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Hydrides compounds for electrochemical applications

Short review for Electrochemical Materials and Engineering 2022 Section: New concepts in Electrochemical Energy Conversion and Storage of the journal *Current Opinion in Electrochemistry*

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Keywords: hydrides; negative electrode; solid electrolyte; Ni-MH or A-ion batteries (A = Li, Na, Mg).

Abstract

Hydrides are used since a long time for solid state hydrogen storage and electrochemical nickel-metal hydride batteries. Beside these applications, growing attention has been devoted to their development as anode materials as well as solid electrolytes for Li-ion and other ion batteries. Herein, we review and summarize the recent advances of hydrides as negative electrode for Ni-MH and A-ion batteries (A=Li, Na), and as electrolyte for all solid-state batteries (ASSB). Metallic hydrides such as intergrowth compounds are highlighted as the best compromise up to now for Ni-MH. Regarding anodes of Li-ion batteries, MgH₂, especially its combination with TiH₂ provides very promising results. Complex hydrides such as Li-borohydride and related closo-borates and monovalent carborate boron clusters appear to be very attractive as solid electrolyte for Li-based ASSB, whereas closo-hydroborate sodium salts and closo-carborates are investigated for Na- and Mg-ASSB. Finally, further research directions are foreseen for hydrides in electrochemical applications.

Introduction

Hydrides are inorganic compounds in which hydrogen is combined with other elements, mainly metallic or semi-metallic. Based on their chemical bonding, hydrides can be classified as metallic, ionic or covalent. In addition, some hydrides are formed by combining ionic and covalent bonds leading to complex ionic-covalent hydrides (such as borohydrides, alanates and amides) and non-classically bonded compounds such as boranes or carboranes. Metallic hydrides crystallize in a large diversity of crystal structures [1]. Solid state hydrogen storage and electrochemical energy storage are key applications for these hydrides. The present review focus on recent trends of hydrides used as negative electrodes for Nickel-Metal Hydride (Ni-MH) and A-ion batteries (A = Li and Na) as well as electrolytes for all solid-state batteries (ASSB) involving different cations (Li, Na and Mg).

1. Hydrides as negative electrodes

a. Ni-MH batteries

Ni-MH batteries consists of a M/MH anode, a NiOOH/Ni(OH)₂ cathode and a KOH alkaline electrolyte. These batteries, commercialized since the 90's, exhibit high capacity and power, safety, and excellent tolerability toward overcharge/discharge processes. The capacity of the positive electrode is limited by its constrained chemistry but there is still room for improvement regarding the negative electrode. Hydrogen storage alloys (HSA) must have high reversible H storage capacity, high-rate capability and good corrosion resistance in alkaline solution. They are based on the association of A and B-type metals

having high and low hydrogen affinity, respectively. According to their stoichiometry, HSA may be classified into AB_x ($2 \leq x \leq 5$), TiV- and Mg-based alloys.

AB_5 alloys based on rare earths (*RE*) and Ni are the first HSA generation developed for Ni-MH batteries. Their electrochemical properties are fully optimized, reaching capacities of 320-350 mAhg⁻¹ for state-of-the-art commercial formulations such as La_{0.62}Ce_{0.27}Pr_{0.03}Nd_{0.08}Ni_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3} [2]. Current researches focus on minimizing the content of expensive Co [3] and improving their electrochemical performance through annealing treatment, additives or non-stoichiometry [4], sometimes supported by theoretical calculation [5].

AB_2 alloys receive high interest as they have higher electrochemical capacities than other AB_x ones. Unfortunately, they suffer from structural amorphization and corrosion during cycling that hinders their use in commercial batteries. However, by stacking AB_2 and AB_5 units in the so-called intergrowth AB_x alloys, the amorphization issue can be mitigated leading to the second generation of commercial Ni-MH batteries. Among the different intergrowth alloys, AB_3 [6], A_2B_7 and A_5B_{19} [7–9] stoichiometries are of particular interest. The richness of the chemistry of these AB_x stacking structures allows for intensive research aiming at improving electrochemical capacities [10,11]¹. Today, AB_x alloys are the most advanced materials for commercial Ni-MH batteries, even if their energy density remains constrained by the weight of *RE*, critical raw materials which content should be minimized. For all AB_x alloys, studies on surface treatments have been explored, either with polyaniline to enhance reaction kinetics by formation of a Ni-overlayer [12] or by hot-alkali treatment to increase low temperature performances of the batteries [13,14]. However, decrepitation phenomena during electrochemical cycling leads to the formation of non-treated surfaces limiting the benefits of such approach.

To overcome the use of *RE*, TiV- and Mg-based alloys are also studied. They are formed by lighter metals that theoretically allow higher capacity (> 500 mAhg⁻¹) though lower reaction kinetics and cycle-life. Aiming at mitigating these issues, coating Ti_{1.4}V_{0.6}Ni with TiN by ball-milling slightly decreases the electrochemical capacity from 270 to 250 mAhg⁻¹, enhances the high-rate discharge capability, slows down the alloy corrosion and increases the cycling stability [15]. Combination of first principle calculations and electrochemical measurement evidences that adding Cr to Ti_{0.5}V_{1.4-x}Ni_{0.1}Cr_x ($0 \leq x \leq 0.3$) increases corrosion resistance as well, even if the discharge capacity is much lower than the theoretical one due to sluggish hydrogen sorption kinetics in these *bcc* alloys [16]. More recent works focus on Mg-Ni-based alloys. Mg₄₆Ti₄Ni₄₅Al₃CO₂ + 50 wt.% Ni with nanocrystalline and amorphous structures show maximum initial capacity of 520 mAhg⁻¹, which falls to 370 mAhg⁻¹ after 12 cycles so with 72% retention capacity [17]. Interestingly, non-alloyed but TiF₃ catalyzed nanosized Mg has been tested with different electrolytes, with encapsulation in a nickel foil in aqueous alkaline electrolyte. A capacity of 146 mAhg⁻¹ is measured in KOH at room temperature (RT), and 399 mAhg⁻¹ is reached in high temperature ionic liquid [18]².

b. A-ion batteries (A = Li, Na)

Nowadays, commercial Li-ion batteries (LiBs) are mainly using graphite as anode material to reversibly store lithium by intercalation of the alkaline ion. Despite reasonable properties in terms of lifetime, kinetics, cost and safety, graphite brings rather low gravimetric and volumetric capacities, a limitation

¹ (*) Article of special interest. This article reports a series of two-phase intergrowth HSAs with a (La,Mg)₂Ni₇ matrix phase and a novel (La,Mg)₇Ni₂₃ secondary phase. These alloys exhibit the highest discharge capacities reported for stacking alloys with 402–413 mAhg⁻¹.

² (*) Article of special interest. This article reports the use of non-alloyed Mg as negative electrode for Ni-MH batteries. The composite MgH₂-TiF₃-Ni has been produced using ball-milling then dehydrogenated before use. Four electrolytes were tested, classical KOH at RT, Triethylsulfonium bis(-trifluoromethylsulfonyl)imide at RT, molten NaOH/KOH at 200°C and polyvinyl alcohol - NaOH/KOH anhydrous alkaline polymer membrane. The best results are obtained at 200 °C with a discharge capacity of 399 mAhg⁻¹

to be overpassed to answer the increasing energy demand for on-board electric energy storage. To overcome this drawback, research is conducted worldwide to find alternatives to graphite. Beside various approaches, conversion reactions are seen as a promising route for developing effective and capacitive anode materials. This type of reaction can take place for various materials including hydrides as shown by Oumellal *et al.* [19]. The reaction consists in a metal hydride conversion into lithium hydride and metal ($MH_x + xLi \rightleftharpoons xLiH + M$) and it takes place as far as $\Delta G_f(MH_x)/x > \Delta G_f(LiH)$, a favorable case for many hydrides. Theoretical capacities (Figure 1) can reach thousands of mAhg^{-1} [20] and the equilibrium potentials of hydrides range between 0.1 and 1 V (vs Li^+/Li^0), a well-adapted window for negative electrodes. Several review papers have been published recently on that topic demonstrating the promising properties of these anode materials [21,22].

Recent works focused mainly on magnesium hydride, a suitable compound with low weight, low voltage, and high hydrogen content. Accordingly, MgH_2 can deliver 2036 mAhg^{-1} and 2880 mAhcm^{-3} at an equilibrium potential of $E_{\text{eq}}=0.55 \text{ V}$ vs. Li^+/Li [23]. Despite these good thermodynamic properties, practical use of MgH_2 encounters some restrictions mainly related to its low electronic conductivity, slow reaction kinetics and the large volume change involved by the conversion reaction (85%) leading to low reversibility at room temperature.

Better results are obtained by increasing the temperature to 120°C , allowing the use of the superionic solid electrolyte LiBH_4 [24,25] exhibiting high ionic conductivity ($> 1 \text{ mScm}^{-1}$) at such temperature. Beside the kinetic improvement brought by the heating process, it was also established the formation of better interfaces at this temperature between LiBH_4 and MgH_2 enhancing the H-transport mechanism into the composite electrode [26].

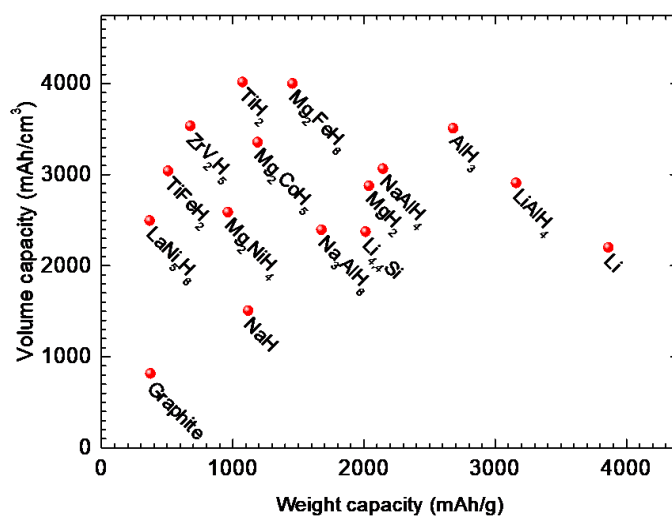


Figure 1: Theoretical specific capacities (per mass and volume) for some binary and ternary hydrides. Reprinted by permission from Springer Nature, Applied Physics A: Materials Science & Processing, Sabrina Sartori *et al.*, [22] COPYRIGHT 2016.

Alongside magnesium hydride, other materials involving transition metals have been studied. The combination of MgH_2 with TiH_2 has been mainly considered. Though not miscible, these two hydrides can form nanocomposites able to take profit of synergetic effects between them leading to enhanced electrochemical properties [27]. This was attributed to a compositional trade-off between the two

constituents as MgH_2 brings high specific capacity whereas TiH_2 provides improved cycling stability [28,29]³.

Getting rid of magnesium, the VH_2 hydride was also recently considered [30] as anode. This compound is not stable at ambient conditions so that the experiment was made starting with vanadium mixed with lithium hydride (charge state) instead of the dihydride. LiBH_4 was used as solid electrolyte at 125°C. In agreement with the V-H phase diagram, a conversion reaction was observed in at least two steps, forming VH_y ($y = 0.8$ and 2) and Li. Unsuitedly, the dihydride formed at the end of the reaction was not stable at such temperature and desorbed hydrogen during the charge, thus limiting the capacity at low values (200 to 400 mAhg^{-1}) for a few cycles.

Beyond lithium, the conversion reaction of metallic hydrides with other alkaline or alkali-earths cannot be ruled out. Indeed, the case of sodium has been already foreseen with MgH_2 [31] though the full mechanism of the reaction taking place at room temperature remains to be better understood. More recently, the properties of the complex lithium-aluminum amide $\text{LiAl}(\text{NH}_2)_4$ was theoretically reported as a possible Na anode material [32] opening the way to new routes for such conversion reactions. To the best of our knowledge, hydrides have not been considered so far as anodes of Mg-ion batteries. Undoubtedly, the possible conversion reaction between hydrides and Mg would be worth to explore.

2. Hydrides as solid electrolytes

a. All solid-state Li-ion batteries

Solid electrolytes should provide high ionic conductivity, chemical stability against anode, compatibility with high voltage cathode, deformability, low environmental impact, and low cost for the development of next ASSBs generation. Among the numerous families of materials proposed as solid electrolyte for LiBs, complex hydrides, generally denoted as $M_x(M'_y\text{H}_z)$ where M is a metal cation ionically bonded to the complex anion $M'_y\text{H}_z$, have received particular attention as a new class of solid electrolytes owing to their high deformability and high chemical/electrochemical stability against Li.

Li-borohydride LiBH_4 was firstly reported with high Li^+ ionic conductivity above 1 mScm^{-1} at 120 °C and wide electrochemical window [33]. This fast Li^+ conduction is observed for the high temperature phase (hexagonal structure), where the dynamics of complex anion reorientation “paddle wheel” rotation favors the Li^+ diffusion. The ionic conduction mechanism in these borohydrides show that the ionic conduction depends on the cation vacancy and the “paddle-wheel” rotation of the complex anion. Recently, researches focus on complex hydrides with large cage-like $B_{10}H_{10}^{2-}$ or $B_{12}H_{12}^{2-}$ anions, namely closo-borates, which are intermediate decomposition products of $M(\text{BH}_4)_w$ compounds and therefore are thermally more stable than the corresponding $M(\text{BH}_4)_w$ compounds. An *in-situ* formed $\text{LiH}[\text{Li}_2\text{B}_{12}\text{H}_{11+1/n}]_N\text{-LiBH}_4$ composite by controlled decomposition of LiBH_4 shows high Li-ion conductivity of 0.27 mScm^{-1} at 35°C [34]⁴. The interface layer between $[\text{Li}_2\text{B}_{12}\text{H}_{11+1/n}]_N$ and LiBH_4 is believed to be responsible for the high ionic conductivity. By replacing one boron by one carbon atom in closo-borates, monovalent carborate boron clusters such as $\text{CB}_9\text{H}_{10}^-$ and $\text{CB}_{11}\text{H}_{12}^-$ can be formed. $\text{LiCB}_{11}\text{H}_{12}$

³ (***) Article of outstanding interest. This article [29] reviews the most advanced results obtained in the field of novel complex hydrides for electrochemical storage. The results were obtained by a large UE consortium of high-level research scientists in the frame of the People Program Marie Skłodowska-Curie Actions (MSCA) of the European Union’s Seventh Framework Program FP7/2007–2013/under REA grant agreement n° 607040 (MSCA ITN ECOSTORE).

⁴ (*) Article of special interest. This article reported a novel “synthesis method” by controlled dehydrogenation of LiBH_4 to get high ionic conduction phases $[\text{Li}_2\text{B}_{12}\text{H}_{11+1/n}]_N$. The closo-borates and carborate are reported with high Li^+ conductivity, their syntheses are very challenging thus very expensive. A new synthesis method open the door even larger for more compounds. The obtained material shows a conductivity of 0.27 mScm^{-1} at 35 °C.

and $\text{NaCB}_{11}\text{H}_{12}$ transform to a disordered phase above 127 and 107 °C respectively with super ionic conductivity of 100 mScm^{-1} [35]. The carbon atom plays an important role, breaks the symmetry of the anion cluster, and produces a dipole creating additional symmetry incompatibilities. The modified interaction between the alkali cation and the monovalent anion as well as the anion reorientation dynamics account for the higher ionic conductivity of $\text{CB}_{11}\text{H}_{12}^-$ salts compared with $\text{B}_{12}\text{H}_{12}^{2-}$ ones. Recent results show that $(1-x)\text{Li}(\text{CB}_9\text{H}_{10})-x\text{Li}(\text{CB}_{11}\text{H}_{12})$ has high ionic conductivity (6.7 mScm^{-1} at 25 °C) allowing the implementation of a high energy density Li-S battery [36,37]. The partial substitution of $\text{CB}_9\text{H}_{10}^-$ by $\text{CB}_{11}\text{H}_{12}^-$ stabilizes the disordered high temperature phase at RT leading to superionic conductivity. However, the synthesis of $\text{LiCB}_9\text{H}_{10}$ is challenging and expensive. A very recent work proposes to replace $\text{LiCB}_9\text{H}_{10}$ by nido-hydroborate $\text{LiB}_{11}\text{H}_{14}$. Ionic conductivities of 0.1 and 1 mScm^{-1} at RT have been reported for $\text{Li}_2(\text{B}_{11}\text{H}_{14})(\text{CB}_{11}\text{H}_{12})$ and $\text{Li}_3(\text{B}_{11}\text{H}_{14})(\text{CB}_{11}\text{H}_{12})_2$, respectively [38], though $\text{LiB}_{11}\text{H}_{14}$ is not chemically stable against Li. Further work is still needed to improve the stability and conductivity.

In the line of playing with the structural order, studies on lithium imide Li_2NH have demonstrated an increase of ionic conductivity from 0.1 to 0.5 mScm^{-1} at RT by ordering of Li^+ cation and NH^- anion in the structure, but no jump of ionic conductivity has been observed at the phase transition (from orthorhombic α phase to cubic β phase) temperature [39].

The ionic conductivity of LiBH_4 can also be enhanced by adding ammonia groups to form lithium borohydrides ammoniates $\text{Li}(\text{NH}_3)_n\text{BH}_4$ ($0 < n \leq 2$). In these compounds, the ionic conductivity is largely enhanced relating to the cell expansion caused by ammonia absorption. An ionic conductivity of 2.2 mScm^{-1} was obtained for $\text{Li}(\text{NH}_3)\text{BH}_4$ at 40°C [40]. Again in order to increase the cell volume, the addition of ammonia borane (AB) to LiBH_4 was performed by ball milling. Two synthesized ammonia borane complexes, $(\text{LiBH}_4)\text{AB}$ and $(\text{LiBH}_4)_2\text{AB}$ exhibit fast Li-ion conduction, being the highest 0.4 mScm^{-1} at 25°C for $(\text{LiBH}_4)\text{AB}$ [41].

The mechanical softness of LiBH_4 is a major advantage of this compound for being used as solid electrolyte. This was recently highlighted by combining soft LiBH_4 with rigid Garnet-type oxide $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ (LLZTO). LLZTO requires high sintering temperature for shaping and suffers from high interface resistance [42]. The composite LiBH_4 -LLZTO was obtained by ball milling and shaped by cold pressing. It provided high Li-ion conduction 0.08 mScm^{-1} at 30 °C using simple mechanical shaping.

Another approach to increase the ionic conductivity consists of mixing LiBH_4 with oxides at the nanoscale. This approach is motivated from the observed conductivity enhancement of nano-confined LiBH_4 in mesoporous silica scaffold (MCM-41) which was attributed to the formation of high Li-mobility layer at $\text{LiBH}_4/\text{SiO}_2$ interfaces [43]. Later, nano-composites elaborated by ball milling of LiBH_4 and different oxides such as SiO_2 , CaO , MgO , Al_2O_3 , TiO_2 and ZrO_2 show ionic conductivity three orders of magnitude higher than that of LiBH_4 at 40 °C. The highest conductivities, 0.26 and 0.18 mScm^{-1} at 40°C, have been obtained for the nanocomposites with ZrO_2 and MgO [44]. The composite LiBH_4 - MgO has been used as solid electrolyte in a TiS_2/Li ASSB working at RT. Though conductivity is high enough for electrochemical cycling, the battery failed after 5 cycles due to electrode/electrolyte interface instability. By cycling at 60 °C, the battery could work for 30 cycles though a resistive electrode/electrolyte interface is formed at the first cycle [45].

To further increase the ionic conductivity, the combination of the two mentioned approaches, anion substitution and interface engineering has been studied. The LiBH_4 - $\text{LiI}/\text{Al}_2\text{O}_3$ and LiBH_4 - LiNH_2 nanoconfined in MCM-41 show that the increase of the conductivity is due to the combined effect of the interface and the stabilization of high temperature phase by anion substitution [46,47]⁵.

⁵ (*) Article of special interest. Further increase of ionic conductivity has been reached by combining two approaches: the complex anion substitution to stabilizing high temperature structure and interface engineering by nano-confinement or ball-milling with oxides.

b. All solid-state Na-ion and Mg-ion batteries

Research on alternative chemistries of Li-ion batteries is driven by its limitations in energy density and shortcomings in natural abundance and safety compared to alternative monovalent (Na^+) and divalent (Mg^{2+}) chemistries [48]. Many current studies focus on ASSBs to both get rid of flammable organic-based solvents and increase the energy density by enabling the use of metal anodes [49]. In this context, novel hydride solid electrolytes with outstanding properties in terms of ionic conductivity, chemical and electrochemical stability as well as processability, have been recently discovered [50,51].

Closo-hydroborate sodium salts, consisting of large cage-like $[\text{B}_n\text{H}_n]^{2-}$ anions and Na^+ cations, are preferred compounds as solid electrolytes for Na batteries [50]. Their ionic conductivity strongly depends on a thermally driven order-disorder structural phase transition eventually leading to superionic conductivity, above 100 mS cm^{-1} , for the high temperature phase ($T_{\text{trans}} \sim 110^\circ\text{C}$) [52]. It results from the reorientational dynamics of the anions and their ability to create a flat energy landscape for the cation diffusion [53]. Intensive efforts have been devoted to suppressing or reducing the temperature of the phase transition below room temperature through nano-sizing and defects [54], partial substitution of boron by carbon to form closo-carborates such as $\text{NaCB}_9\text{H}_{10}$ [52], and anion mixing such as $\text{Na}_4(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})$ [55]. By combining the two latter approaches, ionic conductivity above 1 mS cm^{-1} at room temperature and oxidative electrochemical stability up to 4.5 V vs. Na^+/Na was obtained for $\text{Na}_4(\text{CB}_{11}\text{H}_{12})(\text{B}_{12}\text{H}_{12})$ [55]⁶. This has enabled the implementation of a 4 V – ASSB battery with formulation $\text{Na}_3(\text{VOPO}_4)_2\text{F}|\text{Na}_4(\text{CB}_{11}\text{H}_{12})_2(\text{B}_{12}\text{H}_{12})|\text{Na}$ [56]⁷. As displayed in Figure 2, the galvanostatic curves of this battery show an impressive cycle-life with 76% capacity retention for 800 cycles. The remarkable cycling stability takes benefit from the favorable mechanical properties and solution processability of closo-hydroborates.

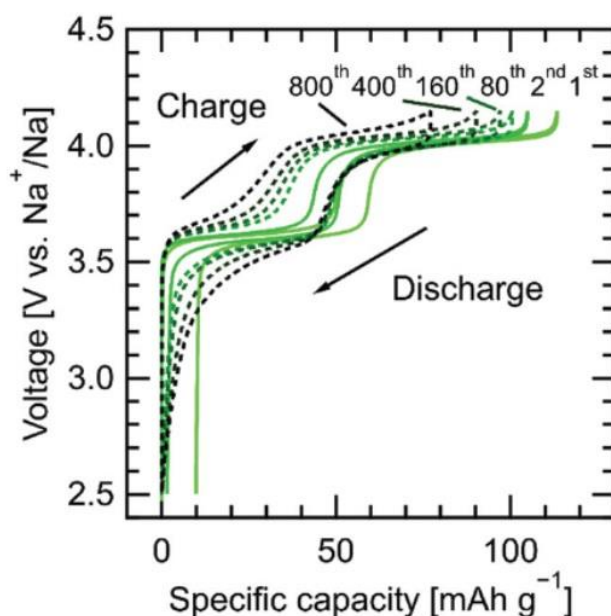


Figure 2: Galvanostatic charge–discharge curves at room temperature of $\text{Na}_3(\text{VOPO}_4)_2\text{F}|\text{Na}_4(\text{CB}_{11}\text{H}_{12})_2(\text{B}_{12}\text{H}_{12})|\text{Na}$ cell cycled between 2.50 and 4.15 V vs. Na^+/Na . The kinetic regime is C/5 for the first two cycles (dashed) and then at C/10 (solid) over 800 cycles. Reproduced from [56] with permission from the Royal Society of Chemistry.

⁶ (*) Article of special interest. Development of superionic hydride-based Na-ion electrolyte at RT based on an original double approach of partial boron by carbon substitution and anion mixing starting from Na closo-hydroborates.

⁷ (**) Article of outstanding interest. First implementation of a 4 V – ASSB battery working at RT using a hydride-based Na-ion electrolyte with good kinetic rate, C/10, and long cycle-life (800 cycles).

As concerns divalent batteries, research on Mg-conducting solid-state hydride electrolytes focuses on enhancing the ionic conductivity and improving the thermal and electrochemical stability of compounds derived from magnesium borohydride $\text{Mg}(\text{BH}_4)_2$. Pioneering works on Mg borohydride–amide $\text{Mg}(\text{BH}_4)(\text{NH}_2)$ showed significant Mg conductivities of $10^{-3} \text{ mScm}^{-1}$ at 150°C [57] and oxidative stability above 3 V vs. Mg/Mg^{2+} . Similar conductivity but at lower temperature, 100°C , have been later obtained in amorphous/crystalline composites of Mg borohydride–amide, showing the interest of defect structures for Mg-mobility [58], as well as for the crystalline compound $\text{Mg}_3(\text{BH}_4)_4(\text{NH}_2)_2$ [59]. A complementary research direction is the association of $\text{Mg}(\text{BH}_4)_2$ to neutral molecules which undergo dynamic exchange with Mg ions and increase the structural flexibility [60]. First studies concern the formation of coordination complexes of $\text{Mg}(\text{BH}_4)_2$ with a bidentate ethylenediamine “en”-ligand $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ with $6 \cdot 10^{-2} \text{ mScm}^{-1}$ at 70°C [61], though at the expense of a narrow potential window of 1.2 V. While keeping the same stability window, the ionic conductivity increases above $10^{-2} \text{ mScm}^{-1}$ at 30°C by replacing the “en”-ligand by ammonia borane NH_3BH_3 [62]. Both thermal stability, 47°C , and oxidation stability, 1.2 V vs. Mg/Mg^{2+} , are however low for this compound. The former issue was recently tackled suppressing the melting of ammine magnesium borohydride by combination with MgO nanoparticles [63]⁸. Thus, ball-milled $\text{Mg}(\text{BH}_4)_2 \cdot 1.6\text{NH}_3 @ \text{MgO}$ nanocomposite turns to be thermally stable up to 90°C with ionic conductivity of 1.1 mScm^{-1} at 70°C . Though this nanocomposite undergoes electrochemical oxidation above 1.2 V vs. Mg/Mg^{2+} , it forms a Mg-conducting stable interface over Mg. Compatibility with a high-voltage positive electrode remains however to be demonstrated for full-battery implementation.

3. Conclusions and outlook

Hydrides continue to be developed as negative electrodes for Ni-MH batteries. The new research directions do not only concern the composition of HSA alloys, as illustrated here, but also modifications in the battery concept itself. As an example, harmless electrolyte to limit metal corrosion effects detrimental for cycle life are foreseen. One interesting solution has been proposed by Meng *et al.* [64] who replaced concentrated aqueous potash by aprotic ionic liquids mixed with acetic acid and obtained significant capacities using a classical $\text{Ni}(\text{OH})_2/\text{AB}_5$ cathode/anode coupling.

Cycle life of Ni-MH batteries can also be extended by proper gas management. Longevity is closely related to corrosion, which consumes water and thus generates internal gaseous hydrogen. Shen *et al.* [65] showed that controlled addition of dioxygen can be used to rebalance the electrodes and replenish the electrolyte by reaction with H_2 to reform water. Proper optimization of the gas addition, combined with a cell design that includes an excess amount of MH hydride, compensates for corrosion, reduces the cell drying and thus significantly increases the life of the battery. Finally, Uesato *et al.* [66] developed a sealed Ni-MH/Ni- H_2 hybrid cell that operates under dihydrogen pressure up to 3 MPa. Charging the battery allows in-cell hydrogenation of the anode by both electrochemical (water reduction) and solid-gas reactions (H_2 sorption). Such accumulator allows to increase by 50% the specific energy of the Ni-MH battery.

Although still in its early stages, the concept of conversion reactions for the development of efficient Li-ion battery anodes could be demonstrated for complete battery systems. Several prototypes have been assembled with cathodes and tested, leading to significant reversible capacities compared to graphite [21,67,68]. Research works are however still needed to improve the reversibility of the reaction at room temperature and to assess significant lifetime for the battery.

The degree of maturity of hydrides as solid electrolytes depends on the different battery chemistries. Monovalent Li and Na already reach high technological levels. For Li and Na ASSBs, main hurdle

⁸ (*) Article of special interest. Hydride-based Mg-ion electrolyte with superionic conductivity at moderate temperature, 70°C and forming a Mg-conducting stable surface over Mg anode.

remains the high cost of closo-borate electrolytes, related to the handling of toxic gases such as diborane and decaborane, but promising synthetic routes starting from cheaper $\text{Li}(\text{Na})\text{BH}_4$ have been established [34,69,70]. In the case of Li, there are two approaches for conductivity enhancement: the complex anion substitution to stabilizing high temperature structure and interface engineering by nano-confinement or ball-milling with oxides. Works have shown the combination of two can further increase ionic conductivity[46,47]. And same concept is applicable to other Li complex hydrides and could be a promising approach to achieve high room temperature ionic conductivity for ASSB application.

For Mg, compatibility and processing with high-voltage cathodes needs to be demonstrated but first full-battery tests have been already implemented [62]. Furthermore, the discovery of novel hydrides as future solid electrolytes of more prospective Ca and Al ASSBs batteries cannot be ruled out. For the former, liquid electrolytes based on $\text{Ca}(\text{BH}_4)_2$ derived compounds have been recently reported [71] and promising compounds are foreseen from theoretical calculations [72]. For the latter, the enormous richness of Al-based borohydrides [73] constitutes a large playground for the discovery of Al solid electrolytes.

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Declaration of interest: none

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