PRINCIPLES AND PROSPECTS OF HIGH-ENERGY MAGNESIUM-ION BATTERIES

Peter J. S. Foot, Materials Research Centre, SEC Faculty, Kingston University London
Kingston upon Thames KT1 2EE (UK)

Email: p.j.foot@kingston.ac.uk

ABSTRACT

In the last decade or so, lithium batteries have gained important niche positions in the market for electrochemical storage systems. Their energy capacities per unit weight (or volume) are remarkably better than those of traditional batteries – yet they appear to be approaching their practical limit, and alternative cell systems are under active investigation.

The potential advantages of replacing lithium by magnesium have long been recognised, but for years it was thought that materials limitations and technical problems would prevent them from being realised. However, a combination of commercial pressures and recent scientific breakthroughs has made it likely that magnesium batteries will soon be available for a wide range of applications; they are expected to be cheaper and safer than those based on lithium, with comparable performance.

This article briefly reviews the current situation and looks at the general background, principles and cell components, outlining some of the technical problems and discussing some promising materials for magnesium-ion batteries.

Keywords: magnesium battery; magnesium anode, Grignard salt; Chevrel phase

AUTHOR

Peter Foot studied Chemistry at the Universities of Southampton and Oxford (Physical Chemistry Laboratory). His doctoral thesis was on lithium battery materials, and he subsequently did postdoctoral research at the University of Sussex on electroactive polymers. He has authored over 100 publications on functional materials, and produced 8 patents. Since 1998 he has been Professor of Materials at Kingston University London.

PRINCIPLES AND PROSPECTS OF HIGH-ENERGY MAGNESIUM-ION BATTERIES

Peter J. S. Foot, Materials Research Centre, SEC Faculty, Kingston University London
Kingston upon Thames KT1 2EE (UK)

Email: p.j.foot@kingston.ac.uk

Introduction

There has been a need for electrical energy storage systems since the early days of electricity generation and the manufacture of automobiles. The commonest method has been batteries of electrochemical cells, a simple example of which comprises an electropositive metal (anode) like zinc and a more electronegative one (cathode) like copper, in an electrolyte medium such as a dilute acid.

For many years, despite the existence of numerous battery designs, the zinc-carbon (Leclanché) cell was the normal system for portable electrical devices, and the lead-acid "accumulator" battery for automobile electronics. The Leclanché cell had the advantages of cheapness, reliability and relatively low toxicity, while the lead-acid cell was simple, robust and capable of supplying the large instantaneous currents needed by the starter motors in petroleum-powered vehicles.

Low-power equipment such as torches and portable radios have been well served by one-shot (primary) zinc-carbon cells, and rechargeable (secondary) batteries such as nickel-cadmium or nickel-metal hydride (Ni-MH) were used for power tools.

The potential of lithium-based batteries as compact, high-energy storage systems has long been recognised: tiny lithium button-cells have been widely used in watches, hearing-aids, heart pacemakers etc., and large secondary lithium batteries were first tested in electric cars in the 1970s. The advent of practical electric vehicles and ultra-compact electronic devices such as lap-tops, smartphones and wearable digital technology drove the research that produced the present range of advanced lithium batteries to power them.

Why then, should we look any further for our future secondary battery needs? What would be the advantage of replacing lithium by another active metal such as magnesium? Well, despite their amazing capacity and performance, lithium batteries are delicate structures to manufacture; moreover lithium can cause fires if it comes into contact with water and even the latest "Li-ion" cells are susceptible to overheating or explosion hazards. Magnesium has no such risks, scarcely reacting even with boiling water. In batteries, it offers the prospect of comparable energy storage to lithium, with no significant toxicity or environmental impact, and the metal itself is cheap and widely available: nearly 17% of the earth's crust is magnesium, whereas lithium only occurs at the level of a few parts per million.

A Generic Magnesium Battery System

A typical magnesium cell (Fig. 1) would have the following active components:

- A metal anode (either the pure metal or another rich source of magnesium)

- An electrolyte/spacer capable of conducting magnesium cations (Mg^{2+}) easily.

- A cathode compound [Q] capable of reacting with magnesium (or with Mg^{2+} plus two electrons) and thereby releasing a lot of energy. For a rechargeable cell, this reaction needs to be highly reversible.
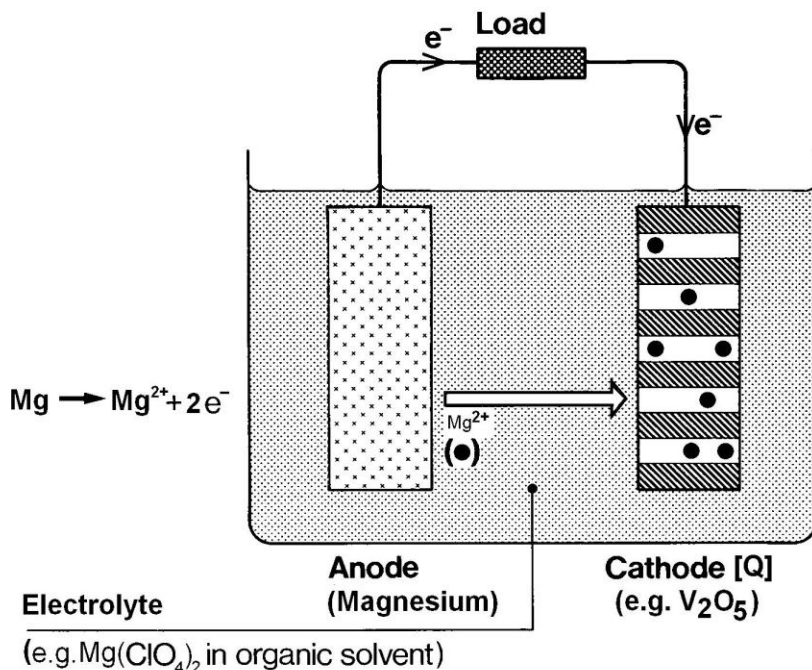
The cell reactions at the two electrodes could be represented thus:

ANODE: Mg $\rightarrow$ Mg^{2+} + 2e$^-$ CATHODE: Mg^{2+} + 2e$^-$ + [Q] $\rightarrow$ Mg[Q]

The electrolyte serves to carry the cations from the anode to the cathode, while the flow of electrons through an external circuit is the useful electric current supplied by the cell.

When such a magnesium cell is recharged, the flow of electrons is reversed: Mg is thereby removed from the cathode and may be "electroplated" back onto the anode. For such a system to be used in commercial storage batteries, all the processes must be reversible over many hundreds of cycles; this requires a high level of chemical and mechanical stability for all the above components, each of which will be discussed in the following sections.

Magnesium anodes

The term "anode" may seem to be a misnomer, since the reactive metal electrode (Li, Zn etc.) in a battery tends to be the negative one. Shouldn't it therefore be called a *cathode*? The reason for the widespread use of this terminology is that the anode is the electrode where oxidation occurs, and when an electrochemical cell supplies a current, it's the metal anode that is being oxidised to cations and releasing electrons.

In some batteries (e.g. the Leclanché cell above), the metal anode (Zn) is also the current collector - usually the outer casing of the cells - which can be very convenient in terms of cell manufacture. This design would of course be impossible for a lithium battery, because of the high reactivity of lithium to air and water.

In fact, lithium batteries seldom use pure lithium anodes anyway, since the metal is quite soft, and it is prone to form dendrites (crystalline whiskers) on its surface after several recharges. There are many cases of metallic dendrites causing short-circuits and even explosions in pure-lithium batteries, and the modern lithium-ion cell typically has an anode of graphite with the lithium stored in between the "chicken-mesh" sheets of carbon atoms in the well-known graphite structure. When the anode is fully charged with Li^+ ions, its limiting composition is LiC_6.

Unlike lithium, pure magnesium is harder, is not dangerously reactive and has little tendency to form dangerous metal dendrites during recharge. It's therefore possible to envisage magnesium cells in which the pure metal could be used as the active anode material, and possibly even as the current collector - hence saving on manufacturing costs and giving better energy storage per kg of battery weight[1].

Liang *et al* reported the preparation of nano-scale magnesium for battery use, the advantage being a very large area of contact between the Mg anode and the electrolyte solution, to ensure rapid transfer of Mg^{2+} ions between them and hence to maximise the current density that can be supplied[2].

For some applications or electrolytes, the active metal may need to be trapped in an alloy or an inert matrix in order to provide efficient charge-recharge cycling and long cell life over thousands of cycles. We have seen that this is necessary for lithium batteries, in which alloys such as LiAl have been used as anodes in the past.

The magnesium-tin alloy $Mg_{2-x}Sn$ is very electropositive and it can supply magnesium ions reversibly with a high theoretical capacity of 903 mA h g^{-1}. The rate of diffusion of Mg^{2+} from the metal alloy structure is fairly slow, so that it is necessary for the anode to have a very porous morphology in order to give acceptable current densities. Singh *et al*, at Toyota, used a commercial Sn nanopowder to fabricate Mg anodes with experimental capacities close to the theoretical value[3].

Unfortunately simple alloys may undergo very large volume changes over a charge-discharge cycle (214% for $Mg_{2-x}Sn$)[3], which can result in amorphization of the alloy and

poor cyclability. The Mg-Sn system may still prove to be an effective practical anode material if new, nanoporous forms can be developed. Nanostructuring has already been used to make the unlikely host matrix, metallic bismuth, into a successful magnesium anode. Despite its high atomic mass, bismuth has a surprisingly large specific capacity for magnesium (limiting composition Mg_3Bi_2; theoretical capacity 385 mA h g^{-1}). Whereas commercial microsphere Bi powder undergoes pulverization on cycling in a magnesium cell (Fig. 2), Shao *et al*[4] at the Pacific Northwest National Laboratory, Washington, demonstrated that bismuth nanotubes could be used in magnesium anodes with fast charge-discharge rates and a capacity of 303 mA h g^{-1}, even after 200 cycles.
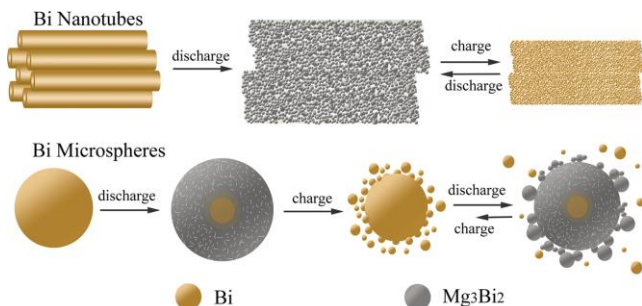

Fig. 2. Structural transformation of Mg_3Bi_2 during the discharge/charge process.
Reprinted with permission from Nano Letters 2014 14 (1), 255-260
DOI: 10.1021/nl403874y. Copyright 2014 American Chemical Society.

Very recently, Parent *et al*, also at the Pacific Northwest National Laboratory produced a Sb-Sn alloy that was electrochemically conditioned to form Sn-rich nanoparticles[5]; scanning transmission electron microscopy indicated that these (<40nm) particles would have excellent performance in Mg battery anodes, although electrochemical data have not yet been reported.

Electrolytes for Mg-Ion Cells

The electrolyte in many electrochemical cells may be a simple aqueous salt or acid solution, but it could take other forms such as a molten salt, an organic salt solution, a semi-solid gel or a thin membrane of polymer or ceramic. It needs to transport electrochemically-active ions (in this case Mg^{2+}) as quickly as possible, to ensure low internal resistance and to avoid loss of cell voltage when high currents are being supplied.

Although magnesium metal is safe in direct contact with water, Mg anodes cannot be recharged efficiently with a water-based electrolyte, and non-aqueous solvents such as organic ethers, esters or ionic liquids have been used in most research on Mg cells.

Early experiments used simple salts such as magnesium perchlorate $Mg(ClO_4)_2$ in a propylene carbonate solvent, analogous to those used in lithium batteries. They provided good current densities, but generally poor cell life and rechargeability, and for some time it looked as if magnesium secondary cells might never live up to their promise; the anodes often reacted with the salt or the solvent to produce insulating films on their surfaces[6].

Pioneering research by Gregory *et al* using organoaluminate or organoborate electrolytes like $Mg(BBu_4)_2$ in tetrahydrofuran (THF) gave better stability in contact with magnesium electrodes, but their overall cycling efficiency was inadequate for use in practical secondary batteries[7]. Aurbach and his colleagues achieved significant advances by developing Gregory's approach to produce compounds such as $Mg(AlCl_{4-x}R_x)_2$, which provided the first electrolytes in which magnesium showed good charge-discharge cycling properties[8].

Grignard reagents (organomagnesium halides) and related salts such as those in Fig. 3, dissolved in ether solvents like tetrahydrofuran (THF), were found to be electrolytes with good stability towards Mg electrodes[9].

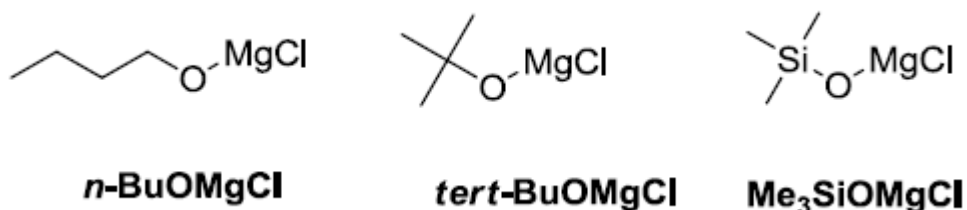**n-BuOMgCl**　　　　**tert-BuOMgCl**　　　　**Me₃SiOMgCl**

Fig. 3. Some simple Grignard-like electrolyte salts

Unlike conventional Grignard reagents, the above salt solutions carried no potential fire hazards and had comparatively high conductivities; Liao and his colleagues at Oak Ridge National Laboratory (ORNL), USA[9], reacted one of these compounds with $AlCl_3$ to produce an even more conductive, air-stable electrolyte salt comprising a THF-trichloromagnesium anion [Fig. 4(a)] and a chloro-bridged cluster cation [Fig. 4(b)].
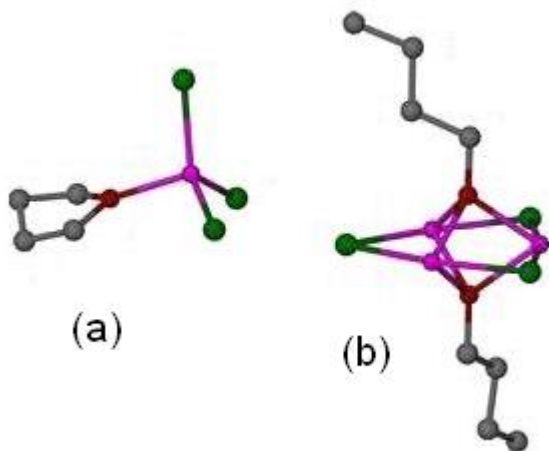

Fig. 4. Structure of a magnesium electrolyte salt developed at ORNL.
Key: Grey = C   Violet = Mg   Red = O   Green = Cl
(Reproduced from Ref. 9 with permission from the Royal Society of Chemistry.)

The coulombic (charge storage) efficiency of the best electrolytes actually increased after the first few conditioning cycles to reach steady values of about 98% (Fig. 5).
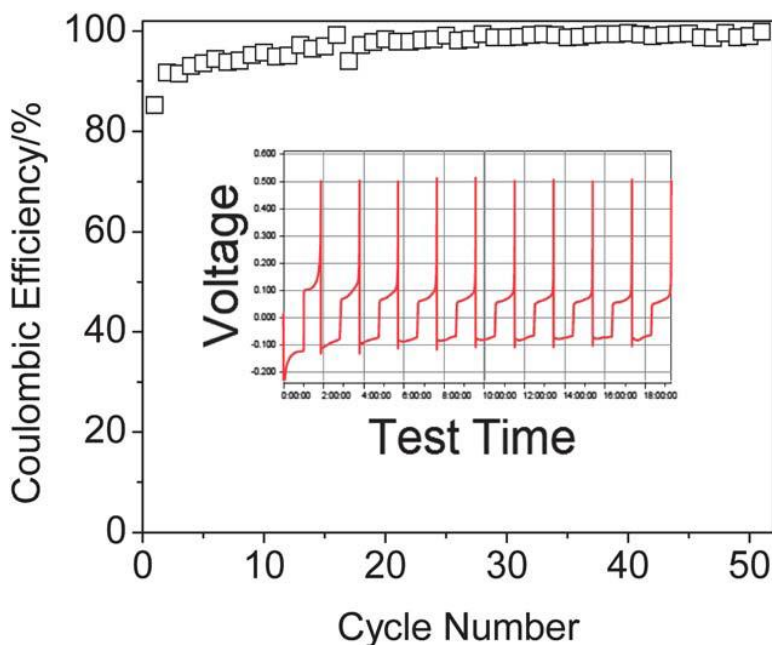
Fig. 5. Effects of cell cycling on the rechargeability of magnesium electrodes in a THF solution of the electrolyte shown in Fig. 4. (The inset shows the first 10 cycling profiles.) *(Reproduced from Ref. 9 with permission from the Royal Society of Chemistry.)*

NuLi *et al* demonstrated in 2005 that magnesium could be reversibly electro-deposited onto inert metal electrodes from a solution of magnesium triflate [$Mg(CF_3SO_3)_2$] in the ionic liquid BMIMBF$_4$ [10]. Other workers, notably Morita *et al* [11] have subsequently published a significant amount of work on ionic liquid solvents for Mg^{2+} ion electrolytes which also show good properties for use in magnesium cells.

Polymer or gel electrolytes based, for example, on Mg triflate or perchlorate have also shown promise[12,13]. They are typically less conductive than liquid systems, but this disadvantage is offset by using them in the form of thin membranes, which can serve as electrode separators and make for a compact cell design that is virtually 100% solid-state.

Cathode Compounds

A good cathode material for a magnesium cell is likely to operate on a similar principle to those in many lithium-ion cells, i.e. it should be a "cation sponge" that can reversibly accommodate Mg^{2+} ions by insertion or intercalation into its structure. Such materials are normally solid solutions, in which the proportion (x) of Mg can be smoothly varied over a wide range without wasting energy by generating completely new product phases.

An energetic redox reaction (high cell voltage) tends to favour a high energy density, and hence compounds of metals in a high oxidation state have been tested. Such a compound was cobalt (IV) oxide, in which the core metal can be reversibly reduced from oxidation state 4+ to 3+. For a commercial lithium battery, the cell reaction may be written as:-

$$xLi^+ + xe^- + CoO_2 \rightleftharpoons Li_xCoO_2 \text{ (with } 0 \le x \le 1)$$

7
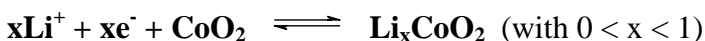
In the case of magnesium, a similar reversible cell reaction can theoretically occur:

$$xMg^{2+} + 2xe^- + CoO_2 \rightleftharpoons Mg_xCoO_2$$
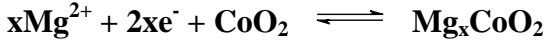
Here, the maximum value of x is 0.5, but the total amount of charge stored is the same. However CoO_2 is not as suitable for magnesium batteries as it is for Li-ion devices; pure CoO_2 has too much oxidising power for most Mg^{2+} electrolytes, and would rapidly destroy the organic solvents or salts that they contain. Many other possible oxide cathodes have been considered (some of which are shown in Table 1); a material with lower oxidising power (and hence cell voltage) tends to give a smaller energy density, but in some cases it may still provide acceptable performance and good cycling properties.

Table 1. Properties of some Mg^{2+} cathode-active compounds.

Cathode Material	Electronic Nature	Cell Voltage	Mg/host ratio (x)	Capacity		Ref.
				Ah/kg	Wh/kg	
MoO_3	ins.	2.28	0.50	143	326	7
WO_3	ins.	2.16	0.50	116	250	7
Co_3O_4	s/c	2.28	0.80	222	505	7
V_2O_5	s/c	2.66	0.66	194	516	7
V_2O_5 xerogel	s/c	~1.6		463	740	14
TiS_2	conductor	1.63	0.5	157	266	7
VS_2	s/c	1.71	0.34	154	263	7
Mo_6S_8	metal	1.1	1.0	90	99	7,15,16
MoS_2	s/c	1.5	0.066	22	33	7
Monolayer MoS_2/C microspheres	s/c	1.4	-	119	167	17
Expanded MoS_2	s/c	0.7	0.224	75	53	18
λ-MnO_2	ins.	2.5	-	156	390	19
$MgFeSiO_4$	ins.	~1.3	0.73	114	148	20
$MgCoSiO_4$	ins.	1.65	0.98	300	495	21
$(CF)_n$ Graphite fluoride	ins.	0.68	-	429	292	22
C_{60} (Buckminsterfullerene)	s/c	1.5	-	35	53	23
2,5-Dimercapto-1,3,4-thiadiazole	ins.	1.6	-	27	43	24
2,5-Dimethoxy-benzoquinone	ins.	0.90	-	250	225	25
Polyaniline	s/c	1.72	0.42	61	105	26, 27

As mentioned above, another important factor is the cell resistance; to minimise the voltage drop at the cathode when supplying (or accepting) a large current, we need to be able to insert (or remove) the Mg^{2+} ions as easily as possible. Therefore the crystal structure of the cathode should not be close-packed; it will typically contain pores,

channels or inter-layer spaces, in which the cations can move quite freely. Most of the oxides and sulfides in Table 1 have this property.

The oxides tend to provide the highest cell voltages, but their more-ionic bonding can lead to a drawback compared to the sulfides: movement of the doubly-charged Mg^{2+} cations within the oxide matrices may be much more hindered than Li^+ by electrostatic traps. At least for ambient-temperature cells, diffusion of Mg cations in comparatively covalent sulfides like TiS_2 is typically much faster than in oxides such as MoO_3, which makes it easier for them to sustain high currents. Although several of the crystalline oxides in Table 1 (e.g. MoO_3 and V_2O_5) have very impressive capacities[7], they are unusable as practical Mg battery cathodes because the mobility of Mg^{2+} ions within their structure is very low; the presence of water molecules in inter-layer sites can greatly enhance the mobilities, but as we have seen, water tends to deteriorate the lifetime of the anode. It seems preferable to give the oxides a more open and amorphous morphology, like that of the V_2O_5 xerogels studied by Inamoto *et al*, which showed much-improved current densities and storage capacities compared with those of the crystalline oxide[14]. The spinel-structured *lambda*-form of another metal oxide, MnO_2, has recently been shown to provide remarkably good initial cathode performance for magnesium, albeit in an aqueous electrolyte[19].

Table 1 also mentions the electronic nature of the selected cathode compounds. Clearly, a good cathode should also have appreciable electronic conductivity, to avoid extra limitations on the current flow to the cathode terminal. In practice, most of the listed compounds acquire sufficient conductivity from the transfer of electrons during the cell reaction to transmit the discharge current, but over-charging could be a problem for a compound such as MoO_3, which would become an insulator if all the Mg were removed.

Some "Chevrel phases" such as $Mg_xMo_6S_8$ have shown themselves to be very effective as magnesium cathode materials. They are typically molybdenum compounds containing octahedral Mo_6 clusters within chalcogenide (S_8, Se_8, etc.) cubes; the arrangement of the cubes in the crystal structure (Fig. 7) provides channels in which the magnesium guest cations can move relatively easily between cavities of types 1 and 2,[16] whereas cations in type 3 cavities are essentially immobile.

The performance of Mo_6S_8 in secondary Mg cells is excellent, with a highly reversible uptake of 1 Mg^{2+} per formula unit at room temperature (2 Mg^{2+} at 60°C), retained for over 3000 cycles[15,16]. The cell voltage is not particularly high, but at least it remains fairly constant over most of the discharge period; this is due to the coexistence of closely-compatible intercalated phases throughout both of the stages of the cell reaction (Fig. 8).
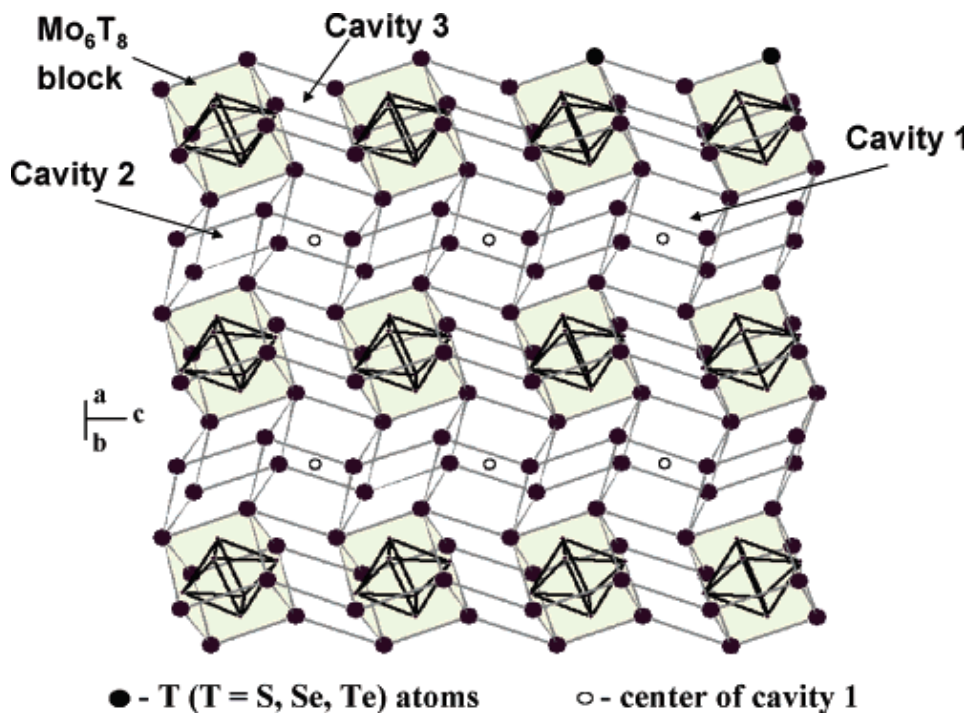
Fig. 7. Indicative structure of the Chevrel phases $Mg_xMo_6T_8$.

(a)

E / V (vs. Mg / Mg^{2+})

1.8
1.4
1.0
0.6
0.2

$Mg \leftrightarrow 2e^- + Mg^{2+}$

$Mo_6S_8 + 2e^- + Mg^{2+} \leftrightarrow Mg\,Mo_6S_8$

$Mg\,Mo_6S_8 + 2e^- + Mg^{2+} \leftrightarrow Mg_2\,Mo_6S_8$

2nd – 3000th cycles

1st cycle

0   20   40   60   80   100   120

Capacity / mAhg^{-1}

(b)

T = 60°C

E [V]

2
1.7
1.4
1.1
0.8
0.5
0.2

① ② ③ ④ ⑤

$Mg^{2+} + 2e^- + Mo_6S_8 \rightarrow MgMo_6S_8$

$Mg^{2+} + 2e^- + MgMo_6S_8 \rightarrow Mg_2Mo_6S_8$

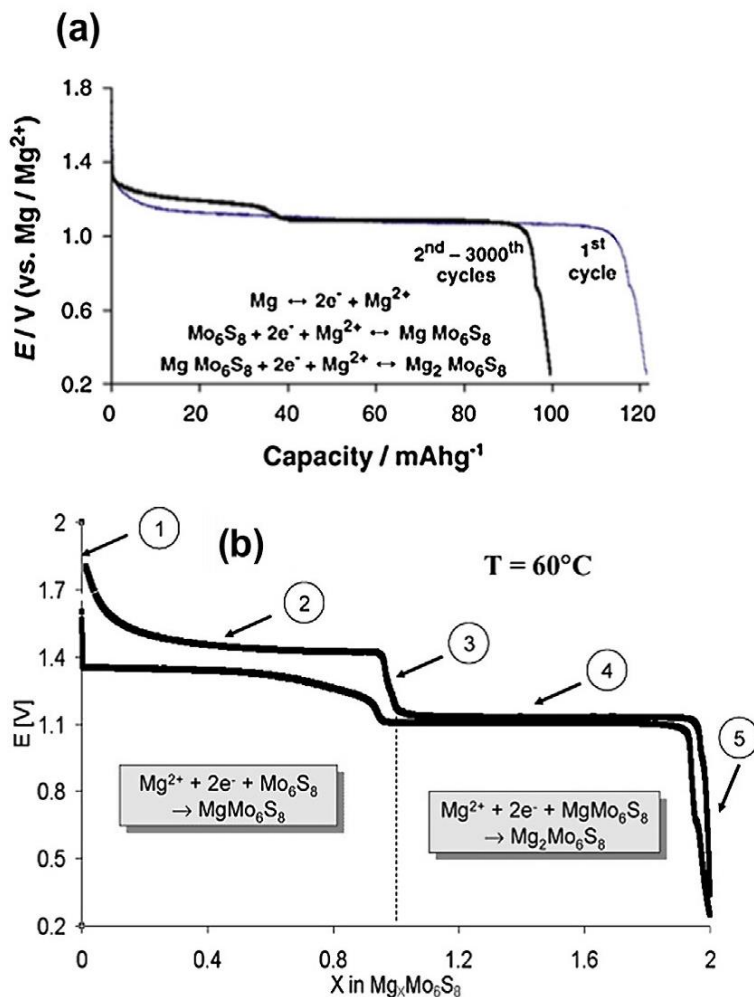0   0.4   0.8   1.2   1.6   2

X in Mg$_x$Mo$_6$S$_8$

Fig. 8. Electrochemical performance of Mg - Mo$_6$S$_8$ cells.

(a) Cell discharge curves at ambient temperature: note the slight loss of capacity after the first cycle and the relatively constant cell voltage throughout.
Reprinted from *Solid-State Ionics*, Vol 179, D. Aurbach, M. D. Levi and E. Levi, "A review on the solid-state ionics of electrochemical intercalation processes: How to interpret properly their electrochemical response", pp. 742–751, Copyright (2008); with permission from Elsevier.

(b) Charge-discharge cycle at 60°C, showing two successive stages of intercalation of magnesium. There are single phases at points 1, 3 and 5, and relatively flat regions in between (e.g. points 2 and 4) with coexisting commensurate phases.
Adapted with permission from *Chem. Mater.*, 2006, 18 (23), pp 5492–5503 DOI: 10.1021/cm061656f. Copyright (2006) American Chemical Society.

The layer-structured sulfide MoS$_2$ is cheap and plentiful, but as Table 1 shows, its capacity for magnesium ions is quite modest; moreover the mobility of Mg^{2+} in the crystalline material is very low. Research to produce a more electroactive form of MoS$_2$ has provided a route to microparticle assemblies of MoS$_2$ nanosheets (Fig. 9) with a five-times greater energy density[17] and much larger current density than the crystalline form of the sulfide.
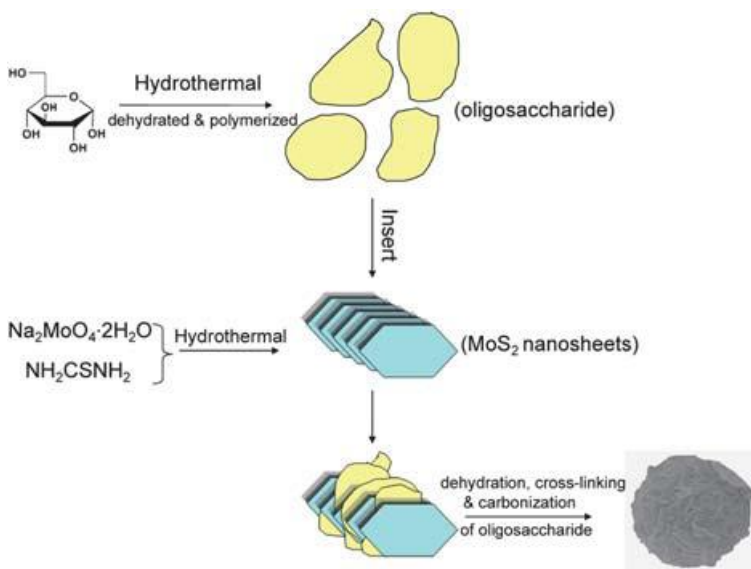
Fig. 9. Graphite-MoS_2 microspheres.
(Reproduced from Ref. 17 with permission from the Royal Society of Chemistry.)

A very recent approach to increase the mobility of Mg ions in MoS_2 has used a polyether to expand the interlayer space, resulting in an enhancement by two orders of magnitude[18].

Transition metal silicate host matrices based on metals such as iron[20] and cobalt[21] have also been the subject of considerable interest as cathode materials, and the energy capacity of $MgCoSiO_4$ is particularly promising.

Some metal-free cathode compounds have also been investigated, including fluorinated graphite[22], buckminsterfullerene[23], redox-active organic molecules[24-25] and conducting polymers[26]. Of these, the graphite fluoride shows the largest capacity, but it lacks reversibility; the other materials show good rechargeable cell performance and are still under active investigation.

Concluding Comments and Possible Future Developments

In the battery industry, old products are often slow to be displaced by new ones; the zinc-carbon Leclanché cell is still in widespread use after 100 years, as is the lead-acid battery in automobiles. Nevertheless, despite the excellent performance of lithium cells, recurring concerns have been expressed about problems with premature loss of capacity (e.g. for electric automobiles such as the Nissan Leaf electric car in hot climates[28]) and more importantly about their safety (e.g. fire on the Boeing 787 Dreamliner[29]). Lithium cells are also quite expensive and unsustainable, so their days are likely to be numbered.

Other proposed high-energy systems are currently under investigation, like the Zn-air cell and new designs for sodium-based batteries, and they certainly show some promise for the post-lithium era. In the past, there were some perceived issues that inhibited the development of magnesium-based batteries, such as lower capacity, operating voltage

and current density than lithium systems, but in spite of a few remaining technical challenges it seems very likely that rechargeable magnesium-ion devices will soon be in wide commercial use.

References

1. Aurbach D., Lu Z., Schechter A., Gofer Y., Gizbar H., Turgeman R., *et al*. (2000). Prototype systems for rechargeable magnesium batteries. *Nature,* **407,** 724–7.
2. Liang Y., Feng R., Yang S., Ma H., Liang J. and Chen J. (2011). Rechargeable Mg batteries with graphene-like MoS_2 cathode and ultrasmall Mg nanoparticle anode. *Adv. Mater.*, **23** 640–3.
3. Singh N., Arthur T.S., Ling C., Matsui M., Mizuno F. (2013). A high energy-density tin anode for rechargeable magnesium-ion batteries. *Chem. Commun.*, **49**, 149–51.
4. Shao Y., Gu M., Li X., Nie Z., Zuo P., Li G., *et al*. (2013). Highly reversible Mg insertion in nanostructured Bi for Mg ion batteries. *Nano. Lett.* **14**, 255−60.
5. Parent, L,R,, Cheng, Y.W., Sushko, P.V., Shao, Y.Y. *et al*. (2015). Realizing the Full Potential of Insertion Anodes for Mg-Ion Batteries through the Nanostructuring of Sn. *Nano. Lett.* **15**, 1177−1182.
6. Lu Z., Schechter A., Moshkovich M. and Aurbach D. (1999). On the electrochemical behavior of magnesium electrodes in polar aprotic electrolyte solutions. *J. Electroanal. Chem.*, **466**, 203–217.
7. Gregory T. D., Hoffman R. J. and Winterton R. C. (1990). Non-aqueous electrochemistry of magnesium. *J. Electrochem. Soc.*, **137**, 775−780.
8. Vestfried Y., Chusid O., Goffer Y., Aped P. and Aurbach D. (2007). Structural Analysis of Electrolyte Solutions Comprising Magnesium-Aluminate Chloro-Organic Complexes by Raman Spectroscopy. *Organometallics*, **26**, 3130–3137, and refs. therein.
9. Liao C., Sun X.-G., Dai S., Guo B., Jiang D.-E., Custelcean R., *et al*. (2014). Highly soluble alkoxide magnesium salts for rechargeable magnesium batteries. *J. Mater. Chem.* A, **2**, 581–4.
10. NuLi Y., Yang J. and Wu R. (2005). Reversible deposition and dissolution of magnesium from BMIMBF4 ionic liquid. *Electrochem. Commun.* **7,** 1105-10.
11. Kakibe T., Hishii J.-Y., Yoshimoto N., Egashira M. and Morita M. (2012). Binary ionic liquid electrolytes containing organo-magnesium complex for rechargeable magnesium batteries. *J. Power Sources,* **203,** 195–200; and references therein.
12. Aravindan V., Karthikaselvi G., Vickraman P. and Naganandhini S. P. (2009). Polyvinylidene Fluoride-Based Novel Polymer Electrolytes for Magnesium-Rechargeable Batteries with $Mg(CF_3SO_3)_2$. *J. Appl. Polym. Sci.* **112**, 3024–3029.
13. Jo, N.-J., Kim, M.-K., Kang, S.-W. *et al*. (2010). The influence of the cations of salts on the electrochemical stability of a solid polymer electrolyte based on segmented poly(ether urethane). *Physica Scripta*, **T139**, Art. No. 014035.
14. Inamoto M., Kurihara H. and Yajima T. (2012). Electrode performance of vanadium pentoxide xerogel prepared by microwave irradiation as an active cathode material for rechargeable magnesium batteries. *Electrochemistry*, **80**, 421–422.

15. Aurbach D., Levi M.D. and Levi E. (2008). A review on the solid-state ionics of electrochemical intercalation processes: how to interpret properly their electrochemical response. *Solid State Ionics* **179**, 742–51.

16. E. Levi, E. Lancry, A. Mitelman, D. Aurbach, G. Ceder, D. Morgan and O. Isnard (2006). Phase Diagram of Mg Insertion into Chevrel Phases, $Mg_xMo_6T_8$ (T = S, Se). 1. Crystal Structure of the Sulfides. *Chem. Mater.*, **18**, 5492-5503.

17. Liu Y., Jiao L., Wu Q., Zhao Y., Si Y., Wang Y. and Yuan H. (2013). Sandwich-structured graphene-like MoS_2/C microspheres for rechargeable Mg batteries. *J. Mater. Chem. A*, **1**, 5822-6.

18. Liang Y., Yoo H. D., Li Y., Shuai J., Calderon H. A., Hernandez F.C.R., Grabow L. C. and Yao Y. (2015). Interlayer-Expanded Molybdenum Disulfide Nanocomposites for Electrochemical Magnesium Storage. *Nano Lett.* **15**, 2194−2202.

19. Yuan C., Zhang Y., Pan Y., Liu X., Wang G. and Cao D. (2014). Investigation of the intercalation of polyvalent cations (Mg^{2+}, Zn^{2+}) into λ-MnO_2 for rechargeable aqueous battery. *Electrochimica Acta* **116** 404– 412.

20. Li Y., NuLi Y.N., Yang J., Yilinuer T. and Wang J.L. (2011). $MgFeSiO_4$ prepared via a molten salt method as a new cathode material for rechargeable magnesium batteries. *Chinese Sci. Bull.*, **56** 386−390.

21. Zheng Y., NuLi Y., Chen Q., Wang Y., Yang J. and Wang J. (2012). Magnesium cobalt silicate materials for reversible magnesium ion storage. *Electrochimica Acta* **66**, 75− 81.

22. J. Giraudet, Claves D., Guerin K., Dubois M., Houdayer A., Masin F. and Hamwi A. (2007). Magnesium batteries: Towards a first use of graphite fluorides. *Journal of Power Sources* **173** 592–598.

23. Zhang R.G., Mizuno F. and Ling, C. (2015). Fullerenes: non-transition metal clusters as rechargeable magnesium battery cathodes. *Chem. Commun.* **51**, 1108-1111.

24. NuLi Y., Guo Z., Liu H. and Yang J. (2007). A new class of cathode materials for rechargeable magnesium batteries - Organosulfur compounds based on sulfur–sulfur bonds. *Electrochem. Commun.* **9**, 1913–1917.

25. Sano H., Senoh H., Yao M., Sakaebe H. and Kiyobayashi T. (2012). Mg^{2+} Storage in Organic Positive-electrode Active Material Based on 2,5-Dimethoxy-1,4-benzoquinone. *Chem. Lett.* **41**, 1594–1596.

26. Foot, P.J.S. (2015). Electroactive polymer cathodes for magnesium-ion battery systems. UK Patent Application.

27. Foot, P.J.S. (2015). Novel polyaniline-based magnesium battery materials. *Polymers and Polymer Composites*; accepted for publication.

28. Battery_Capacity_Loss - Electric vehicle wiki. http://www.electricvehiclewiki.com/Battery_Capacity_Loss#mw-head

29. http://batteryuniversity.com/learn/article/possible_solutions_for_the_battery_problem_on_the_boeing_787