**Article:**
Pryke, J.J., Kennard, R.M. and Cussen, S.A. (2022) Cathodes for Mg batteries: a condensed review. Energy Reports, 8 (Supplement 11). pp. 83-88. ISSN: 2352-4847

https://doi.org/10.1016/j.egyr.2022.07.124

Available online at www.sciencedirect.com
ScienceDirect
Energy Reports 8 (2022) 83–88
www.elsevier.com/locate/egyr

Multi-CDT Conference on Clean Energy and Sustainable Infrastructure, Professor Solomon Brown, 5th and 6th April 2022, The University of Sheffield

# Cathodes for Mg batteries: A condensed review

Jethro J. Pryke, Rhiannon M. Kennard, Serena A. Cussen*

*Department of Materials Science and Engineering, The University of Sheffield, Sheffield, S1 3JD, UK*

Received 27 June 2022; accepted 21 July 2022
Available online 20 August 2022

**Abstract**

Magnesium batteries offer several advantages over commercial lithium batteries, including predicted lower cost due to the greater abundance of Mg, and better theoretical performance. Currently, there are numerous challenges to overcome in delivering commercial Mg batteries, such as the high charge density of $Mg^{2+}$ that hinders its intercalation in and out the cathode, or strict requirements for coordination of $Mg^{2+}$. In this condensed review, we present an overview of some of the key challenges and strategies for high performance, focusing on the cathode. We highlight some promising cathode compositions, including manganese oxides, the seminal $Mo_6S_8$ that is still used to evaluate novel electrolytes and anodes, and vanadium oxides, such as $H_2V_3O_8$. Correlations between structure, chemistry and performance are discussed for each composition.


Peer-review under responsibility of the scientific committee of the Multi-CDT Conference on Clean Energy and Sustainable Infrastructure, Professor Solomon Brown, 2022.

*Keywords:* Magnesium batteries; Energy storage; Cathodes

## 1. Introduction

The transition to a self-sustaining and greener economy requires the development of new and more sustainable energy technologies. Batteries are attractive for powering electric transportation and small electronic devices, as well as energy storage at grid-scale [1]. Commercial lithium-ion batteries already find applications for such purposes. However, the raw materials required for Li batteries are concentrated in a few countries, including conflict zones. Such considerations also coincide with a greater demand for more sustainable energy storage [1,2]. Thus, we must develop new battery chemistries, that use intercalating ions other than $Li^+$, and avoid critical raw materials such a cobalt [2].

Magnesium-ion batteries are attractive candidates for overcoming this challenge. Mg batteries are potentially less expensive since Mg is $>$ 300 times more abundant than lithium and because Mg ores are distributed across many countries [1,3]. In addition, magnesium is divalent ($Mg^{2+}$), while lithium is monovalent ($Li^+$), which gives Mg batteries a higher theoretical volumetric capacity (3833 Ah/L for Mg, versus 2062 Ah/L for Li) [1]. Despite these advantages, commercialization of Mg batteries has not yet been realized, in part due to a lack of suitable cathodes.

* Corresponding author.
*E-mail address:* s.cussen@sheffield.ac.uk (S.A. Cussen).

https://doi.org/10.1016/j.egyr.2022.07.124


Peer-review under responsibility of the scientific committee of the Multi-CDT Conference on Clean Energy and Sustainable Infrastructure, Professor Solomon Brown, 2022.

The cathode releases $Mg^{2+}$ during charge, and incorporates $Mg^{2+}$ during discharge, so it is crucial to develop a cathode that can accept large concentrations of $Mg^{2+}$ reversibly and quickly. Few materials meet this requirement currently, highlighting the demand for new cathode chemistries. Below, we review key challenges associated with finding suitable cathodes, as well as strategies to achieve high performance. We then highlight some interesting cathode compositions, and finally discuss correlations between structure, chemistry and performance.

## 2. Challenges and strategies for high performance in cathodes

We focus here on obstacles and strategies associated with the cathode, although we note that improvements to the electrolyte and anode are also needed in tandem [1]. First, the cathode must accommodate the high charge density of $Mg^{2+}$, which originates from its small ionic radius (0.72 Å), [4] and from its divalency. [5] In contrast, $Li^{+}$ is slightly larger (0.76 Å) [4] and is monovalent, resulting in lower charge density. The high density of $Mg^{2+}$ produces strong Coulombic interactions between $Mg^{2+}$ and the cathode. These interactions can slow the migration of $Mg^{2+}$ and cause large lattice distortions during cycling, both of which limit the capacity [1,6,7]. In addition, this high charge density can increase the energy barrier for $Mg^{2+}$ to hop between sites, [8] and complicates redistribution of charge within the cathode, which is needed to maintain local electroneutrality. [9]

Using sulfides can mitigate some of these challenges: the sulfide anion $S^{2-}$ is larger and more polarizable than the $O^{2-}$, making $S^{2-}$ better suited to accommodate the high charge density [7]. This results in better $Mg^{2+}$ conduction and in larger capacities [10]. Notable sulfide cathodes include the seminal Chevrel phase $Mg_xMo_6S_8$ (see below) or the spinel $Mg_xTi_2S_4$, which delivers a promising capacity of 195 mAh/g at C/20 [10,11]. However, the greater capacity of sulfides often comes at the expense of high voltage, which is needed to achieve good energy density [5–7,10–14].

Such high voltages can be obtained by using oxides, which often yield voltages of between 2 and 3 V vs. $Mg^{2+}$/Mg. This is in part because the metal–oxygen bond is more ionic than the metal–sulfur bond [5–7,10–16]. However, the large electronegativity of oxygen worsens the strong Coulombic interactions and large lattice distortions described above. Several strategies can mitigate these effects. Nanosizing shortens the diffusion distance of mobile ions, which can improve cathode performance [16–18]. Alternately, small amounts of $H_2O$ can shield $Mg^{2+}$ from the host lattice, allowing reversible intercalation [16]. However, $H_2O$ reacts with the Mg metal anode to form an Mg-blocking layer, which limits the choice of anode to carbon or other non-Mg metal compositions [8].

Other challenges include inversion and coordination. Inversion refers to $Mg^{2+}$ exchanging locations with a nearby transition metal, which modifies the migration pathways of $Mg^{2+}$ and can decrease the capacity [19]. In addition, migration is favored when $Mg^{2+}$ sits in an unfavorable coordination site; i.e., when the coordination of $Mg^{2+}$ with neighboring anions is different than 6 (octahedral), which further restricts the cathode chemistries available. [20,21]

## 3. Highlighted cathodes

Many inorganic compositions have been investigated as Mg-cathodes. These include 3D structures, such as spinels (e.g., $Mg_xMn_2\ O_4$, $Mg_xTi_2S_4$), polyanionics (e.g., $Mg_xTi_2(PO_4)_3$), Wadsley–Roth phases (e.g., $V_4Nb_{18}O_{55}$), or layered materials, in which $Mg^{2+}$ migrates between 2D sheets of metal-anion polyhedra (e.g., $TiS_2$) [1,6,22,23]. Comprehensive reviews of these phases can be found elsewhere. [1,13,22–24] Here, we highlight a few select compositions, and explain correlations between structure, chemistry and performance.

### 3.1. Chevrel phase $Mo_6S_8$

The seminal phase $Mo_6S_8$ (or $Mo_3S_4$), was first synthesized by Chevrel in 1974, [25] and later used to make the first rechargeable Mg battery in 2000 by Aurbach et al. (Fig. 1; adapted from prior crystallographic information) [11,26]. Rapid diffusivity of $Mg^{2+}$ in this structure is thought to be encouraged by (1) the use of $S^{2-}$ which compensates for the high charge density of $Mg^{2+}$, (2) the large numbers of vacant $Mg^{2+}$ sites with short distances between them, (3) the 4-fold or 5-fold coordination of $Mg^{2+}$ in the Chevrel structure, and (4) the presence of $MoS_6$ octahedral clusters with delocalized electrons, which are thought to rapidly redistribute charge as $Mg^{2+}$ intercalates. [5,26,27] Consistent with the use of sulfide, the voltage attained is rather low ($< 2$ V vs. $Mg^{2+}$/Mg). [7,8] The theoretical capacity of $Mo_6S_8$ is 129 mAh/g, as the $Mo_6$ octahedral clusters can sustain up to 4 additional electrons (corresponding to two $Mg^{2+}$ ions). [5] While this is lower than the experimental capacity of other sulfides, [10] $Mo_6S_8$ retains $> 80\%$ capacity retention after hundreds of cycles. [8,11,28] This reliable stability renders $Mo_6S_8$ useful for evaluating novel electrodes or electrolytes. [23,28–30]

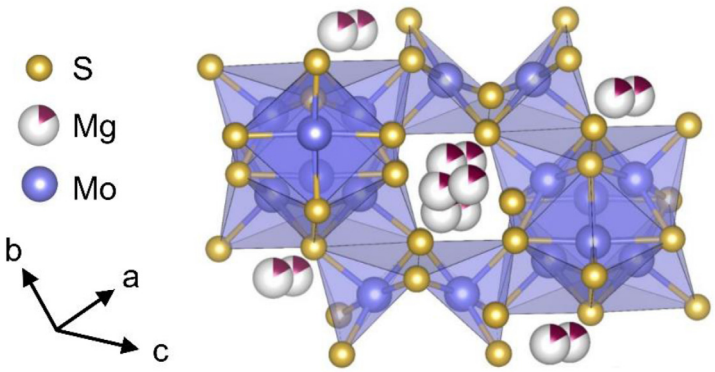


**Fig. 1.** Structure of the $Mo_6S_8$ Chevrel phase, with 1 $Mg^{2+}$ intercalated. (i.e., $MgMo_6S_8$). The possible $Mg^{2+}$ sites are shown, each with partial occupancy.

### 3.2. Manganese oxides

Mn oxides promise high capacities, low cost, and decent voltage [24]. Interestingly, $MnO_2$ crystallizes as both 2D and 3D polymorphs (Birnessite, Hollandite, Spinel, Ramsdellite), which have been tested as cathodes for Mg-batteries [24]. The elevated voltages achievable using $MnO_2$ polymorphs (2–3 V vs. $Mg^{2+}$/Mg) make these materials attractive for commercialization [24]. $MnO_2$ cathodes can also exhibit high initial capacities, with reports of up to 545 mAh/g reported for the spinel [31]. However, this high capacity fades significantly, with $\leq$ 75% retained after 50 cycles. [31] Capacity fade is also a concern for other $MnO_2$ polymorphs. [24] The Hollandite $\alpha$-$MnO_2$ produced an initial discharge capacity of 280 mAh $g^{-1}$ that decreased to 100 mAh $g^{-1}$ after the fourth cycle (36% capacity retention). [32] This decrease was attributed to a collapse in the Hollandite's tunnel structure, possibly due to a Jahn–Teller distortion that causes instability in the structure and traps $Mg^{2+}$ ions [32]. Some capacity fade may be inherent to the use of Mn, as Mn chalcogenides are predicted to undergo larger volume changes during cycling compared with other metal-chalcogenides. [33] Thus, it is useful to examine the performance of other metal-oxides.

### 3.3. Vanadates: the case of $H_2V_3O_8$

Despite the toxic and critical nature of vanadium, [2] vanadates present many attractive qualities. Vanadium is a multi-redox transition metal ($V^{5+/4+/3+/2+}$), and therefore well-suited to cycling the divalent $Mg^{2+}$. The availability of many oxidation states helps to preserve local electroneutrality, which is thought to aid intercalation [9]. In addition, V or Ti oxides are predicted to have lower volume changes during cycling, as non-bonding orbitals are filled during reduction [33]. In contrast, for Mn or other metals, the anti-bonding orbitals are filled instead, making the volume change much greater [33]. These structural characteristics have motivated evaluating vanadates for Mg cathodes, such as $VO_2$, [23] $V_4Nb_{18}O_{55}$, [6] or the famous $V_2O_5$ [24].

One such promising cathode is $H_2V_3O_8$. This structure consists of $VO_6$ and $VO_5$ octahedra, joined together to form 1D needles, [34] which have nanowire morphology (Fig. 2 – structure adapted from prior work [34]) [30,34]. TGA analysis suggests the presence of structural water, which is thought to share oxygen with the V-O polyhedra [34]. When employed in Li-batteries, this water helps to accommodate the $Li^+$ and enhances $Li^+$ mobility between the V-O needles [35]. It is likely that water similarly enhances the intercalation of $Mg^{2+}$. Moreover, the coordination of $Mg^{2+}$ in the structure is 5, [34] meeting the requirement of non-octahedral coordination [20,21]. Encouragingly, over 300 mAh/g are attainable experimentally for $Mg^{2+}$ cycling using a carbon anode, with capacity retention of $>$ 85% after 20 cycles [30]. Other work reports lower initial capacity (231 mAh/g) with $>$ 70% retention after 100 cycles [34]. The performance of $H_2V_3O_8$ depends strongly on the anode employed, with carbon being more successful than Mg metal [30,34]. It was suggested that finding an appropriate electrolyte would improve cycling against Mg metal, [34] although perhaps slight leakage of the structural water could create an Mg-blocking layer [8] on the metal anode. While the reported plateau voltage varies between reports, it is consistently decent (2–3 V vs. $Mg^{2+}$/Mg), as expected for an oxide [30,34]. Thus, $H_2V_3O_8$ is a promising cathode for Mg batteries.

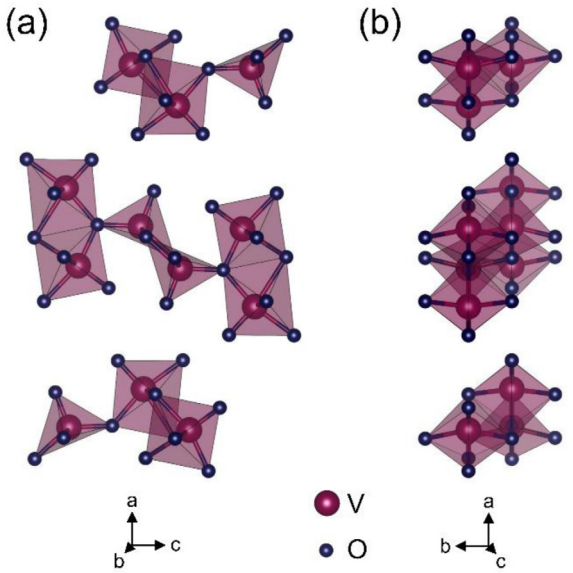


**Fig. 2.** Structure of $H_2V_3O_8$, looking (a) down the *b*-axis and (b) down the *c*-axis.

## 4. Conclusion

While Mg batteries promise higher capacity than their Li counterparts, a lack of suitable cathodes hinders their commercialization. Here, we have given an overview of the main considerations for obtaining good ion migration, capacity and voltage from Mg-cathodes. Oxides often afford higher voltages, which is needed to deliver good energy densities. However, this comes at the expense of fast intercalation of $Mg^{2+}$, which can be achieved using sulfides. $Mg^{2+}$ also has strict requirements for coordination within the cathode structure. Nanosizing and shielding can improve ion migration and capacity in oxides, but some shielding agents, such as water, may be incompatible with a Mg-metal anode. We have highlighted here several key cathode chemistries, including the seminal $Mo_6S_8$, which due to its high stability is still employed to evaluate novel electrodes and electrolytes. Manganese oxides exhibit promising voltages and capacities, but can also experience significant capacity fades. Despite the critical nature of vanadium, vanadates are particularly interesting, as the many redox states of vanadium and smaller volume changes during cycling can more easily accommodate the divalent $Mg^{2+}$. Of note is $H_2V_3O_8$, which can deliver $>$ 300 mAh/g capacity, but is difficult to cycle vs. Mg metal. Further optimization of existing cathodes, as well as discovery of new chemistries, are needed for commercialization of Mg batteries.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No data was used for the research described in the article.

## Acknowledgments

JP and SC thank the EPSRC, United Kingdom for financial support via grant [EP/L016818/1] which funds the Centre for Doctoral Training in Energy Storage and its Applications. RK and SC gratefully acknowledge the support of the Faraday ISCF Faraday Challenge projects FutureCat [grant no. FIRG017] and Nexgenna [grant no. FIRG018].

## References


[1] Liu F, Wang T, Liu X, Fan LZ. Challenges and recent progress on key materials for rechargeable magnesium batteries. Adv Energy Mater 2021;11(2):2000787.

[2] Hasa I, Mariyappan S, Saurel D, Adelhelm P. Challenges of today for Na-based batteries of the future : From materials to cell metrics. J Power Sources 2021 2020;482:228872.

[3] Statista. Magnesite reserves worldwide as of 2020 https://www.statista.com/statistics/264953/global-reserves-of-magnesium-by-major-countries/.

[4] Shannon RD. Revised effective ionic radii and systematic studies of interatomie distances in halides and chaleogenides. Acta Crystallogr A 1976;(32):751–67.

[5] Muldoon J, Bucur CB, Gregory T. Quest for nonaqueous multivalent secondary batteries: Magnesium and beyond. Chem Rev 2014;114(23):11683–720.

[6] Johnson ID, Nolis G, Mccoll K, Wu YA, Thornton D, Hu L, et al. Probing Mg intercalation in the tetragonal tungsten bronze framework V4Nb18o55. Inorg Chem 2020;59:9783–97.

[7] Liu M, Jain A, Rong Z, Qu X, Canepa P. Evaluation of sulfur spinel compounds for multivalent battery cathode applications. Energy Environ Sci 2016;9:3201–9.

[8] Shterenberg I, Salama M, Gofer Y, Levi E, Aurbach D. The challenge of developing rechargeable magnesium batteries. MRS Bull 2014;39(5):453–60.

[9] Levi E, Levi MD, Chasid O, Aurbach D. A review on the problems of the solid state ions diffusion in cathodes for rechargeable Mg batteries. J Electroceramics 2009;22(1–3):13–9.

[10] Sun X, Bonnick P, Duffort V, Liu M, Rong Z, Persson KA, et al. A high capacity thiospinel cathode for Mg batteries. Energy Environ Sci 2016;9:2273–7.

[11] Aurbach D, Lu Z, Schechter A, Gofer Y, Gizbar H, Turgeman R, et al. Prototype systems for rechargeable magnesium batteries. Nature 2000;407:724–7.

[12] Kaveevivitchai W, Jacobson AJ. High capacity rechargeable magnesium-ion batteries based on a microporous molybdenum-vanadium oxide cathode. Chem Mater 2016;28(13):4593–601.

[13] Michail A, Silván B, Tapia-Ruiz N. Progress in high-voltage MgMn2O4 oxyspinel cathode materials for Mg batteries. Curr Opin Electrochem 2022;31:100817.

[14] Lau J, DeBlock RH, Butts DM, Ashby DS, Choi CS, Dunn BS. Sulfide solid electrolytes for lithium battery applications. Adv Energy Mater 2018;8(27):1800933.

[15] Saha S, Assat G, Sougrati MT, Foix D, Li H, Vergnet J, et al. Exploring the bottlenecks of anionic redox in Li-rich layered sulfides. Nat Energy 2019;4(November):977–87.

[16] Levi E, YGofer, Aurbach D. On the way to rechargeable Mg batteries: The challenge of new cathode materials. Chem Mater 2010;22(3):860–8.

[17] Chen W, Zhan X, Luo B, Ou Z, Shih PC, Yao L, et al. Effects of particle size on $Mg^{2+}$ ion intercalation into λ-$MnO_2$ cathode materials. Nano Lett 2019;19(7):4712–20.

[18] Blanc LE, Sun X, Shyamsunder A, Duffort V, Nazar LF. Direct nano-synthesis methods notably benefit Mg-battery cathode performance. Small Methods 2020;4(5):2000029.

[19] Sai Gautam G, Canepa P, Urban A, Bo SH, Ceder G. Influence of inversion on Mg mobility and electrochemistry in spinels. Chem Mater 2017;29(18):7918–30.

[20] Canepa P, Bo SH, Sai Gautam G, Key B, Richards WD, Shi T, et al. High magnesium mobility in ternary spinel chalcogenides. Nature Commun 2017;8(1):1–8.

[21] Rong Z, Malik R, Canepa P, Sai Gautam G, Liu M, Jain A, et al. Materials design rules for multivalent ion mobility in intercalation structures. Chem Mater 2015;27(17):6016–21.

[22] Maroni F, Dongmo S, Gauckler C, Marinaro M, Wohlfahrt-Mehrens M. Through the maze of multivalent-ion batteries: A critical review on the status of the research on cathode materials for $Mg^{2+}$ and $Ca^{2+}$ ions insertion. Batter Supercaps 2021;4:1–32.

[23] Rashad M, Asif M, Wang Y, He Z, Ahmed I. Recent advances in electrolytes and cathode materials for magnesium and hybrid-ion batteries. Energy Storage Mater 2020 2019;25:342–75.

[24] Canepa P, Sai Gautam G, Hannah DC, Malik R, Liu M, Gallagher KG, et al. Odyssey of multivalent cathode materials: Open questions and future challenges. Chem Rev 2017;117(5):4287–341.

[25] Chevrel R, Sergent M, Prigent J. Un nouveau sulfure de Molybdène: Mo3S4. Préparation, propriétés et structure cristalline. Mater Res Bull 1974;9:1487–98.

[26] Levi E, Mitelman A, Isnard O, Brunelli M, Aurbach D. Phase diagram of Mg insertion into chevrel phases, $Mg_xMo_6T_8$ (T=S, Se). the crystal structure of triclinic $Mg_2Mo_6Se_8$. Inorg Chem 2008;47(6):1975–83.

[27] Aurbach D, Weissman I, Gofer Y, Levi E. Nonaqueous magnesium electrochemistry and its application in secondary batteries. Chem Rec 2003;3(1):61–73.

[28] Kang SJ, Lim SC, Kim H, Heo JW, Hwang S, Jang M, et al. Non-grignard and lewis acid-free sulfone electrolytes for rechargeable magnesium batteries. Chem Mater 2017;29(7):3174–80.

[29] Brouillet EV, Amores M, Corr SA, Robertson SD, Robertson SD. Exploiting cation aggregation in new magnesium amidohaloaluminate electrolytes for magnesium batteries. Inorg Chem Front 2020;7(12):2305–12.

[30] Tang H, Xu N, Pei C, Xiong F, Tan S, Luo W, et al. $H_2V_3O_8$ nanowires as high-capacity cathode materials for magnesium-based battery. ACS Appl Mater Interfaces 2017;9(34):28667–73.

[31] Yuan C, Zhang Y, Pan Y, Liu X, Wang G, Cao D. Investigation of the intercalation of polyvalent cations ($Mg^{2+}$, $Zn^{2+}$) into λ-$MnO_2$ for rechargeable aqueous battery. Electrochim Acta 2014;116:404–12.
[32] Zhang R, Yu X, Nam KW, Ling C, Arthur TS, Song W, et al. α-$MnO_2$ as a cathode material for rechargeable Mg batteries. Electrochem Commun 2012;23(1):110–3.
[33] Liu M, Rong Z, Malik R, Canepa P, Jain A, Ceder G, et al. Spinel compounds as multivalent battery cathodes: A systematic evaluation based on Ab initio calculations. Energy Environ Sci 2015;8(3):964–74.
[34] Rastgoo-Deylami M, Chae MS, Hong ST. $H_2V_3O_8$ as a high energy cathode material for nonaqueous magnesium-ion batteries. Chem Mater 2018;30(21):7464–72.
[35] Kuhn A, Pérez-Flores JC, Prado-Gonjal J, Morán E, Hoelzel M, Díez-Gómez V, et al. Lithium intercalation mechanism and critical role of structural water in layered H2V3O8High-capacity cathode material for lithium-ion batteries. Chem Mater 2022;34(2):694–705.