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COMMUNICATION

Metal hydride-based materials towards high performance negative electrode for all-solid-state lithium-ion batteries

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Electrode performances of MgH₂-LiBH₄ composite material for lithium-ion batteries have been studied with using LiBH₄ as the solid-state electrolyte, which shows a highly reversible capacity of 1650 mAh g⁻¹ with extremely low polarization of 0.05 V, durable cyclability and robust rate capability.

In nowadays, lithium-ion batteries (LIBs) are absolutely imperative devices to power mobile phones, laptops, electric vehicles (EVs), etc. Moreover, LIBs are expected as energy storage devices to easily handle the renewable energy resources such as wind and solar energy.^{1, 2} Developing high capacity materials for LIBs is necessary to meet the sustained growing demand for energy. Although advances have been made to improve the performance for LIBs in the past decades, carbonaceous materials with low theoretical Li storage capacities are still mainly used as negative electrode material for commercial LIBs. That's to say, seeking suitable high capacity negative electrode materials is essential and urgent.³

Recently, metal hydrides have been studied as conversion-type negative electrode materials for LIBs owing to their high theoretical Li storage capacities (> 1000 mAh g⁻¹), relatively low volume expansions (< 200%) and suitable working potential (0.1–1.0 V vs Li⁺/Li).^{4–10} Especially magnesium hydride MgH₂, which has a theoretical capacity of 2038 mAh g⁻¹ and small polarization at an average potential of 0.5 V vs Li⁺/Li. The Li⁺ insertion/extraction processes can be written by the following hydride conversion reaction:



From those reported results, the optimized MgH₂ electrode shows a large reversible capacity of 1480 mAh g⁻¹ in the first full discharge-charge cycle using conventional organic liquid

electrolyte (1M LiPF₆ in 1:1 dimethyl carbonate/ethylene carbonate). However, the capacity fades rapidly and reduces to less than 200 mAh g⁻¹ after only 10 full cycles.⁴ A more recent report using nanoconfinement for MgH₂ shows improved cycle life stability with a reversible capacity of 500 mAh g⁻¹ after 20 cycles,¹¹ but it's still far from sufficiency. Therefore, to enhance the cyclability of MgH₂ is one of the most important issues to realize its practical application.

In our earlier attempt, a sulfide-based solid-state electrolyte Li₂S-P₂S₅ was used to assemble with MgH₂ and Li metal for an all-solid-state battery cell in order to obtain better cyclability.¹² It shows that the Li⁺ incorporation into MgH₂ almost reaches the theoretical value, however, only ~30% coulombic efficiency in the first cycle and lack of cyclability indicate the drawback had still not been overcome.

When seeking a suitable medium to achieve such a reversible hydride conversion reaction shown by Equation (1), the Li⁺ conductivity is only one side to be considered, the another important factor is the H⁻ conductivity. As we know, the MgH₂-LiBH₄ composite is a well-known material in hydrogen storage field.^{13–15} In this system, the mobility of H⁻ in MgH₂ can be strongly enhanced by LiBH₄, due to a superior hydrogen exchange effect between MgH₂ and LiBH₄, which is revealed in our earlier work for hydrogen storage.¹⁵ In other words, this effect may lead to an excellent H⁻ conductivity when applying this material as negative electrode for LIB. At the meanwhile, it was reported that LiBH₄ exhibited remarkable high Li⁺ conductivity to the order of 10⁻³ S cm⁻¹ at its high temperature phase (> 115 °C) with a stable operating window between 0–5 V vs Li⁺/Li, which can be considered as a promising candidate as solid-state electrolyte for LIBs.^{16–20} Combining the above two effects, when using MgH₂-LiBH₄ as negative electrode and

LiBH₄ as solid-state electrolyte, the hydride conversion reaction of Equation (1) could be dramatically accelerated, which lead to a much better battery performance.

In this paper, a battery cell constructed of MgH₂-LiBH₄|LiBH₄|Li (illustrated in Fig. 1) had been fabricated for electrochemical tests. The MgH₂ used in this study was doped with 1 mol% Nb₂O₅ (named c-MgH₂ hereafter), which had been proved to have positive effect in electrochemical performance for MgH₂ in our previous study.¹² The working electrode was prepared by simply ball-milling c-MgH₂, LiBH₄ and conductive carbon (acetylene black) with no further optimization. The thermal stability of c-MgH₂-LiBH₄ composite was measured by thermogravimetry with differential thermal analysis (TG-DTA), which shows a weight loss of less than 1 wt% in the temperature of RT~275 °C (Figure S1), indicates the good thermal stability and wide operating temperature window of the electrode material. To obtain the fast Li⁺ conduction from LiBH₄, all electrochemical measurements in this study were conducted at 120 °C by using oil bath as the heating source. The electrode evolution upon discharge-charge process at different stages was investigated by means of powder X-ray diffraction (XRD).

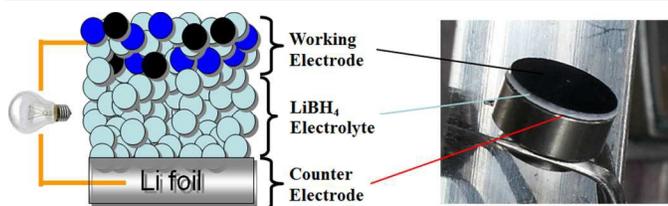


Fig. 1 The schematic (left) and practical (right) illustrations of the MgH₂-LiBH₄|LiBH₄|Li all-solid-state battery. The deep blue, black, and light blue dots in the schematic stand for MgH₂, acetylene black and LiBH₄, respectively.

Fig. 2(a) shows the first galvanostatic discharge-charge curves for c-MgH₂-LiBH₄ composite electrode with using LiBH₄ as solid-state electrolyte between 0.3 and 1.0 V vs Li⁺/Li at a current density of 100 mA g⁻¹. On the discharge curve (Li⁺ incorporation into MgH₂), the potential gradually drops to around 0.5 V and shows a long flat plateau, corresponding to the hydride conversion reaction shown by Equation (1). The discharge process was cut at 0.3 V to avoid the Li-Mg alloying reaction: Mg + x Li⁺ + x e⁻ ↔ MgLi_x, which is a partial irreversible reaction and would weaken the cyclability of MgH₂.^{4,7} On the charge curve (Li⁺ extraction), a plateau slightly above 0.5 V is observed. The polarization between Li insertion and extraction is only 0.05 V, which is much smaller than that of the MgH₂ electrodes working with organic liquid based electrolyte in some earlier reports.^{4,7} For comparison, this extremely low polarization is superior to all known metal oxide-based conversion-type negative electrode materials and even comparable with the well-recognized low polarization material of spinel Li₄Ti₅O₁₂.²¹⁻²³ The reason of such a low polarization could be owing to the fast diffusion of H⁻ species and the high working temperature of 120 °C, which

brings better kinetic properties to the hydride conversion reaction. The initial reversible capacity is 1650 mAh g⁻¹ with a high initial coulombic efficiency of 94.7%. The above results indicate the existing of LiBH₄ significantly promotes the hydride conversion reaction due to its dual effects on Li⁺ conductivity and H⁻ conductivity, results in such a low polarization and a high initial coulombic efficiency. In addition, the discharge/charge plateau voltage of around 0.5 V is much higher than the lithium plating voltage, making it a safe candidate as negative electrode material for LIBs.

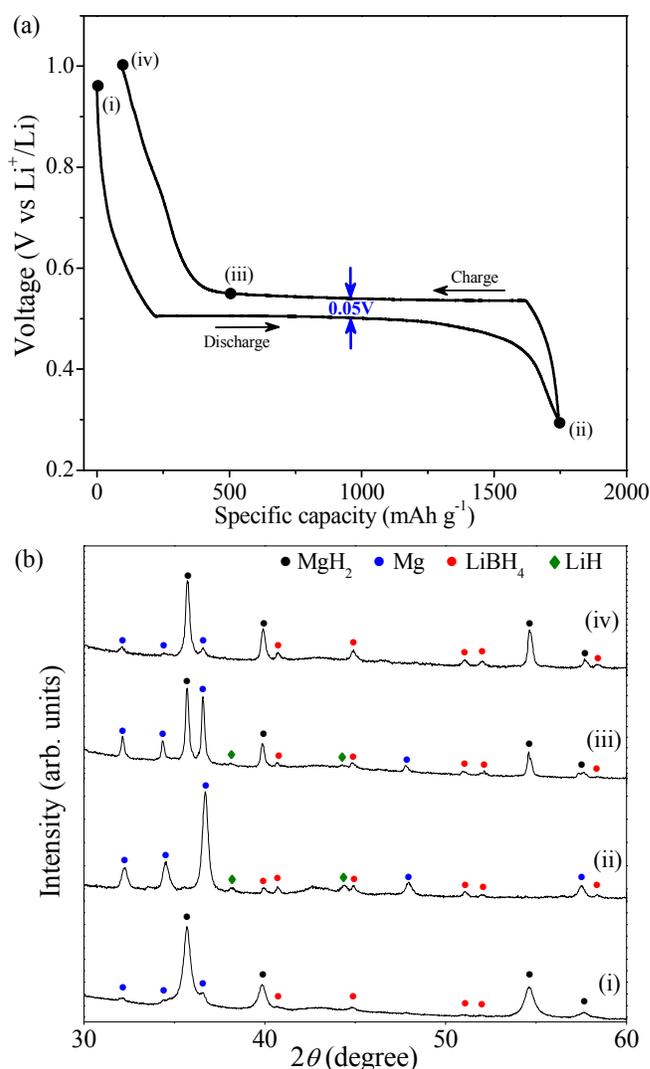
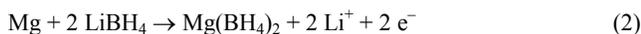


Fig. 2 (a) The first galvanostatic discharge-charge curves for c-MgH₂-LiBH₄ composite electrodes in the voltage range of 0.3–1.0 V at a current density of 100 mA g⁻¹ at 120 °C; (b) *Ex-situ* XRD patterns of MgH₂-LiBH₄ composite electrode evolution upon the first electrochemical discharge-charge process at different stages.

The *ex-situ* XRD measurement had been carried out at different stages upon the initial discharge-charge process shown by Fig. 2(b). LiBH₄ phase is observed in all stages since

it is included in the electrode material. At open circuit voltage (OCV) stage (i), small amount of Mg phase is shown as impurity which comes from the as-received MgH_2 sample. As Li reacts with MgH_2 , the MgH_2 peaks disappeared while LiH and Mg peaks appeared at 0.3 V (ii), which suggests the conversion reaction shown by Equation (1) was occurred. When recharging the battery cell, clear MgH_2 peaks emerged again together with Mg and LiH phases at the intermediate stage (iii). Finally, LiH peaks totally disappeared with only small amount of Mg at 1.0 V (iv), which is equivalent to the OCV stage. These results verify the good reversibility of the conversion reaction. Interestingly, a new phase $\text{Mg}(\text{BH}_4)_2$ was generated (Fig. S2) when further charging the battery cell to 2.0 V, which implies a side reaction shown by Equation (2) might be occurred between 1.0 and 2.0 V.



To avoid this side reaction, the galvanostatic discharge–charge cycling test was performed between 0.3 and 1.0 V at a current density of 800 mA g^{-1} as shown in Fig. 3. It shows that the c- MgH_2 - LiBH_4 electrode delivers a highly reversible capacity of 1586 mAh g^{-1} in the first cycle, and this capacity rapidly fades in the first 5 cycles and stabilized to around 924 mAh g^{-1} within 50 cycles (Fig. 3 insert). It can be seen that the plateau voltage for discharge and charge processes nearly has not been changed during cycling up to 50 times, with coulombic efficiency over 99.5%, indicates the electrode material works properly between 0.3 and 1.0 V without any side reactions.

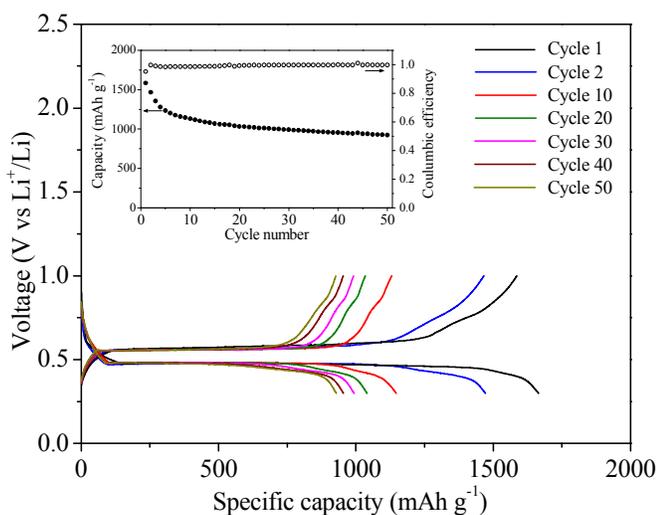


Fig. 3 Cyclic performances of the c- MgH_2 - LiBH_4 composite electrode in the voltage range of 0.3–1.0 V at a current density of 800 mA g^{-1} at 120°C .

The rate capability of the c- MgH_2 - LiBH_4 electrode was also investigated shown by Fig. 4. Each discharge profile on this figure is created by the initial discharge cycle of independent cells at different current densities from 100 to 3200 mA g^{-1} . It

shows that the c- MgH_2 - LiBH_4 electrode possesses excellent rate capability, in which the discharge capacity is 1742, 1704, 1659, 1600 and 1510 mAh g^{-1} at current density of 100, 400, 800, 1600 and 3200 mA g^{-1} , respectively. The fast kinetics could be ascribed to rapid Li^+ and H^- diffusion in the electrode material and on the electrode–electrolyte interface. It is noteworthy that the average voltage gradually decreases along with increasing discharge rate, which could be caused by the insufficiency of electronic conductivity at high current density. Generally, the electronic conductivity of electrode material can be markedly improved by surface modification such as carbon coating,²⁴ which can be considered in this system for future working direction in order to obtain better high rate performance.

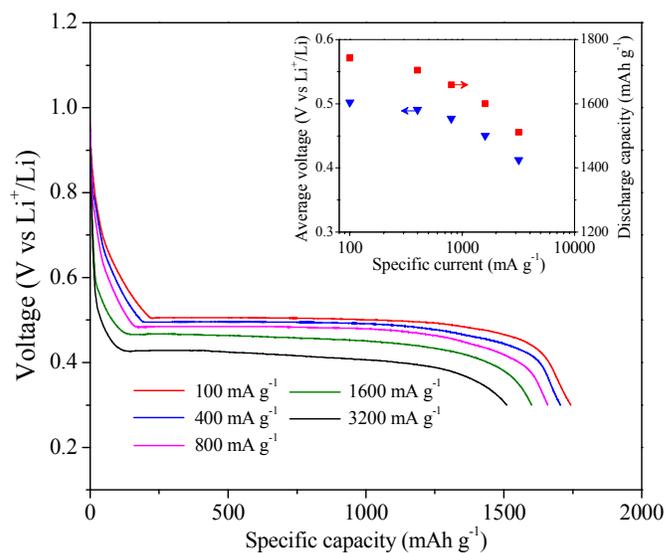


Fig. 4 The first galvanostatic discharge profiles of c- MgH_2 - LiBH_4 composite electrodes at the current densities of 100– 3200 mA g^{-1} at 120°C , respectively. Inset shows the average voltages and discharge capacities at different specific current densities respectively.

In summary, we have demonstrated a metal hydride–based material MgH_2 - LiBH_4 composite as a high performance negative electrode for lithium–ion batteries with using LiBH_4 as solid–state electrolyte. LiBH_4 here acts as multifunctional ion conductor, promotes not only Li^+ but also H^- conductivity, resulting in much higher reversibility for the hydride conversion reaction. The large reversible capacity, durable cyclability, suitable Li^+ insertion/extraction voltage of around 0.5 V (vs Li^+/Li) and the extremely small polarization are particularly remarkable to make this material a promising candidate as negative electrode material for lithium–ion batteries with the art of all–solid–state. Besides LiBH_4 , a large number of hydride–based solid–state alternatives e.g., $\text{Li}_m(\text{BH}_4)_n\text{X}$ ($X = \text{Cl}, \text{Br}, \text{I}$),^{16, 25} $\text{LiM}(\text{BH}_4)_3\text{Cl}$ ($M = \text{La}, \text{Gd}, \text{Ce}$),^{26, 27} LiBH_4 - LiNH_2 ,^{25, 28} and $\text{LiAlH}_4/\text{Li}_3\text{AlH}_6$ ²⁹ can also be considered for this system. The working temperature can be altered by substituting to these various candidates, some of

which even show high Li⁺ conductivity at room temperature. Moreover, this work opens a new way to look for suitable negative electrode materials for lithium-ion batteries. The electrochemical performance of numerous metal hydride-based materials will be investigated as negative electrode material in this system.

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