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Alloys to Replace Mg Anodes in Efficient and Practical Mg-ion/Sulfur Batteries

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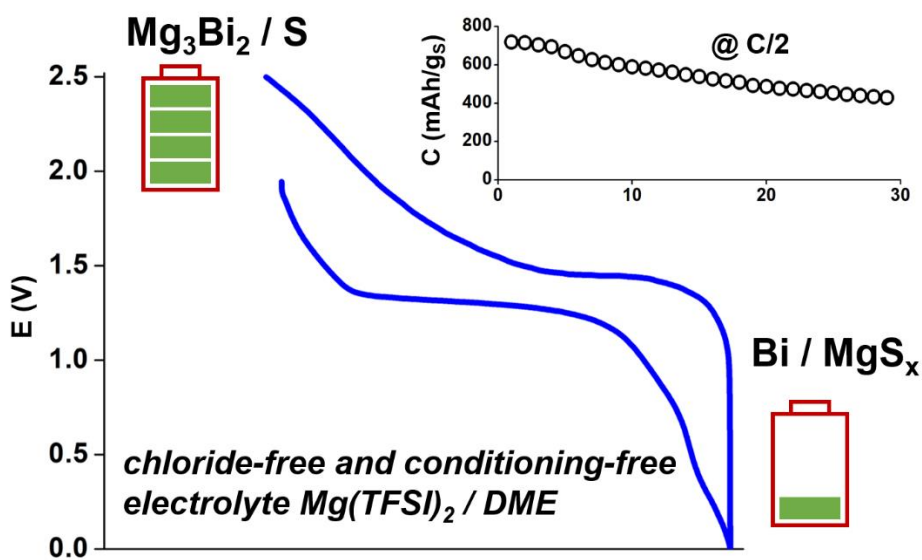
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Abstract. The development of rechargeable Mg/S battery is driven by the design of reliable electrolytes. So far, they seem not suitable for industrial transfer as they are either corrosive or necessitate a complex formulation. The innovative strategy reported here which replaces magnesium by Mg alloys at the negative electrode enables employing facile electrolyte formulations as well as proposing an easier shaping process of the electrode. As proof-of-concept, $\text{Mg}_3\text{Bi}_2/\text{S}$ cells were evaluated with simple $\text{Mg}(\text{TFSI})_2/\text{DME}$ electrolyte. Electrochemical mechanisms including Mg_3Bi_2 de-alloying and sulfur magnesiation was probed by XRD and XPS, respectively. On top of that, very promising cycling performance at elevated current density is obtained. This preliminary findings pave the way for further improvements towards further practical applications.

TOC GRAPHICS



A smart and more efficient energy management is required for drawing a better world. This encompasses greener ways to produce energy, and more coherent and eco-friendly systems to store and transport it. A revolutionary innovation has been the incorporation of electrochemical energy storage in the form of batteries into our energy life cycle. Among the different storage systems, the lithium-ion technology has revolutionized portable electronics and is making long-range electric vehicles a reality. However, after continuous improvements over the last decades, Li-ion batteries are approaching their limits in terms of energy density and cost. Moreover, the ever-increasing need of batteries might face limited resources (for lithium and more likely cobalt or nickel), generating cost rise and geopolitical tensions. It is therefore important to look at alternative systems combining sustainability and satisfactory storage performance. In this context, Mg batteries have received a considerable attention in the past two decades since the first rechargeable prototype reported by Aurbach.¹ Indeed, the use of Mg theoretically offers high volumetric capacity (3.8 Ah/cm³ compare to 2.1 Ah/cm³ for Li) and the combination with its relatively low standard reduction potential (2.4 V vs. NHE) enables considering high volumetric energy density systems. However, the sluggish diffusion of Mg²⁺ ions into typical electrode hosts such as layered or polyanionic compounds is a major hurdle toward the development of practical and high performance Mg batteries.²⁻⁵ Shifting from insertion to conversion electrochemical process, using sulfur-based electrodes is now a widely established way to access high capacities at the positive side as well.⁶ In theory, a Mg/S cell could deliver high specific gravimetric and volumetric energy densities of 1300-1700 Wh/kg and 2500-3200 Wh/L, respectively. Moreover, combining magnesium and sulfur in the same rechargeable batteries seems very attractive nowadays, when sustainability becomes as important as performance.

The design of the electrolyte is driven and constrained by the peculiar chemical and electrochemical features of magnesium and sulfur. The electrolyte needs to be non-nucleophilic and must prevent the passivation of the Mg surface, which could hinder any electrochemical plating/stripping process. In 2011, the research group of Toyota reported the first example of rechargeable Mg/S battery using an electrolyte containing an electrochemical active complex created in situ from HMDSMgCl and AlCl₃ salts.⁷ After that, the use of bisamides salt Mg(HMDS)₂ has been generalized by Fichtner and Zhao-Karger,⁸⁻¹² while working with Mg(TFSI)₂ salt has been more and more considered (Table S1). However, in both cases the mandatory presence of chloride additives (AlCl₃, MgCl₂) increases the corrosive nature of the

electrolyte and compel the use of noble metal current collectors that are not suitable for practical large-scale production. When chloride-free formulations are evaluated, a preliminary conditioning treatment based on successive voltammetry sweeps appears necessary but barely suitable for practical applications.^{13,14} Indeed, the electrochemically cleaned volume is limited, and the ready-to-use electrolyte should be transferred from the electrochemical cell to the Mg/S cell. In 2017, Zhao-Karger *et al.* reported a new class of non-corrosive and efficient electrolytes using fluorinated alkoxyborate magnesium salt $\text{Mg}[\text{B}(\text{HFIP})_4]_2$;^{15,16} however the synthesis of the latter is complex and still far from industrial transfer.

The novel concept introduced with this Letter is the replacement of the Mg anode by an alloy containing magnesium allowing the use of simple, non-corrosive electrolytes with a preparation that is suitable for future practical application. The concept lies on the ability of some *p*-block elements (*e.g.*, In, Sn, Sb, Pb and Bi) to reversibly electrochemically alloy with magnesium.^{17–20} The electrochemical formation of MgIn , Mg_2Sn , Mg_3Sb_2 , Mg_3Bi_2 and Mg_2Pb occurs during a relatively flat biphasic plateau at low voltage and corresponds to high capacities (Table S2). The significant volume changes induced by successive alloying/de-alloying processes has been thought for long time as an important drawback. However, thanks to an appropriate electrode formulation, long-time cycling with high capacity retention could be achieved.^{21,22} Considering that these alloys are more compatible with conventional electrolyte formulations than Mg metal, they represent top-ranking negative electrode materials for rechargeable Mg-ion batteries. The direct use of alloys enables one to investigate Mg-free positive electrode materials. Very recently Mg_2Sn and Mg_3Bi_2 were implemented in full cells to evaluate vanadium oxide, Chevrel phase and Prussian blue analogs with easy-made and non-corrosive electrolytes based on $\text{Mg}(\text{TFSI})_2$ dissolved in diglyme or acetonitrile.^{23,24} Believing that sulfur-based positive electrodes are the most promising choice to access high energy density Mg batteries, here we prepared a $\text{Mg}_3\text{Bi}_2/\text{C}$ composite and evaluated it for the first time in a Mg-ion/S battery with a very simple electrolyte formulation.

Figure 1 compares the first cycles of both Mg/S and $\text{Mg}_3\text{Bi}_2/\text{S}$ batteries with 1 M $\text{Mg}(\text{TFSI})_2/\text{DME}$ electrolyte, importantly without any added chloride additive and without any prior electrochemical conditioning, evaluated at $C/10$ (~ 160 mA/g of sulfur – gs). The $\text{Mg}_3\text{Bi}_2/\text{C}$ composite was prepared

in few hours by high energy ball-milling and simply blended with conducting carbon and binder to get a sufficiently thick negative electrode. Sulfur-impregnated activated carbon cloth (ACC/S) served as positive electrode (details in supporting information).

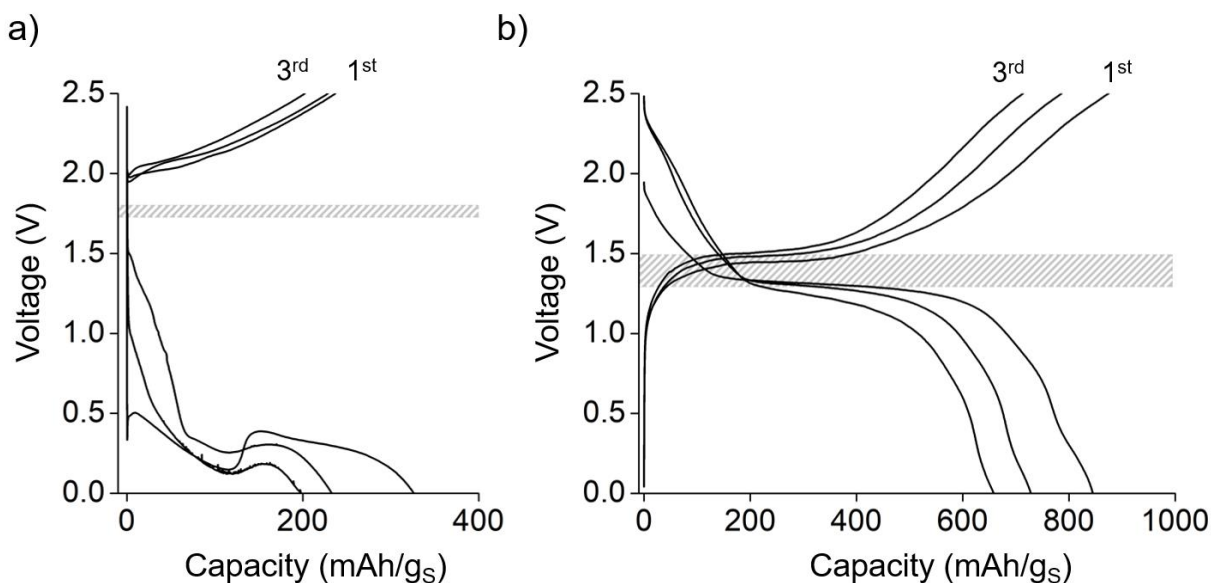


Figure 1: Comparison between first cycles obtained at C/10 for Mg/S cell (a) and Mg₃Bi₂/S cell (b) with Mg(TFSI)₂/DME electrolyte. The grey band represents the theoretical working voltage of each cell and highlights the very high over-potential when Mg anode is used.

A very large overpotential is observed for the Mg/S cell, with a rapid potential drop down below 0.5 V in discharge. The corresponding capacity is consequently very limited below 400 mAh/g_S. A very high over-potential is also observed in charge, and the shape of the subsequent cycles questions the electrochemical mechanisms that really occur. According to the literature, this over-potential should come from the chemical passivation of the Mg surface occurring as soon as the latter comes in contact with the electrolyte, but could also have an electrochemical origin with the reduction of magnesium polysulfide on the surface.^{25,26} The electrochemical signature strongly differs from that of the Mg₃Bi₂/S battery. The first discharge starts with a short slope followed by a relatively flat plateau around 1.3 V. A second slope down to 0 V enables reaching a very high capacity exceeding 800 mAh/g_S. A similar curve profile is obtained during charge, with a very low

polarization around 0.3 V. The subsequent cycles demonstrate a quite reversible electrochemical process. The theoretical operation voltage for a Mg/S battery cell (1.7 V) should be decreased by about 0.2 – 0.3 V when substituting Mg by Mg_3Bi_2 according to the de-alloying process of the alloy.²⁷ The experimental working potentials observed here agree with the theory (1.3 and 1.5 V in discharge and charge, respectively) and underline a very low polarization in spite of the relatively high current density. As similar cathode material and electrolyte formulation were used, the change of cycling profile logically comes from a different behavior at the anode-electrolyte interface. The latter has been further investigated using 3-electrode setup. Comparison between the galvanostatic profiles of $\text{Mg}_3\text{Bi}_2/\text{S}$ and Mg/S cells (Figure S5) highlights the very high polarization of the Mg anode (~ 2 V), whereas the potential gap observed at the Mg_3Bi_2 anode is very low (170 mV). Polarization test of a $\text{Mg}_3\text{Bi}_2/\text{Mg}$ cell confirms the strong passivation that occurs on a Mg electrode (Figure S6). Lastly, EIS has been performed on both $\text{Mg}_3\text{Bi}_2/\text{S}$ and Mg/S cells at OCV and after the 1st and the 3rd cycle (Figure S7). The impedance of the Mg_3Bi_2 anode is maintained below 50 Ohm cm^2 , whereas for the Mg anode the already-high OCV impedance increases becoming impossible to measure upon cycling, indicating an extremely strong passivation process. (Fig S7)

Focusing now on the $\text{Mg}_3\text{Bi}_2/\text{S}$ battery, our early-stage characterizations by *operando* X-ray diffraction (XRD) confirm the de-alloying process from Mg_3Bi_2 to Bi at the negative side (Figures 2a and S3). Indeed, the formation of Bi is clearly evidenced through the growing peak at 32 °, in agreement with the biphasic electrochemical process reported by Murgia *et al.*²⁷ Regarding Mg_3Bi_2 peaks, the intensity decreases only slightly because of the large excess of Mg_3Bi_2 in the negative electrode with respect to the nominal amount of sulfur on the positive side of the cell. Such a low sulfur loading makes all possible crystalline sulfur species practically invisible by XRD. Conversely, X-ray photoelectron spectroscopy (XPS), allows tracking the evolution of the sulfur species in metal/sulfur battery even at such low loadings. Here, XPS spectra collected *ex situ* at different battery states shows the conversion of elemental sulfur into polysulfides MgS_x with a characteristic S 2p_{3/2} at 162 eV (Figure 2b).^{7,13,14,16} The formation of bridging sulfur is also evidenced during the subsequent charge. However, the detection of sulfur species is biased by the presence of the contributions of Bi 4f_{7/2} and Bi 4f_{5/2} peaks at 158.6 and 163.9 eV attributed to a

slight unexpected Bi dissolution. It seems reasonable to assume that the Bi particles generated through the electrochemical de-magnesian of Mg_3Bi_2 have a highly reactive freshly exposed surface, which possibly reacts with sulfur or polysulfide species from the electrolyte, creating bismuth sulfides species which shuttle back to the positive electrode side. Further investigations are actually in progress to confirm or complete this early-stage hypothesis and will be the object of a forthcoming article. Bearing in mind the very simple negative electrode formulation, there is no doubt that a smarter electrode engineering will help circumventing this effect. The sulfite peak (S 2p_{3/2} at 167.3 eV) highlights the degradation of the TFSI⁻ anion, as often observed in metal/sulfur batteries.

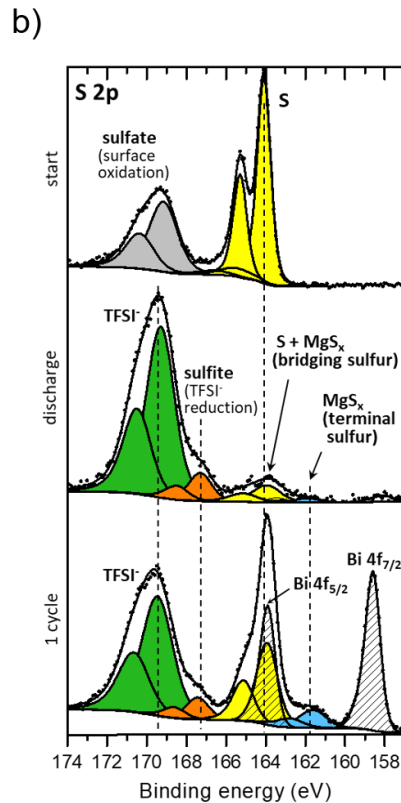
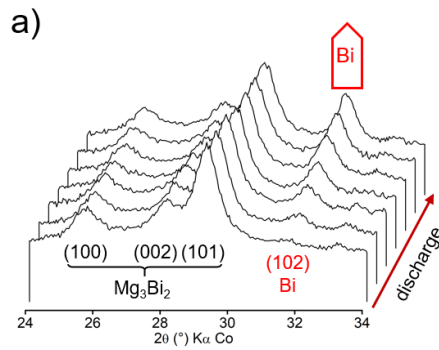


Figure 2: (a) operando XRD monitoring of the negative electrode showing Bi formation during the Mg₃Bi₂/S battery discharge. The peaks shift in the figure is not real but comes from the waterfall plotting format. (b) ex situ S 2p XPS showing the change of sulfur species at the surface, but also the unexpected presence of Bi species.

The discharge-charge profiles exhibit three distinct regions (slope – plateau – slope), as previously observed with similar ACC/S electrodes and ascribed to the successive formation of MgS₈, MgS₂ and lastly solid MgS.¹⁴ Nevertheless, other profiles have been reported in the literature, with alternative scenarios and different intermediate polysulfide species involved.^{16,28,29} The weak shift of the galvanostatic profiles between each cycle (Fig. S4) certainly accounts for polysulfide species dissolution as commonly reported in all metal/sulfur batteries. Unraveling the detailed mechanism of the electrochemical magnesiation of sulfur in such systems is under investigation but is out of the scope of this Letter.

The promising behavior of Mg₃Bi₂/S cell obtained at C/10 is substantiated also by its cycling performance at higher current density. Figure 3 shows the combined evolution of the discharge capacity and the Coulombic efficiency obtained at the high rate of C/2 (~840 mAh/g_S). The first cycle capacity is considered high as it exceeds 700 mAh/g_S, while its regular decay upon cycling is not surprising if compared to previous works on Mg/S battery, and might be ascribed to polysulfide dissolution causing loss of active matter and/or the typical shuttle effect. However, the loss is quite moderate as a capacity of 400 mAh/g_S is reached after 30 cycles. In order to better evaluate this performance, it was decided to compare it with other pioneering works dealing with similar ACC/S cathodes. Zhao-Karger and coworkers observed similar performance in a Mg/S cell using a Mg[B(HFIP)₄]₂-based electrolyte. However, the cycling rate was limited to C/10 (167 mAh/g_S).¹⁶ The group of Wang reported a very stable capacity around 600 mAh/g at 100 mAh/g_S for more than 100 cycles.¹³ However, the cell containing a concentrated 1M Mg(TFSI)₂/MgCl₂/DME electrolyte which needed to be first conditioned by cyclic voltammetry, and Mo or W current collectors had to be employed to avoid corrosion. There is no doubt that the very low over-potential observed with alloy-type anode participates in these extremely high

cycling performance. Further investigations are ongoing to evaluate the influence of the simple electrolyte formulation through a systematic benchmarking of other alloy electrodes.

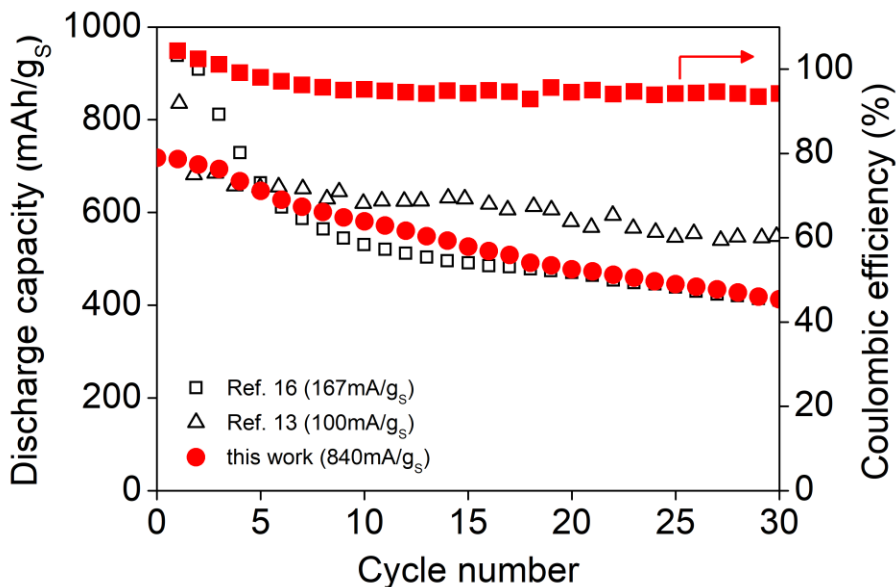


Figure 3: Cycling performance of Mg_3Bi_2/S coin-cell with $Mg(TFSI)_2/DME$ electrolyte at $C/2$ current rate and comparison with literature using similar ACC/S cathode material.^{13,16}

At such an early-stage of the investigation, the cycling performance described above focuses only on the reversible capacity of the sulfur cathode. However, it is important to remind again the average high working potential and the very low polarization increasing the overall energy density of the system. In this regard, it is interesting to simply compare ideal Mg/S and $Mg-ion/S$ batteries only using electrode capacities and working potential. Although the effect of the casing is neglected, such calculation still enables one to point out the electrode materials (anode and cathode) that are promising to combine. As shown in Figure 4, replacing Mg by an alloy involves lower energy densities, because of (i) the alloying/de-alloying process that reduces the working potential and (ii) the lower capacities of alloys with respect to Mg . However this comparison needs to be mitigated considering the nominal volume excess of Mg that must be added in a practical system. The theoretical gap between $Mg-ion/S$ and Mg/S reference cells should be significantly decreased, consequently strengthening the interest of using alloy-type anode.

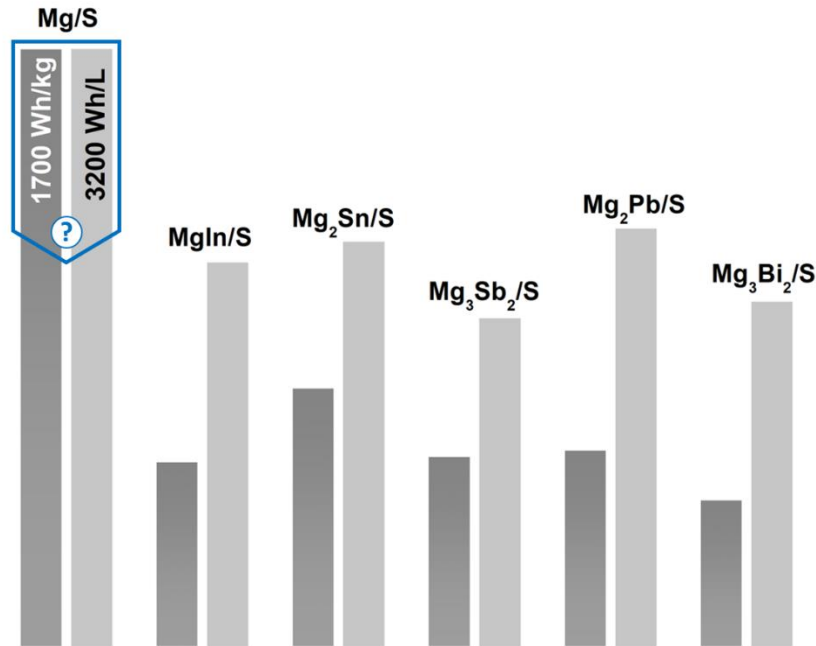


Figure 4: Comparison of theoretical specific or volumetric energy densities between Mg/S and various Mg_xM/S cells. Values are normalized by those for Mg/S cell. The down-pointing blue arrow questions the practical decrease that could result from an initial excess of Mg metal at the anode side.

Summarizing, a first proof-of-concept rechargeable Mg-ion/S battery is shown here. The most important point of this concept is the possible use of a simple Mg(TFSI)₂-based electrolyte made possible by the replacement of Mg by Mg₃Bi₂. The absence of corrosive chloride species and the unnecessary preliminary conditioning treatment pave the way to a possible industrial transfer. Staying on practical considerations, a good electrode material should also be easily integrated in a suitable electrode formulation. Lamination technology seems adapted to design Mg thin film but required specific manufacturing conditions. On the contrary, high energy ball milling could easily produce alloy/carbon composite slurries that could then efficiently shaped in electrode by common tape casting. On top of that, the relatively low air-sensitivity of Mg alloys allows one to work in the absence of a controlled atmosphere.

Such early-stage results will be followed by an in-depth investigation of the chemical and electrochemical mechanisms occurring during cycling, with a special effort on probing the anode-

electrolyte interface to evaluate the chemical reactions between metallic particles and sulfides species and to propose possible strategies to mitigate them.

The very promising cycling performance obtained even at elevated current density might be possibly improved by implementing alternative strategies, for instance by targeting other alloys. Indeed, Mg_3Bi_2 was selected in this first work as a model alloy-type negative electrode owing to the particularly good behavior of bismuth in Mg-batteries, but higher theoretical energy densities could be expected using Mg_2Sn or Mg_2Pb anodes (Figure 4). Significant progress can be expected also by playing with the cathode formulation, and especially by targeting higher sulfur loadings. Lastly, such a very simple electrolyte formulation offers room to further optimizations, in particular to tackle the polysulfide shuttle effect and propose battery prototypes with high energy densities and long cycle lives.

Supporting Information

The Supporting Information section is available free of charge on the ACS Publications website at DOI: xxx.

It includes the preparation and characterization of materials (electrodes and electrolyte), and additional electrochemical analyses performed in 3-electrode cells.

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Notes

The authors declare no competing financial interest.

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References

1. Aurbach, D. *et al.* Prototype systems for rechargeable magnesium batteries. *Nature* **407**, 724–727 (2000).
2. Canepa, P. *et al.* Odyssey of Multivalent Cathode Materials: Open Questions and Future Challenges. *Chem. Rev.* **117**, 4287–4341 (2017).
3. Bucur, C. B., Gregory, T., Oliver, A. G. & Muldoon, J. Confession of a Magnesium Battery. *J. Phys. Chem. Lett.* 3578–3591 (2015). doi:10.1021/acs.jpcclett.5b01219
4. Muldoon, J., Bucur, C. B. & Gregory, T. Quest for Nonaqueous Multivalent Secondary Batteries: Magnesium and Beyond. *Chem. Rev.* **114**, 11683–11720 (2014).
5. Yoo, H. D. *et al.* Mg rechargeable batteries: an on-going challenge. *Energy Environ. Sci.* **6**, 2265–2279 (2013).
6. Zhao-Karger, Z. & Fichtner, M. Magnesium-Sulfur battery: its beginning and recent progress. *MRS Commun.* 1–15 (2017).
7. Kim, H. S. *et al.* Structure and compatibility of a magnesium electrolyte with a sulphur cathode. *Nat. Commun.* **2**, 427 (2011).
8. Zhao-Karger, Z., Zhao, X., Fuhr, O. & Fichtner, M. Bisamide based non-nucleophilic electrolytes for rechargeable magnesium batteries. *RSC Adv.* **3**, 16330–16335 (2013).
9. Zhao-Karger, Z. *et al.* Performance Improvement of Magnesium Sulfur Batteries with Modified Non-Nucleophilic Electrolytes. *Adv. Energy Mater.* **5**, 1401155 (2015).
10. Zhao-Karger, Z. *et al.* Selenium and selenium-sulfur cathode materials for high-energy rechargeable magnesium batteries. *J. Power Sources* **323**, 213–219 (2016).
11. Zhao-Karger, Z. *et al.* Novel transmetalation reaction for electrolyte synthesis for rechargeable magnesium batteries. *RSC Adv.* **4**, 26924–26927 (2014).
12. Vinayan, B. P. *et al.* Performance study of magnesium-sulfur battery using a graphene based sulfur composite cathode electrode and a non-nucleophilic Mg electrolyte. *Nanoscale* **8**, 3296–3306 (2016).
13. Gao, T. *et al.* Reversible S^0/MgS_x Redox Chemistry in a $MgTFSI_2/MgCl_2/DME$ Electrolyte for Rechargeable Mg/S Batteries. *Angew. Chem. Int. Ed.* **129**, 13711–13715 (2017).
14. Gao, T. *et al.* Thermodynamics and Kinetics of Sulfur Cathode during Discharge in $MgTFSI_2 - DME$ Electrolyte. *Adv. Mater.* 1704313 (2017).
15. Zhao-Karger, Z., Gil Bardaji, M. E., Fuhr, O. & Fichtner, M. A new class of non-corrosive,

- highly efficient electrolytes for rechargeable magnesium batteries. *J. Mater. Chem. A* **5**, 10815–10820 (2017).
16. Zhao-Karger, Z. *et al.* Toward Highly Reversible Magnesium–Sulfur Batteries with Efficient and Practical $\text{Mg}[\text{B}(\text{hfiip})_4]_2$ Electrolyte. *ACS Energy Lett.* **3**, 2005–2013 (2018).
 17. Singh, N., Arthur, T. S., Ling, C., Matsui, M. & Mizuno, F. A high energy-density tin anode for rechargeable magnesium-ion batteries. *Chem. Commun.* **49**, 149–151 (2013).
 18. Arthur, T. S., Singh, N. & Matsui, M. Electrodeposited Bi, Sb and $\text{Bi}_{1-x}\text{Sb}_x$ alloys as anodes for Mg-ion batteries. *Electrochem. Commun.* **16**, 103–106 (2012).
 19. Murgia, F., Weldekidan, E. T., Stievano, L., Monconduit, L. & Berthelot, R. First investigation of indium-based electrode in Mg battery. *Electrochem. commun.* **60**, 56–59 (2015).
 20. Periyapperuma, K., Tran, T. T., Purcell, M. I. & Obrovac, M. N. The Reversible Magnesiumation of Pb. *Electrochim. Acta* **165**, 162–165 (2015).
 21. Darwiche, A. *et al.* Better cycling performances of bulk Sb in Na-ion batteries compared to Li-ion systems: an unexpected electrochemical mechanism. *J. Am. Chem. Soc.* **134**, 20805–20811 (2012).
 22. Sougrati, M. T. *et al.* TiSnSb a new efficient negative electrode for Li-ion batteries: mechanism investigations by operando-XRD and Mossbauer techniques. *J. Mater. Chem.* **21**, 10069–10076 (2011).
 23. Nguyen, D. & Song, S. Magnesium stannide as a high-capacity anode for magnesium-ion batteries. *J. Power Sources* **368**, 11–17 (2017).
 24. Tan, Y.-H. *et al.* High Voltage Magnesium-ion Battery Enabled by Nanocluster Mg_3Bi_2 Alloy Anode in Noncorrosive Electrolyte. *ACS Nano* **12**, 5856–5865 (2018).
 25. Tutusaus, O., Mohtadi, R., Singh, N., Arthur, T. S. & Mizuno, F. Study of Electrochemical Phenomena Observed at the Mg Metal/Electrolyte Interface. *ACS Energy Lett.* **2**, 224–229 (2017).
 26. Salama, M. *et al.* On the Feasibility of Practical Mg-S Batteries: Practical Limitations Associated With Metallic Magnesium Anodes. *ACS Appl. Mater. Interfaces* **10**, 36910–36917 (2018).
 27. Murgia, F., Stievano, L., Monconduit, L. & Berthelot, R. Insight into the electrochemical behavior of micrometric Bi and Mg_3Bi_2 as high performance negative electrodes for Mg

- batteries. *J. Mater. Chem. A* **3**, 16478–16485 (2015).
28. Robba, A. *et al.* A Mechanistic Study of Magnesium Sulfur Batteries. *Chem. Mater.* **29**, 9555–9564 (2017).
29. Xu, Y. *et al.* In-situ X-ray absorption spectroscopic investigation of the capacity degradation mechanism in Mg/S batteries. *Nano Lett.* **19**, 2928–2934 (2019).