence of water molecules in the crystal structure, 2) the increased surface area of the xerogel, or a combination of the two factors. To probe this question, high surface area vanadium oxide cathodes with almost no water content have been tested in rechargeable magnesium batteries [17]. The deposited thin film V_2O_5 electrodes were tested with activated carbon cloth counter and reference electrodes in 0.1 M MgTFSI₂ electrolyte in acetonitrile with no water content. The cells were cycled over a potential range of 2.2-3.0 V vs. Mg/Mg²⁺ at a 0.1 C rate. An initial capacity of 180 mAh/g was observed, and the reversible capacity remained above 150 mAh/g over 35 cycles. The observed capacity was significantly lower than the V_2O_5 xerogel results [20, 33] and may be attributed to cycling with a smaller voltage window. Previous studies operated from 0.3 to -1.0 V vs. Ag/Ag⁺ [20] and from 1.0 to -1.0 V vs. Ag/Ag⁺ [33], which correspond to approximately 3.5 to 2.2 V vs. Mg/Mg²⁺ and 4.2 to 2.2 V vs. Mg/Mg²⁺, respectively. Regardless, the thin film geometry provides large surface area and minimizes the diffusion lengths for the intercalating magnesium ions. With an increased surface area, favorable cyclability and rate performance were observed. Further studies are warranted to investigate how water molecules in the cathode influence the usable voltage window.

A microwave synthesis of sulfur-doped vanadium pentoxide (V_2O_5) has also been developed with the premise of incorporating the magnesium insertion/deinsertion attributes of both oxides and sulfides [21]. Metal oxides tend to have stronger bonding energies than the corresponding metal sulfides, and thus these metal oxide cathodes retain their structure with magnesium insertion, but the strength of the oxygen bonds with magnesium will trap the magnesium ions inside the cathode. Conversely, for metal sulfides with weaker bonding energies, magnesium deinsertion should require less energy, but the weak metal sulfide bonds also make metal sulfides susceptible to structural damage upon magnesium insertion. Other metal oxides (MnO_2 , MoO_3 , Fe_2O_3 , NiO and ZrO_2) were included in the composite as additives in order to prevent sulfur from leaching out from the sulfur doped V_2O_5 into the electrolyte. The highest capacity of 420 mAh/g was observed when MnO_2 was added to the sulfur-doped V_2O_5 and discharged in the range of 2.25 to 0.9 V vs. Mg/Mg²⁺. The bulk of the synthesized material was orthorhombic V_2O_5 , while the surface consisted of xerogel-like V_2O_5 and a solid solution of sulfur and MnO_2 . The results of this work are interesting due to the high delivered capacity, but the reduction mechanism is complex due to the incorporation of two different metal oxides and sulfur. Further analysis of the effects of doping metal oxides with sulfur is warranted.

2.2. Prussian Blue Analogs

Figure 5. The structure of the Prussian Blue analog copper hexacyanoferrate, with interstitial A sites indicated [85].

Much magnesium-ion battery research to date has focused on using transition metal oxides, sulfides and olivines for cathode materials, but recently reports of Prussian Blue analogs as cathodes for rechargeable magnesium batteries have been published. Prussian Blue analogs are metal-organic framework materials with an open and tunable crystal structure. The most common Prussian Blue analogs in electrochemical studies are hydrated copper hexacyanoferrate (**Figure 5**) ($\text{K}_{0.1}\text{Cu}[\text{Fe}(\text{CN})_6]_{0.7} \cdot 3.6\text{H}_2\text{O}$) [35], or nickel hexacyanoferrate ($\text{K}_{0.6}\text{Ni}_{1.2}\text{Fe}(\text{CN})_6 \cdot 3.6\text{H}_2\text{O}$) [86]. In general Prussian Blue materials have the formula of $\text{A}_x\text{PR}(\text{CN})_6 \cdot y\text{H}_2\text{O}$, of which A represents interstitial alkaline ions or water and P and R are metal ions. The stable and open framework contains large interstitial A sites which allow for the kinetically easy and fast insertion and removal of ions. Thus, this material can display long cycle life and high rate performance. Prussian Blue analogs were used to create batteries with divalent ions (including magnesium) that could cycle over 2,000 times with over 99.4% coulombic efficiency producing 60 mAh/g with a 1M $\text{Mg}(\text{NO}_3)_2$ aqueous electrolyte [34]. Furthermore, 63% capacity was retained between cycling at C/5 rate and increasing by 50-fold to 10C. This high rate performance is unmatched by the long cycle-life Chevrel Phase Mo_6S_8 [87]. These Prussian Blue batteries operated at approximately +0.7 V vs. Standard Hydrogen Electrode (SHE) which corresponds to +1.7 V vs. Mg/Mg^{2+} . Future investigation of Prussian Blue based magnesium batteries may yield an appropriate battery for large scale stationary electric storage applications.

In addition to their long cycle lives and high rate performance, Prussian Blue analogs are also able to operate in aqueous electrolytes. Water based electrolytes can be safer and environmentally friendlier relative to organic based electrolytes. Magnesium nitrate in an aqueous solution has been used as the electrolyte in recent magnesium-ion battery studies utilizing Prussian Blue cathodes [34, 35]. For these studies, either platinum or magnesiated Prussian Blue was used as the counter electrode. Notably, water in the electrolyte and cathode crystal appear to play important roles in the function of aqueous Prussian Blue magnesium-based batteries. Similar to the effect of water in hydrated V_2O_5 [32], the water located in some of the interstitial A sites in the Prussian Blue structure help disperse the divalent charge of magnesium ions. However, a significant problem when using water in magnesium-based batteries is that the formation of magnesium oxides will occur on the surface of magnesium metal based anodes [30]. Magnesium oxides are stable and inhibit ion diffusion, which can lead to current and power loss.

2.3. Molybdenum Sulfide

2.3.1. Chevrel Phase: Mo_6T_8 where $T=S$ or Se

Figure 6. Chevrel Phase Mo_6S_8 crystallographic structure [50].

Yoo et al. (2013) recently published a review that details the progress that has been made in regards to the Chevrel Phase from 2000 to 2013 [5], therefore this review will include only several notable reports.

The Chevrel phase can be viewed as the stacking of Mo_6S_8 blocks (**Figure 6**). Six molybdenum atoms form an octahedron inside a cube of eight sulfur atoms. Magnesium ions insert and occupy two main interstitial sites between these Mo_6S_8 blocks. Electrochemical performance of the Chevrel Phase Mo_6S_8 was first investigated using magnesium organo-haloaluminate complex electrolyte solutions [9]. This initial report claimed that the Chevrel Phase could be cycled over 2000 times at 100% depth of discharge with capacity fading of less than 15%. The impressive cycle life spurred a surge in interest in the topic, despite the material only producing a maximum discharge capacity of 130 mAh/g and an average discharge voltage of around 1.2 V vs. Mg/Mg^{2+} .

Magnesium insertion into Mo_6S_8 first occupies the ring arrangement in insertion site 1 which has a lower potential energy than insertion site 2. Intercalation into site 1 involves the first transfer of 2 electrons to create MgMo_6S_8 . The ring of magnesium atoms is very stable with a large activation barrier to prevent magnesium migration. Thus, there is an overvoltage upon reduction and trapping upon oxidation for $x < 1$ in the formula $\text{Mg}_x\text{Mo}_6\text{S}_8$. Once the first equivalent of magnesium is inserted into site 1, the proceeding magnesium insertion ($x > 1$) is fast due to the repulsion of inserting cations [88]. Charge trapping in site 1 was reduced when substituting selenium for sulfur in the Chevrel Phase with the formula Mo_6T_8 ($\text{T} = \text{S}, \text{Se}$ or a combination) [53]. Substituting selenium into the host created a triclinic distortion to the crystal structure which lowered the activation barrier, facilitating the migration of magnesium ions from insertion site 1. The selenium ions increased the lattice constants of the crystal relative to sulfur ions, which promoted magnesium ion mobility. Also, the selenium-based material was more polarizable which allows for faster diffusion of magnesium ions through the solid matrix. However, selenium is denser than sulfur, which results in a lower specific capacity of 89 mAh/g. Mo_6S_8 cannot be directly synthesized and is obtained by creating $\text{Cu}_2\text{Mo}_6\text{S}_8$ with high temperature solid-state hydrothermal or molten salt synthesis followed by several days of leaching to remove the copper [40, 89]. The solid-state hydrothermal synthesis is not easily scaled up because it requires a high temperature (1100° C) and a sealed vacuum. Under these condition sulfur vapor can evolve. The molten salt synthesis is a better candidate for large scale production because the system is not pressurized and less reactive precursors can be used. However, the molten salt procedure requires melting KCl at 850° C and several days of leaching. The Chevrel Phase has provided great insight to the desirable characteristics of a successful host magnesium-ion cathode [4, 90-92].

2.3.2. Molybdenum Disulfide MoS_2

Figure 7. MoS₂ crystallographic structure [93].

Molybdenum disulfide has been the subject of study in part due to the layered MoS₂ structure (**Figure 7**). Electrochemical testing of an MoS₂ electrode at 80° C indicated that reversible magnesium insertion was not possible with a molten salt magnesium-based electrolyte [94]. A reversible magnesium-ion battery utilizing several different nanostructures of MoS₂ and an electrolyte consisting of Mg(AlCl₃Bu)₂ dissolved in THF was reported [55]. MoS₂ with hollow-cage fullerene-like particles, fibrous floccus, and spherical nanovesicle structures were employed as the cathode material. However, the cells only had a capacity of 2-25 mAh/g, a coulombic efficiency of 10-40%, and a discharge voltage around 1.5 V. The reactions for rechargeable magnesium batteries with a MoS₂ cathode and a magnesium metal anode are:

Further work combined an exfoliated graphene-like MoS₂ cathode with a magnesium nanoparticle anode to increase the active surface areas for both electrodes [56]. This battery had a reversible capacity of 170 mAh/g over 50 cycles with a nominal voltage of 1.8 V. These results exceed those typically reported for Chevrel Phase Mo₆S₈ based batteries. A first-principles study of zigzag nanoribbon MoS₂ cathodes, which are thin strips of MoS₂ ribbons that have about five layers of MoS₂ trilayers, suggested that the increased surface area and unique geometry of nanoribbon MoS₂ could reach the theoretical capacity of 232.2 mAh/g [59]; however, nanoribbon MoS₂ has not yet been synthesized. Cathodes with graphene-like MoS₂ composited with conductive carbon, where carbon layers are proposed to be sandwiched between the trilayers of S-Mo-S, have been constructed [57, 58]. Cathodes having an optimal amount of carbon, which maximized the surface area contact of active material with carbon while maintaining a complete conductive matrix, had an initial discharge capacity of 213 mAh/g and showed good cycling capability for 50 cycles. In addition, the discharge plateau occurred at 1.4 V and the charging plateau at a voltage of 2.2 V vs. Mg/Mg²⁺ in a cell with an AZ31 magnesium alloy anode in AlCl₃-PhMgCl electrolyte.

For future research, combining the enhanced conductivity of carbon composite cathodes with the nanostructured cathodes and anodes may result in a molybdenum disulfide magnesium-ion battery that operates near the theoretical capacity with good cycling.

2.4. Molybdenum Oxide

Figure 8. MoO₃ crystallographic structure [95].

Molybdenum oxides have been studied less than molybdenum sulfides as electrode materials in magnesium based batteries. Similar to molybdenum disulfide (MoS₂), molybdenum trioxide (MoO₃) forms a double layered structure (**Figure 8**). MoO₃ was observed to have an open circuit potential of 2.8 vs Mg/Mg²⁺ and an intercalation capacity of 143 mAh/g when paired with a magnesium metal anode and 1 M Mg(ClO₄)₂ in THF electrolyte [18]. In (C₄H₉)₂Mg solution, only 0.05 moles of magnesium could be chemically inserted per mole of MoO₃ [16]. The first MoO₃ rechargeable cells were studied using different two electrolytes, a molten salt and magnesium perchlorate in acetonitrile with magnesium metal anode [61]. The addition of water to the magnesium perchlorate based electrolyte resulted in an improved battery performance, but charge trapping was observed after the first 3 cycles (**Figure 9**).

The Mg²⁺ cycling performance of poly(vinylidene fluoride-co-hexafluoropropylene)-based magnesium-ion conducting gel polymer electrolytes with MoO₃ cathodes and magnesium metal/multi-walled carbon nanotube composite anodes has also been investigated [60]. These cells yielded a discharge capacity of 175 mAh/g over 10 cycles with an operating voltage around 1.0 to 1.2 volts. In another study, synthesized thin films of orthorhombic MoO₃ were observed to have a reversible capacity of 210 mAh/g for 10 cycles and an operating voltage of 2.2 to 2.8 V vs. Mg/Mg²⁺ when utilizing 0.1 M magnesium bis(trifluoromethane sulfonyl) imide (MgTFSI₂) electrolyte [17]. Additionally, MoO₃ was observed to have a much larger overpotential than V₂O₅, which may be attributed to differences in particle sizes between the V₂O₅ and MoO₃.

particles. Molybdenum oxide is an intriguing material with a layered crystal structure suitable for ion insertion, but oxide bonds are stronger and more rigid than sulfide bonds, which may result in more structural damage due to cycling for oxides relative to sulfides.

Figure 9. Specific charge by cycle number for MoO₃ cathode using MgCl₂/EMIC/AlCl₃ salt melt and 1M Mg(ClO₄)₂/acetonitrile with 3 mol% H₂O. Cycling was performed between -1.5 V to 0.5 V vs. Ag/Ag⁺ at a scan rate of 20 μV/s for the 1M Mg(ClO₄)₂/acetonitrile with 3 mol% H₂O system [61].

2.5. Manganese Oxides

The various crystal phases of manganese oxide have also been investigated as cathodes for magnesium-ion batteries. The natural abundance and low toxicity of manganese would make these materials desirable for large-scale energy storage. The spinel phase LiMn₂O₄ is used commercially in lithium ion batteries, due to its high energy density and rate capability [96]. The first studies of electrochemical magnesium insertion into manganese oxide compounds examined Mn₂O₃ and Mn₃O₄ in THF / magnesium perchlorate electrolytes [18]. The open circuit potentials of the materials versus Mg/Mg²⁺ were observed to be the same and equal to 2.40 V.

Additionally, both compounds inserted 0.66 moles magnesium per mole of host, correlating to capacities of 224 mAh/g and 154 mAh/g for Mn_2O_3 and Mn_3O_4 , respectively. Manganese can form several stable phases with oxygen and recent research for manganese oxide cathodes for magnesium-ion batteries has focused on the various phases of MnO_2 .

2.5.1. Tunneled MnO_2 (Hollandite and Todorokite)

Figure 10. Tunneled MnO_2 crystal structures: Hollandite (2x2 tunnel) left [97], Todorokite (3x3 tunnel) right [98].

Tunneled cathodes are encouraging materials as they provide easy transport channels that should promote cation mobility, which is a major limitation preventing the success of high-rate, reversible magnesium batteries. Hollandite has a 2x2 tunnel and todorokite has larger 3x3 sized tunnels surrounded by edge-sharing MnO_6 octahedra (**Figure 10**). Todorokite $\text{Mg}_{0.21}\text{MnO}_{2.03} \cdot 0.24\text{H}_2\text{O}$, prepared via the hydrothermal treatment of a Mg busserite precursor, was observed to insert 0.3 equivalents of magnesium when using a 1 M magnesium perchlorate in propylene carbonate electrolyte, corresponding to a capacity of 85 mAh/g [63].

The magnesium electrochemistry for the hollandite 2x2 tunneled MnO_2 structure has also been investigated. Hollandite MnO_2 was reported to have a capacity of 280 mAh/g capacity in the voltage range 3.0-0.8 V vs. Mg/Mg^{2+} when using a high voltage electrolyte 0.2 M $(\text{Mg}_2(\mu\text{-Cl})_3 \cdot 6(\text{OC}_4\text{H}_8))(\text{N}(\text{Si}(\text{CH}_3)_3)_2)_n\text{AlCl}_{4-n}$ ($n=1,2$) (Mg-HMDS) in THF [66]. An additional study reported pristine hollandite as having a capacity of 85 mAh/g when discharged with a magnesium metal anode and magnesium perchlorate in acetonitrile electrolyte [64]. To improve performance of the hollandite material, cathode composites consisting of hollandite MnO_2 with acetylene black have been investigated [64, 65]. The acetylene black additive increased the

conductivity and pore size of the cathode and ultimately boosted the capacity to 310 mAh/g when cycled at a 100 mAh/g rate at 20°C (**Figure 11**). For this study, K^+ cations were used to stabilize the hollandite tunnels. Notably, significant capacity fade was observed for hollandite MnO_2 /acetylene black composites (**Figure 12**). Significant capacity fade for hollandite MnO_2 has also been reported [66], with nearly 50% capacity lost between the first and second cycles. For this study, X-ray Absorption Near Edge Spectroscopy (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) analyses were used to determine the oxidation state and coordination of manganese atoms during discharge and linked the battery's failure to the collapse of hollandite tunnels and incomplete extraction of Mg^{2+} ions upon charging. **Figure 13** shows both normalized manganese K-edge XANES spectra and Fourier transform (FT) magnitudes of k^2 -weighted EXAFS spectra for α - MnO_2 electrodes at various states of discharge and recharge. The position of the manganese K-edge upon recharge was not equivalent to the edge position in the pristine state, indicating that Mg^{2+} ions may not be completely removed from the material after charging. Furthermore, upon discharge, the FT peak at ~ 3.0 Å associated with corner-shared MnO_6 octahedra interactions disappeared, suggesting that magnesium insertion may cause collapse of the hollandite tunnels (**Figure 13**). At the point of final discharge, the EXAFS spectra for the cathode was broadened and resembled a significantly different pattern from the pristine MnO_2 cathode. For this work, MnO_2 was used as received and no mention was made of the stabilizing cation used. An additional structural study on potassium stabilized hollandite MnO_2 indicated that the surface of the material undergoes a conversion reaction during discharge to gradually form Mn_2O_3 and MnO phases [62].

Figure 11. Charge/discharge profiles for a hollandite- MnO_2 /Acetylene black (Hol/AB 65:35 wt %) composite. 1M $Mg(ClO_4)_2$ in acetonitrile was used as the electrolyte with magnesium metal counter and Ag/Ag^+ reference [65].

Figure 12. Cycling performance of hollandite-MnO₂/Acetylene black (Hol/AB 65:35 wt %) composites tested at 20 C, 60 C, and with K⁺ removed from the hollandite tunnels [65].

Figure 13. Figure shows (a) normalized K-edge XANES spectra and (b) Fourier transform magnitudes of k^2 -weighted EXAFS spectra for α - MnO_2 electrodes at various states of discharge and recharge [66].

2.5.2. Layered MnO_2 (Birnessite)

Figure 14. Two dimensional layered crystal structure of birnessite MnO_2 [99].

The structure of layered manganese oxide, birnessite-type $\delta\text{-MnO}_2$, provides a two dimensional pathway for ions to intercalate and deintercalate (**Figure 14**). The magnesium electrochemistry of the layered birnessite phase of MnO_2 was studied using a metallic magnesium anode and acetonitrile electrolyte with magnesium perchlorate salt [65]. The magnesium ion exchanged birnessite has a lower discharge capacity (109 mAh/g as an acetylene black composite) than the hollandite phase (310 mAh/g as an acetylene black composite), but the birnessite material was able to retain more of its original capacity over a longer cycle life when cycled at a 1 C rate in the voltage range of +1.0 to -1.8 V vs. Ag/Ag^+ (corresponds to about 4.2 to 1.4 V vs Mg/Mg^{2+}). Comparison of the cycling performance of various birnessite- MnO_2 microstructures is shown in **Figure 15**. Hollandite tunnels underwent significant charge trapping and almost all capacity was lost after 20 cycles. Meanwhile the birnessite composites retained nearly 50% of the initial capacity after 25 cycles. In lithium-ion batteries, the decomposition of the birnessite phase leads to the formation of a spinel phase [65]. Because of this decomposition behavior, birnessite- MnO_2 is mostly disregarded in lithium-ion applications [100]. However, for the magnesium ion chemistry, formation of a spinel structure was not observed and degradation of capacity was attributed to the leaching of Mn^{2+} into the electrolyte [65].

Figure 15. Cycling performance of birnessite-MnO₂, magnesium ion exchanged birnessite-MnO₂, and the corresponding acetylene black composites for the two materials (MnO₂/AB 50:50 wt %) [65].

Figure 16. Crystal structure of spinel MnO_2 [101].

2.5.3. Spinel MnO_2

The tunnel structure of spinel $\lambda\text{-MnO}_2$ is shown in **Figure 16**. Spinel $\lambda\text{-MnO}_2$ has been synthesized using a microwave reactor [67]. When utilized as a cathode, the material had an OCV of 1.2 V vs. Mg/Mg^{2+} and delivered a specific capacity up to 80 mAh/g on the first discharge to 0.7 V in 0.1 M $\text{Mg}(\text{ClO}_4)_2$ -0.5 M H_2O in THF electrolyte. Materials synthesized at lower power settings displayed poor cycling properties, while materials created at higher microwave power retained some capacity over 8 cycles. Recent work has studied the electrochemical intercalation of divalent ions into spinel MnO_2 with a graphite sheet anode and aqueous electrolytes with magnesium sulfate, magnesium nitrate and magnesium chloride salts [68]. An initial discharge capacity of 545.6 mAh/g at 13.6 mA/g current was observed and a capacity of 155.6 mAh/g was maintained over 300 cycles in the potential range of -0.8 to 1.0 V vs. SCE (corresponding with 2.5 to 4.3 V vs. Mg/Mg^{2+}). The cycling performance of the $\lambda\text{-MnO}_2$ electrode in various aqueous electrolytes is shown in **Figure 17**. The high initial capacity, cycling properties and compatibility in water based electrolytes make $\lambda\text{-MnO}_2$ worthy of future research.

Figure 17. Cycling performance of $\lambda\text{-MnO}_2$ electrode using a 136 mA/g current in various electrolytes (1M MgSO_4 , $\text{Mg}(\text{NO}_3)_2$, MgCl_2 in H_2O). Graphite sheet and saturated calomel electrode are used as the counter and reference electrodes [68].

2.5.4. Post-Spinel MnO_2

A first-principles method was used to calculate the phase stability, activation energy required for Mg^{2+} migration, voltage window, and energy density of post-spinel MnO_2 [102]. The calculations predict that the post-spinel phase is stable, due to a high energy barrier preventing the rearrangement of MnO_6 octahedra. Additionally, the Mg^{2+} migration activation energy for the phase was calculated to be 0.4 eV, which is comparable to the mobility of Li^+ in Li-ion batteries. The possible voltage window lies in between 2.84 and 1.68 V vs. Mg/Mg^{2+} . These calculations may draw future attention to this material.

2.6. Transition metal silicates

The ability of Li_2MSiO_4 (M =transition metal) materials to transfer two electrons per transition metal atom suggest that these transition metal silicates should have high energy densities. Further, the structural stabilities and multi-valent transition metal cores of these materials allow for reversible magnesium ion insertion without much structural damage or magnesium ion trapping. Silicates are also environmentally friendly and inexpensive materials. Sparked by these intriguing qualities, several studies have probed the electrochemical and physical properties of magnesium manganese silicate ($\text{Mg}_{1.03}\text{Mn}_{0.97}\text{SiO}_4$), magnesium iron silicate (MgFeSiO_4) and magnesium cobalt silicate (MgCoSiO_4).

Figure 18. Olivine crystal structure, yellow octahedra represent transition metals (Mn, Fe, or Co) coordinated with 6 oxygen atoms [103].

Olivine materials crystallize in orthorhombic structures with isolated silicate tetrahedra (**Figure 18**). The first report of rechargeable magnesium batteries utilizing silicate based cathodes electrochemically tested $\text{MgMn}_{1.03}\text{Mn}_{0.97}\text{SiO}_4$ synthesized using two methods, a solid-state and a modified sol-gel approach [70, 71]. All electrochemical studies were conducted using $\text{Mg}(\text{AlCl}_2\text{EtBu})_2$ in THF electrolyte. Voltage profiles for magnesium intercalation in $\text{Mg}_{1.03}\text{Mn}_{0.97}\text{SiO}_4$ prepared by solid state and modified sol gel approaches are shown in **Figure 19**. The material prepared by the sol-gel procedure delivered a discharge capacity of 244 mAh/g with an operating voltage around 1.6 V vs. Mg/Mg^{2+} and good capacity retention over 15 cycles. From CV and constant current discharge tests, two reduction peaks and plateaus were observed, respectively. These results indicated that there are two insertion sites for magnesium ions, and that there may be a crystal reordering during the discharge process. Further work on this topic applied Density Functional Theory (DFT) calculations on olivine structures in magnesium batteries and predicted that the transition metal reduces in a two-step process [69]. The transition metal first reduces from 4+ to 3+ and then from 3+ to 2+, which correlates with the two CV peaks that were observed in the experimental study. Crystal reordering could be detrimental to the cycle life of this material, as it can cause structural damage or magnesium ion trapping.

Figure 19. Voltage profiles for magnesium intercalation in $\text{Mg}_{1.03}\text{Mn}_{0.97}\text{SiO}_4$ prepared by (a) solid state approach (with and without 20% acetylene black additive) and (b) prepared by a modified sol gel (MSG) approach at varying current densities [71].

Additional research on the manganese silicate has focused on strategies to increase the cathode's active surface area and the inclusion of conductive materials to create an electronically conductive matrix around the active material. When nanosized, the manganese silicate had good capacity retention for 80 cycles and showed improved performance at high peak currents [73]. These results were obtained with nanosized manganese silicate cathodes, magnesium metal ribbon anode and 0.25 M $\text{Mg}(\text{AlCl}_2\text{EtBu})_2$ in THF electrolyte and cycled at C/20 from 2.0 to 0.4 V vs. Mg/Mg^{2+} . The optimized delivered capacity of 300 mAh/g closely approached the theoretical capacity of 314 mAh/g [72]. Additionally, close to 100% capacity retention was observed through 20 cycles. The most recent work involving manganese silicates involved adding carbon multi-walled nanotubes (MWNT) to the cathode [74]. The nanotubes provided a conductive network to enhance electrical conductivity, but they also increased structural strength. MWNTs have an extremely high elastic modulus, which aids in holding the cathode together during cycling.

Magnesium iron silicate (MgFeSiO_4) prepared using a molten salt method has additionally been tested as a magnesium ion cathode material [75]. The synthesis temperature was modified to optimize the electrochemical properties of the product material. Coin cells were constructed with MgFeSiO_4 cathodes, magnesium ribbon anodes and 0.25 M $\text{Mg}(\text{AlCl}_2\text{EtBu})_2$ in THF electrolyte. Cathodes prepared at 900° C had a capacity of 125.1 mAh/g at initial discharge and retained 91.4 % capacity on the 20th cycle at 0.1 C rate. When the discharge rate was increased to 0.3 C, the initial capacity dropped to approximately 95 mAh/g. Additional results using higher discharge currents were not provided, but it is noteworthy that nearly 25% of the capacity was lost from a small increase in discharge current from 0.1 C to 0.3 C. MgFeSiO_4 has also been prepared using an ion-exchange method [76]. The ion-exchange method involves the electrochemical extraction of 2 Li^+ ions from $\text{Li}_2\text{FeSiO}_4$ and electrochemically replacing them with Mg^{2+} . The ion-exchanged MgFeSiO_4 cathode was paired with a magnesium metal anode and $\text{Mg}(\text{TFSI})_2/\text{triglyme}$ electrolyte. The two electrode cell was heated to 100° C and cycled at C/50, producing a reversible capacity of 166 mAh/g. Further work needs to address the high temperature and slow rate used for cycling.

In magnesium cobalt silicate (MgCoSiO_4), cobalt is an attractive choice for the transition metal because cobalt has a standard reduction potential 0.7 volts higher than manganese. Thus, cobalt silicate should have a higher operating voltage than the analogous manganese silicate, and a higher voltage should lead to a higher power density. When used as a cathode in a magnesium-ion battery, MgCoSiO_4 had an operating voltage plateau of around 1.6 V vs. Mg/Mg^{2+} [78]. However, the observed voltage did not increase compared to the manganese and iron silicate. **Figure 20** shows charge-discharge curves for MgCoSiO_4 material synthesized by a solid state approach, a molten salt approach, and a mixed solvothermal approach. Two electrode cells with a magnesium anode and 0.25 M $\text{Mg}(\text{AlCl}_2\text{EtBu})_2$ in THF electrolyte were used to collect the measurements. The mixed solvothermal synthesis yielded a mesoporous MgCoSiO_4 material which had a first discharge capacity of approximately 170 mAh/g. Additional cycling indicated

that capacity continued to increase within the first ten cycles, reaching a maximum of 300 mAh/g [77]. Further testing showed little capacity loss through 30 cycles, with the capability to cycle up to 200 times. These results suggest that a new electrolyte with better anodic stability will allow for this material to fully reach its maximum capacity.

Figure 20. The figure shows discharge capacity vs. cycle number for MgCoSiO₄ material synthesized by a solid state approach, a molten salt approach, and a mixed solvothermal approach. Current rate was 0.1C [78].

2.7. Other Cathode Materials

In addition to manganese dioxide and vanadium oxide, other oxide materials have been studied as cathode materials for rechargeable magnesium batteries. Co₃O₄ and RuO₂ were investigated using electrolytes based on organic solvents containing Mg(ClO₄)₂ but demonstrated limited electrochemical activity [94]. More recent investigations of Co₃O₄[104] and RuO₂[105] coupled the materials with Mg(ClO₄)₂ in ionic liquid as the electrolyte, but linear decrease in capacity with cycle number indicated that deintercalation of divalent magnesium was

problematic. The cation-deficient mixed oxide $\text{Mn}_{2.15}\text{Co}_{0.37}\text{O}_4$ was investigated but exhibited similarly low capacity [106].

Sulfide based compounds, including copper sulfide [36], nickel sulfide [36], niobium sulfide [107], titanium sulfide [16, 18, 36, 108, 109], vanadium sulfide [18], and zirconium sulfide [18] have been investigated as cathode materials for magnesium-ion batteries but in general have exhibited poor performance. The most promising of these materials is TiS_2 nanotubes, for which a preliminary report indicated that discharge capacity was 180 mAh/g after 80 cycles at a 10 mA/g rate using a magnesium foil anode. The electrolyte utilized was 1 M $\text{Mg}(\text{ClO}_4)_2$ in acetonitrile [109]. Boride based compounds were also investigated as magnesium-ion cathodes [18] and exhibited open circuit voltages that were not viable, while a recent computational study [110] has suggested that the development of layered magnesium boride sheets may could be promising if synthesized appropriately.

Other classes of materials that have been tested as magnesium-ion battery cathode materials include organosulfur compounds [111], graphite fluorides [112], and organic materials [113]. The investigations on these materials are preliminary in nature and will require further study. Organosulfur materials employing an organothiols (-SH)/disulfide (S-S) redox couple were proposed as novel cathode materials [111]. The most promising of the materials tested exhibited a discharge capacity above 70 mAh/g after 30 cycles, though strategies such as increasing the density of S-S bonds through the use of polysulfide compounds, or using a catalyst that enhances the disulfide redox reaction, could result in improvement [111]. The use of graphite fluorides as magnesium cathodes has also been investigated, based on their success as cathodes in lithium ion systems. The graphite fluoride cathodes were paired with magnesium foil anodes with 1M $\text{Mg}(\text{ClO}_4)_2$ salt dissolved in ACN, DMSO, PC or THF as the electrolyte. However, when the electrodes were discharged at a 10 A kg^{-1} rate (**Figure 21**) the capacity was approximately half of the theoretical value due to slow diffusion of Mg^{2+} into the cathode [112].

The use of cathode materials that are primarily organic in nature represents a novel approach to Mg^{2+} ion storage. The electrochemical performance of redox active 2,5-dimethoxy-1,4-benzoquinone has been reported [113]. The organic powder was mixed with a conductive additive and PTFE binder to form the cathode in a three electrode cell with magnesium foil counter and reference electrodes and electrolyte consisting of 0.5M $\text{Mg}(\text{ClO}_4)_2$ dissolved in γ -butyrolactone. When discharged at 20mA/g, the material had a capacity of 260 mAh/g and average voltage of 0.9V versus a magnesium reference, providing evidence that redox active organic crystals have promise for multi-electron energy storage.

Figure 21. Galvanostatic discharge curves at a rate of 10 A/kg for various graphite fluoride samples used as cathodes in lithium and magnesium batteries [112].

3.0. Conclusions

Magnesium-ion battery research is a growing field of study, based on publication rates. However, there are a number of issues which prevent magnesium-based batteries from commercial implementation, including low capacities, low operating voltages and low current capabilities. Further, the discovery of safe, non-corrosive electrolytes for magnesium-based batteries is critical.

Cathode materials for magnesium and magnesium-ion based batteries include vanadium oxide, Chevrel phases, Prussian Blue, molybdenum sulfide, molybdenum oxide, manganese oxide, and transition metal silicates. The layered vanadium oxides provide high operating voltage and high capacity, development of small crystallite size, high surface area material with appropriate water content has improved Mg^{2+} ion transfer properties. Manganese oxides offer a variety of structural forms with diverse electrochemistry, where the layered (birnessite) and spinel structured materials showed improved cycling relative to the tunneled (hollandite) structured material. Orthorhombic structured molybdenum oxides show charge trapping, where prolonged insertion and removal of divalent charges may cause irreversible structure changes; however thin films may address this issue. Molybdenum sulfides are likely the most studied cathode material in magnesium-based batteries, where little fade upon multiple cycles is observed. The molybdenum sulfides exhibit less structural rigidity relative to oxides, resulting in less structural degradation upon cycling. Magnesium ion charge trapping and slow ion diffusion remain issues; however, improved performance by using nanostructured materials and cycling at

higher temperature in order to increase diffusional rates has been demonstrated. Silicates with manganese, iron, or cobalt have been prepared via molten salt and sol-gel synthesis methods, where the use of high surface area mesoporous materials was the key to generating viable electrochemical performance in magnesium systems. Recent reports in this area have involved molecularly based aqueous systems incorporating cathode active materials with structures analogous to Prussian blue (nickel and copper hexacyanoferrate). The advantage of this approach is the open framework structure, providing pathways for Mg^{2+} mobility.

Gravimetric capacity and volumetric capacity may not be critical issues to large-scale secondary stationary batteries, relative to portable secondary batteries. Thus, it is possible that magnesium-ion batteries may emerge as a viable solution for integrating energy storage with the electrical grid, playing a key role in the future large-scale energy landscape.

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