Editorial

Anodes for magnesium batteries: State-of-the-art and prospects. A viewpoint ☆

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1. Motivation

There is an increasing demand for rechargeable batteries in high-performance energy storage systems. The current dominating Li ion batteries are limited by price fluctuations of resources, resource availability, as well as their theoretical capacities so that the community is exploring alternative battery chemistries to expand the portfolio of available battery types. As a promising multivalent battery type, rechargeable magnesium batteries (RMBs) have attracted increasing attention because of high safety, high volumetric energy density, and low cost due to the high geological abundance of Mg. The high theoretical energy density comes from the fact that Mg can be used in undiluted form as a metal anode in RMB. This anode can provide high coulombic efficiency without dendrite formation upon charging with selected electrolytes and under reasonable conditions [1]. However, despite these benefits, the implementation of magnesium batteries has been obstructed by several significant roadblocks.

This little perspective article aims to provide a selective overview on progress with various anode materials used in nonaqueous RMBs, with the hope to inspire more attention and research efforts for the achievement of overall better performance of future RMBs.

2. Challenges

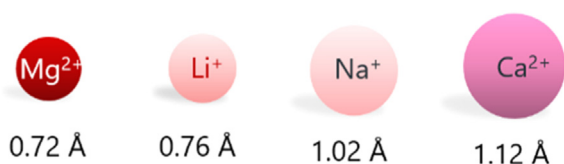It has been mentioned that the divalence of magnesium is advantageous because more charge can be transported and stored per ion. In practice, however, this fundamental advantage is compromised by the fact that the small and doubly charged Mg^{2+} ion has a high charge density and therefore strongly polarizes the ion's chemical environment, which negatively affects its mobility in liquids and solids, see Fig. 1.

Hence, any strategy for developing a viable system with high and stable reversible capacity and good reaction rates needs to take this circumstance into account and a specific environment must be tailored for the Mg ion. A particular challenge is, that the affinity to oxidic groups is strong and must be kept under control either by geometrical measures such as pillaring or by replacing the oxide by other elements such as sulfur. The strong polarization may also be a reason why the formation of thin deposition layers on the anode (similar to the "Solid Electrolyte Interface" with Li ion batteries) may lead to either blocking the ionic transfer completely or imposing serious energetic barriers which can lead to high overpotentials.

In recent years, there has been good progress with Mg metal and alloy electrodes, and with reducing the overpotential by electrolyte additives and artificial SEIs. Stable electrolytes with good ionic conductivities have been identified, as well, and meanwhile, a "reference" electrolyte with wide applicability has emerged [2]. Still, little progress can be noticed in the development of inorganic insertion hosts where the mobility challenges seem to prevail. At the same time, a series of impressive results with stable organic cathode active materials has been published. Progress has also been made with the stabilization of conversion-based cathodes such as sulfur.

Fig. 1. Charge, ionic radii and order of charge densities of the first alkaline and alkaline-earth elements.

3. Progress

Without the claim of being complete, selected examples from recent work anodes for rechargeable Mg battery are presented and discussed in the following. In brief, progress on anodes for RMB has been made by expanding the candidates list of anode active materials. Moreover, artificial coatings have been presented which protect the anode surface and lead to lower overpotential and higher stability upon cycling – one of the major roadblocks on the way to practical systems.

3.1. Mg alloys

Pure Mg is not only expensive but has also unfavorable mechanical properties, such as low cold formability and machinability, low strength, low fracture strain and its tendency to microcracking and fatigue under cyclic loading. Therefore, it would be advantageous to replace it with a more cost-effective, machineable and durable alternative. In this regard, several studies have recently been conducted with the aim of exploring alloy anodes made of Mg alloyed with transition metals and other elements such as Al, Ga, In, Si, Ge, Sn, Pb, P, As, Sb, and Bi. The alloys were tested for their voltage stability, cycling efficiency, and internal resistance in [3]. A different and larger set of materials is summarized in a review article, in [4].

Among the various options investigated, $Mg_{17}Al_{12}$ (2812 mAh/g), Mg_2Si (3816 mAh/g), Mg_2Ge (1476 mAh/g) and Mg_2Sn (903 mAh/g) offer the highest theoretical capacities. However, Ge is expensive, with Mg_2Si a reversible de-/magnesiation could not be demonstrated and Mg_2Sn has shown only a limited reversibility so far [4] so that only the Mg-Al alloy seems to hold promise at the moment. Moreover, its $Mg_{17}Al_{12}$ phase offers an average potential of 0.07 V versus Mg^{2+}/Mg.

In the second study [3], the Mg-Al alloy was found to exhibit a high efficiency (over 85% after 100 cycles) and a comparably stable voltage. The alloy reduces internal resistance and improves cycling stability. When compared to a Mg-Ag alloy, the Mg-Al alloy demonstrated superior voltage stability over longer cycles. After 100 cycles, the open-circuit poten-

tial (OCP) of the Mg-Al alloy had decreased by only 0.05 V, from 2.1 V to 2.05 V, while a similar experiment showed a more significant decrease of 0.12 V for the Mg-Ag alloy. Overall, the studies published so far point out that proper design of the alloy can be an effective strategy for improving cycling stability and efficiency. But, unfortunately, a direct comparison of pure Mg and Mg-Al alloy is still lacking and more research is needed to learn about the effect of alloying and obtain further guidelines for research and development.

It should be mentioned that these studies were all performed with either Grignard-based, APC (All-Phenyl Complex, $PhMgCl + AlCl_3$), or $Mg(TFSI)_2$ based electrolytes, which limits their meaningfulness. In practical systems, other electrolytes may be preferred, such as borate-based or amide-based electrolytes [5–7]. This is particularly necessary, if the electrolyte is in contact with a cathode that can be easily reduced such as a sulfur cathode [2]. Hence, it would be necessary to conduct additional studies, with different electrolyte formulations.

3.2. Protective and functional layers

There is currently a general trend toward integrating metal anodes into batteries, as these promise theoretical full-cell capacities that can exceed current ones by 30 percent or more, as in the case of lithium-ion metal batteries [8]. However, light and electropositive metals such as Mg can have a strongly reducing effect, and layers of molecular deposits can form on the anode, which can severely impair stripping and coating behavior. As a solution, artificial layers have been proposed that prevent direct contact of the Mg metal with the electrolyte and keep deleterious materials away from the actual Mg interface. Various material strategies have been proposed for this purpose.

There have been several hints in the past that surface protection by elements like Bi or Sn can lower the high overpotential at Mg anodes and maintain stable cycling [8]. In the following years, strategies have been proposed to create such interfaces by, e.g., simple addition of a Bi containing additive [9]. Recently, an electrodeposition of Mg-Sn@Mg and Mg-Bi@Mg layers on Mg led to significant prolongation of cycle life, lowering of the hysteresis and the impedance of the electrode. Interestingly, similarly prepared Mg-Sn@Mg and Mg-Bi@Mg anodes, coupled in full cells with Chevrel cathode, exhibited an ultrastable electrochemical performance, even after 5000 cycles [10].

While extensive studies have revealed great potential of COF (Covalent Organic Framework) protecting layers on Li, Na, and Zn anodes, little is known about the potential of COFs for stabilizing Mg anodes. COFs can form dense protective layers which can alleviate passivation caused by ongoing side reactions between the metal anode and the electrolyte. The layers have demonstrated similar electronic insulation properties to conventional SEIs, along with many other merits such as high designability, chemical robustness, and ordered pore structure. Their tunability, their synthesis, challenges in obtaining a well-defined pore structure, dealing with

potential side reactions and benefits of COFs are highlighted in a series of overview articles, with a collection further references therein [11,12].

To push the gravimetric and volumetric density limits further, it would be desirable to extend the concept of zero-excess or "anode-free" systems which is currently explored for Li batteries, also to RMB. However, the practical application of anode-free magnesium metal batteries is plagued by low Mg plating/stripping efficiency due to nonuniform Mg deposition on conventional anode current collectors. In a proof-of-concept, a first "anode-free" magnesium cell has been developed on the basis of a $Ti_3C_3T_x$ MXene foil coating as the current collector [13]. The layer promoted exceptionally uniform Mg plating and almost complete stripping with efficiencies of 99.7% over 364 cycles and 99.4% over 164 cycles, respectively, with high Mg yield at 5 mA g^{-1}. It was demonstrated that when the $Ti_3C_2T_x$ film was coupled with a pre-magnetized Mo_6S_8 cathode, the anode-free Mg-metal full-cell prototype exhibited a volumetric energy density five times higher than its standard Mg-metal counterpart.

4. Future directions

From the little selection above the author sees a high potential for progress in further developing Mg alloys which do not only have favorable mechanical properties but also offer an electrochemical potential close to Mg/Mg^{2+}. Moreover, it might be of advantage to integrate trace elements which can lower the kinetic barriers for ion transfer at the interface with the electrolyte.

Another successful approach with enormous potential for stabilizing the interface is the development of protective or functional layers that maintain the stable function of the anode. A particular challenge will be the development of functional interfaces that enable a smooth Mg coating in the context of a "zero-excess" Mg battery cell. One of the biggest challenges will be achieving this even at high rates. Mg would be particularly promising for this new type of battery cell because, unlike Li or even Na metal, Mg offers a higher volumetric capacity, it has significantly better safety properties and does not react with water in the event of an accident.

Declaration of competing interest

None.

CRediT authorship contribution statement

Maximilian Fichtner: Writing – review & editing, Writing – original draft, Project administration, Investigation, Funding acquisition, Conceptualization.

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References

[1] L. Leuppert, A. Reupert, T. Diemant, T. Philipp, C. Kranz, Z. Li, M. Fichtner, RSC Applied Interfaces 1 (2024) 1142–1155, doi:10.1039/d4lf00124a.

[2] P. Jankowski, Z. Li, Z. Zhao-Karger, T. Diemant, M. Fichtner, T. Vegge, J.M.G. Lastra, Energy Storage Mater 45 (2022) 1133–1143, doi:10.1016/j.ensm.2021.11.012.

[3] B.I. Oladapo, M.A. Olawumi, F.T. Omigbodun, Batteries 10 (2024) 1–24, doi:10.3390/batteries10110383.

[4] D. Setiawan, H. Lee, J. Pyun, A. Nimkar, N. Shpigel, D. Sharon, S.T. Hong, D. Aurbach, M.S. Chae, Journal of Magnesium and Alloys 12 (2024) 3476–3490, doi:10.1016/j.jma.2024.09.018.

[5] Z. Zhao-Karger, X. Zhao, D. Wang, T. Diemant, R.J. Behm, M. Fichtner, Adv Energy Mater 5 (2015) 1401155, doi:10.1002/aenm.201401155.

[6] Z. Zhao-Karger, M.E. Gil Bardaji, O. Fuhr, M. Fichtner, J Mater Chem A Mater 5 (2017) 10815–10820, doi:10.1039/c7ta02237a.

[7] Z. Zhao-Karger, R. Liu, W. Dai, Z. Li, T. Diemant, B.P. Vinayan, C. Bonatto Minella, X. Yu, A. Manthiram, R.J. Behm, M. Ruben, M. Fichtner, ACS Energy Lett 3 (2018), doi:10.1021/acsenergylett.8b01061.

[8] F. Murgia, L. Stievano, L. Monconduit, R. Berthelot, J Mater Chem A Mater 3 (2015) 16478–16485, doi:10.1039/C5TA04077A.

[9] Z. Meng, Z. Li, L. Wang, T. Diemant, D. Bosubabu, Y. Tang, R. Berthelot, Z. Zhao-Karger, M. Fichtner, ACS Appl Mater Interfaces 13 (2021) 37044–37051, doi:10.1021/acsami.1c07648.

[10] X. Chai, Y. Xin, B. He, F. Zhang, H. Xie, H. Tian, Nanoscale 16 (2024) 9123–9135, doi:10.1039/d4nr00842a.

[11] J. Sun, F. Kang, D. Yan, T. Ding, Y. Wang, X. Zhou, Q. Zhang, Angewandte Chemie - International Edition 63 (2024) e202406511, doi:10.1002/anie.202406511.

[12] X. Li, Z. Zhang, D. Chen, F. Ma, J. Huang, Y. Wang, L. Wang, Y. Wu, Y. Chen, Adv Funct Mater (2025) 2505390, doi:10.1002/adfm.202505390.

[13] Y. Li, X. Feng, W.Y. Lieu, L. Fu, C. Zhang, T. Ghosh, A. Thakur, B.C. Wyatt, B. Anasori, W. Liu, Q. Zhang, J. Lu, Z.W. Seh, Adv Funct Mater 33 (2023) 2303067, doi:10.1002/adfm.202303067.