

Borohydride Solid-State Electrolytes: Ion Transport Mechanisms and Modifications

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Abstract: The ongoing global transition toward higher energy density and enhanced safety in energy systems has positioned all-solid-state lithium batteries as a pivotal solution to current energy storage limitations, owing to their intrinsic safety characteristics and lithium metal anode compatibility. Borohydride-based solid-state electrolytes demonstrate exceptional performance characteristics, including high ionic conductivity exceeding 10^{-3} S/cm at room temperature, broad electrochemical stability windows, and structurally tunable $[\text{BH}_4]^-$ anion frameworks. This paper systematically describes the structural features of borohydride solid-state electrolyte and analyzes the conductive mechanism of this electrolyte from the point of view of defect chemistry; At the same time, this paper not only nearly reviews the progress of modification of borohydride solid-state electrolytes in the direction of solid solution and elemental doping in recent years, but also reveals the technical challenges of borohydride solid-state electrolytes in their own performance and scale-up preparation. Based on this, this paper looks at future research directions for borohydride solid-state electrolytes in terms of material properties, interface engineering and process optimization.

Keywords: all-solid-state battery, solid-state electrolyte, borohydride, ionic conductivity, interface engineering

1. Introduction

The global energy system is undergoing systematic restructuring, and the new electrochemical energy storage technology characterized by high energy density and high safety has become a key supporting technology to support the scale-up of grid-connected renewable energy and the industrial upgrading of electric vehicles [1]. Although lithium-ion batteries have formed a mature industrial ecology, there are inherent flaws in their liquid electrolyte system: Thermodynamic instability leads to the risk of thermal runaway, the upper limit of theoretical energy density is difficult to exceed 500 Wh/kg, easy polarization, etc [2,3]. These technological bottlenecks seriously constrain the demand for high safety and performance in new generation energy storage systems. All-solid-state Li-ion batteries currently stand as the most viable path to overcome existing energy density limitations. Their appeal lies in three critical attributes: inherent safety due to non-flammable solid electrolytes, an exceptionally wide window of electrochemical stability exceeding 5 V versus Li^+/Li , and seamless compatibility with high-capacity lithium metal anodes.

As the core component of the full battery system, the physical and chemical properties of the solid electrolyte directly determine the practical progress of the device. The current mainstream solid-state electrolyte systems (oxide-based, sulfide-based, polymer-based) have significant technical

shortcomings: The oxide has an interfacial contact resistance of up to $10^3 \Omega \cdot \text{cm}^2$ due to grain boundary impedance; Although sulfides have superior ionic conductivity, they are chemically unstable, insufficiently incompatible and sensitive to humidity; The ionic conductivity of polymer electrolytes is generally very low at 25°C , severely limiting their low-temperature performance [4]. Notably, since the 2010s, the borohydride electrolyte system represented by LiBH_4 has triggered extensive research due to its unique combination of properties [4]. This material has low density, a wide chemical window, and excellent room temperature ionic conductivity. The system's key innovation lies in its functionalized $[\text{BH}_4]^-$ units, which enable precise control of Li^+ transport pathways via topological modification and anion substitution. This approach establishes a novel design paradigm for developing solid-state electrolytes with tunable structure-performance relationships. This provides a new research paradigm for the construction of “structure-performance” designable solid-state electrolytes.

In this paper, we will sort out the research progress in the field of borohydride solid state electrolytes. Meanwhile, this paper will analyze its structural design and discuss its conductive mechanism. In addition, this paper will investigate its modification strategies and reveal the technical bottlenecks in the current research. Finally, we evaluate the material's practical applicability in all-solid-state battery systems.

2. Structure of borohydride

Ionic conductivity is a key factor in determining the internal resistance and multiplier performance of a cell. For nearly a decade, researchers have been working to enhance the ionic conductivity of borohydrides at room temperature. Some of the research results have even enabled the conductivity of borohydrides to exceed that of organic liquid electrolytes by an order of magnitude of 10^{-2} S/cm . Initial research efforts were primarily directed toward LiBH_4 and its derivatives. $[\text{BH}_4]^-$ exhibits an orthorhombic symmetric structure, where the B-H bond lengths are between 0.1118 and 0.1151 nm, and the $\angle\text{H-B-H}$ is about 98.7° - 113° . As the temperature increases, the structure of $[\text{BH}_4]^-$ undergoes a transition from an orthorhombic to a hexagonal crystal system. Its symmetry is enhanced, the B-H bond length is extended to between 0.127 and 0.129 nm, and the bond angle is increased to 106.4° - 112.4° [5]. The above structural changes fit with the findings of Nakamori et al. They experimentally confirmed that microwave heating can significantly enhance the ionic conductivity of lithium borohydride [6].

3. Conductivity mechanism of borohydrides

3.1. Ion migration dominated by point defects

Point defects are zero-dimensional defects in crystals that consist mainly of vacancies, interstitial atoms, and replacement atoms. In borohydrides, these defects play a non-negligible role in ionic conductivity by altering ion migration paths and energy barriers. Li^+ diffuses through a vacancy-leaping mechanism, and the vacancy concentration (CV) is positively correlated with the conductivity (σ) ($\sigma \propto \text{CV} \cdot D$; D is the diffusion coefficient). For example, in the $\text{Li}_{1-2x}\text{Mg}_x\text{BH}_4$ system, the doping of Mg^{2+} increases the Li^+ vacancies by a charge compensation mechanism, which results in an increase in conductivity to 10^{-2} S/cm . As for interstitial diffusion, in the case of LiBH_4 , for example, due to its compact lattice structure, the interstitial diffusion energy barrier is high ($E_a > 0.5 \text{ eV}$), resulting in a negligible contribution of interstitial diffusion to the ionic conductivity [6].

3.1.1. Mechanisms for space jumps

Due to atomic vacancies and gaps in crystals, individual atomic leaps in solids have a fixed length. In most solid electrolytes, increased cation vacancy concentration creates more hopping sites for charge carrier migration [3]. Cations diffuse through a vacancy-jumping mechanism, and the higher the vacancy concentration, the higher the ion mobility usually is. But anion vacancies may change the local lattice distortion and affect the cation migration path. However, anionic vacancies are not involved in ion transport and contribute less directly to electrical conductivity. The ionic conductivity of LiBH_4 in its high-temperature phase ($>380\text{ K}$) reaches up to 10^{-3} S/cm , attributed to the increased concentration of point defects at elevated temperatures.

3.1.2. Gap diffusion

The contribution of interstitial atoms to ionic conductivity is small. In the case of LiBH_4 , for example, although Li^+ may occupy interstitial sites and diffuse through interstitial mechanisms at high pressures or high defect concentrations, the compact structure of borohydrides usually results in high interstitial diffusion barriers, and diffusion is not easy to occur. In the modification strategy, on the one hand, high-valent cations (e.g., Mg^{2+}) can be introduced to replace some of the low-valent cations (e.g., Li^+) to increase the concentration of Li^+ vacancies, which can enhance the ionic conductivity. For example, in $\text{Li}_{1-2x}\text{Mg}_x\text{BH}_4$, the charge compensation mechanism generates more Li^+ vacancies. On the other hand, smaller radius cations (e.g., Na^+) can be introduced to replace some of the larger radius cations (e.g., Li^+), potentially widening the lattice channel and lowering the energy barrier for Li^+ migration. In $\text{Li}_{1-x}\text{Na}_x\text{BH}_4$, lattice distortions may form more continuous ion migration paths.

The introduction of atomic defects enhances ionic conductivity by lowering activation energy or expanding migration pathways, offering a viable strategy for optimizing borohydride-based solid-state electrolytes [3].

3.2. Synergistic effects of face defects

Facet defects are two-dimensional defects in crystals, including grain boundaries, stacking dislocations, and phase interfaces. They affect electrical conductivity by changing the localized structure and charge distribution. The grain boundary-phase interface optimizes the electrical conductivity of borohydrides through a specific mechanism. The relatively loose arrangement of atoms in the grain boundary region has the potential to form ion migration paths with low energy barriers, but the phenomenon of segregation of impurities at grain boundaries may increase the local resistance. The oxidized surface of LiBH_4 was observed to form a vacancy-rich interfacial layer, leading to a two-order-of-magnitude enhancement in ionic conductivity. In multiphase systems, such as $\text{LiBH}_4\text{-LiCl}$ composites, the phase interface can promote Li^+ transport through stress field coupling, and the conductivity can reach $5 \times 10^{-3}\text{ S/cm}$ at 25°C .

Atoms in the grain boundary region are more loosely arranged and may form ion migration paths with low energy barriers, while disordered structures or impurity bias at grain boundaries may increase the local resistance, which needs to be optimized by doping. Luo et al. found that when borohydride particles are in contact with oxygen and undergo an oxidation reaction, the atoms on their surfaces are rearranged, and the large number of vacancies generated by cation polarization significantly increases the ionic conductivity of borohydride [7]. In addition, stacking laminar errors may introduce localized regions of high symmetry, creating diffusion paths with low energy barriers.

In terms of modification strategies, the phase interfaces of multiphase borohydrides (e.g., $\text{LiBH}_4\text{-LiCl}$ composites) can be used to enhance the electrical conductivity through interfacial ion transport or stress field coupling.

4. Advances in the modification of borohydrides

The research on borohydride solid electrolytes has shown a blossoming trend, with significant breakthroughs in theoretical frameworks, multiphase composites, and coating treatments.

In 2019, Yuepeng Pang et al. proposed the preparation of multiphase composite solid-state electrolyte materials by partial hydrogen release treatment of metallic borohydrides to optimize ionic conductivity and electrode compatibility [8]. The LiBH_4 -derived electrolyte demonstrates stable operation at 1 mA/cm^2 (35°C) while maintaining compatibility with diverse cathode materials.

In 2022, the study by Ziqiang Wu et al. induced deformation of the $[\text{BH}_4]^-$ structure of LiBH_4 through h-BN defects to weaken Li-H interactions [9]. The LiBH_4/BN composites realized an ionic conductivity of $1.15 \times 10^{-4} \text{ S/cm}$ with a 97% migration number at 40°C , significantly improving their low-temperature performance.

In 2023, a team from Zhejiang University developed LiBH_4 -based composites containing a polymer capping layer. This composite inhibits lithium dendrite growth over a wide temperature range of $-30 \sim 150^\circ\text{C}$ while maintaining high ionic conductivity ($>10^{-4} \text{ S/cm}$ at 25°C) for extreme environment batteries [10].

In 2024, Qingbo Zhang et al. used V_2C MXene-loaded $\text{LiBH}_4\text{-Mg}(\text{BH}_4)_2$ composites to achieve 8.1 wt% of hydrogen storage and 5 wt% of reversible capacity at 350°C , with a 30% reduction in activation energy, and the $\text{VH}_2.01$ material as a “hydrogen pump” for improved cycle stability [11].

5. Challenges and developments

To address the above bottlenecks, future research can focus on four directions: material design, interface engineering, process optimization, and multi-scale simulation. Material design can be devoted to the development of novel borohydrides with intrinsic wide temperature domain stability, e.g., by introducing rare earth elements or neutral ligands. Modulation of borohydride lattice distortion and enhancement of structural thermal stability by rare earth elements (e.g., La, Ce) doping; Dynamic coordination of neutral ligands (crown ethers, ionic liquids) allows the construction of self-repairing hydrogen bonding networks but requires a balance between coordination strength and ion transport efficiency.

Constructing adaptive interfacial layers by interfacial engineering to inhibit the occurrence of side reactions. For example, the design of biomimetic CEI draws on the principle of biomineralization to construct a gradient interface layer, which can dynamically adjust the components with the electrochemical environment to achieve the in-situ passivation of side-reaction products.

In terms of process optimization, low-temperature synthesis and scale-up preparation technologies can be actively explored. On the one hand, the mechanical energy of the ball milling process is utilized to induce the generation of substable phases. As described in the patent by Ouyang Liuzhang et al. of South China University of Technology, sodium borohydride can be synthesized at room temperature by mechanical ball milling, but large-scale production needs to solve the problem of particle agglomeration[12]. On the other hand, the low-temperature solvothermal method can enhance the electrode-electrolyte interface compatibility by modulating the nucleation kinetics to construct a porous structure.

In addition, multi-scale simulations can be used to combine DFT calculations with machine learning methods to predict material properties and accelerate the screening of optimal components.

6. Conclusion

From the point of view of borohydride's own performance, although some borohydrides exhibit high lithium ion conductivity at room temperature, their performance is highly dependent on temperature, and it is usually necessary to improve the low-temperature performance with the help of heat

treatment or nanocomposites. In addition, some borohydrides are prone to phase change or decomposition at elevated temperatures, which greatly limits their application over a wide temperature range.

The production of borohydride materials typically requires sophisticated synthetic approaches, including high-energy ball milling and high-temperature sintering processes. Although strategies such as nano-restricted domains and doping can optimize material properties, there are greater difficulties in accurately controlling the microstructure of materials during large-scale production, resulting in poor product batch consistency.

Overall, the research on borohydride-based solid-state batteries is still in its infancy, and its core principles are not yet fully understood. In key areas such as interfacial behavior, electrochemical stability, battery composition, and structure, the academic community's knowledge is still limited, and further in-depth exploration is urgently needed. In addition, borohydride solid-state electrolytes need to find a balance between material intrinsic properties, interfacial stability, and process economics in the commercialization process. Advances in relevant disciplines will significantly accelerate the commercialization of all-solid-state battery technologies.

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