Research on Battery Technology of Borohydride New Hydrogen Energy Material

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Abstract. Vehicle-mounted hydrogen storage is a "bottleneck" link in promoting the large-scale commercial application of hydrogen fuel vehicles. The development of high-performance vehicle-mounted hydrogen storage material technology has become a hot spot in the current energy and materials field. In recent years, with the continuous expansion of the field of hydrogen storage materials, high-storage coordination metal hydrides represented by lithium borohydride (LiBH₄) have gradually become a new research focus of hydrogen storage materials. This article summarizes the latest modification research and application of metal borohydride hydrogen storage materials from the perspectives of substitution, recombination, doping, nanostructure confinement and corresponding reaction mechanism, and puts forward the existing problems and corresponding countermeasures, and points out the future research direction.

Keywords: Hydrogen storage materials, thermodynamic kinetics, metal borohydride, performance control.

1. Introduction
Hydrogen energy is a completely clean, resource-rich secondary energy source that is easy to exchange with electricity and heat. The use of hydrogen energy to replace fossil fuel-based energy has become a hot spot of global concern and a major demand for the sustainable development of my country's economy. The large-scale application of hydrogen energy needs to solve the three major technologies of hydrogen production, storage, transportation, and application, and hydrogen storage technology is currently the main bottleneck of hydrogen energy utilization. Solid-state hydrogen storage is an efficient hydrogen storage technology, but the performance of existing hydrogen storage materials cannot or cannot meet the application requirements of vehicle-mounted hydrogen source systems and secondary energy carriers such as wind energy and biomass energy. The research and development of new hydrogen storage materials has become the primary task of hydrogen energy application researchers [1]. The direct borohydride fuel cell (DBFC) using alkali metal borohydride (MBH₄⁺) solution as fuel has the characteristics of high hydrogen storage energy density, convenient storage and carrying, and high safety. It is considered as a mobile power source with development potential. Received more widespread attention.
2. Principle of alkaline metal borohydride ($MBH_4$) solution battery

The alkali metal borohydride ($MBH_4$) used in DBFC is a methane-like tetrahedral anion compound containing hydrogen anion H-, which is widely used as a reducing agent and is also an ideal hydrogen storage material, such as: $NaBH_4$ contains 10.6% (mass Percentage) of the element hydrogen. The theoretical specific capacity and specific energy density of DBFC composed of $NaBH_4$ as fuel are 5.678Ah/g and 9.296Wh/g, which are much higher than the 5.03Ah/g and 6.081Wh/g of methanol. The anodizing reaction of DBFC is

$$BH_4^- + 8OH^- = BO_2^- + 6H_2O + 8e$$

(1)

If $H_2O_2$ in acid solution is used as oxidant, the cathode reaction is

$$4H_2O_2 + 8H^+ + 8e^-= 8H_2O$$

(2)

The total response is

$$BH_4^- + 4H_2O_2 = BO_2^- + 6H_2O$$

(3)

The theoretical open circuit voltage of its DBFC can reach 3.02V, which is higher than 1.229V of hydrogen fuel cell and 1.214V of DMFC, and also higher than 1.64V of DBFC with $O_2$ as oxidant, which is beneficial to increase output power. In view of the above advantages, DBFC is expected to be used in space power supplies, underwater power supplies and portable power supplies with high energy and high-power density, and it is worthy of further study. It can be seen from the electrode reaction formula (1) that when each $BH_4^-$ undergoes an electrochemical oxidation reaction, the hydride ion H in $BH_4^-$ loses two electrons in the 1s electron shell, and it exists in the product $H_2O$ in the form of proton $H^+$, releasing 8 electrons [2]. However, in the actual discharge process, the $BH_4^-$ hydrolysis reaction that does not release electrons but releases hydrogen is always accompanied to varying degrees:

$$BH_4^- + 2H_2O \rightarrow BO_2^- + 4H_2$$

(4)

Therefore, the comprehensive reaction measurement formula can be written as

$$BH_4^- + nOH^- = BO_2^- + (n-2)4H_2O + (4-n/2)H_2 + ne$$

(5)

In formula (5), n represents the number of apparent electrons actually released on the anode by each $BH_4^-$, which can theoretically be equal to any value from 0 to 8. The value of n determines the Faraday efficiency of the electrode reaction, and its size is related to the electrode material and reaction conditions. $BH_4^-$. The generation of hydrogen during the anodization of the DBFC not only reduces the Faraday efficiency, but also reduces the performance of the battery due to the hydrogen bubbles hindering the migration of ions, and also brings certain safety hazards to the operation of the battery. Therefore, finding an anode catalyst with good performance has become an important issue facing the practical application of DBFC. In order to develop catalytic materials with high selectivity and high catalytic activity, a lot of researches have been done on DBFC electrode catalytic materials. The electrocatalytic materials currently used in DBFC anodes mainly include precious metals Pt, Pd, Au and Ag, non-precious metals Ni, Cu, and some hydrogen storage materials and alloys. In the
literature, metal electrodes are usually divided into "catalytic" and "non-catalytic" according to whether the BH$_4^-$ oxidation process "catalyses" the hydrolysis reaction. For electrode materials such as Pt, Pd, Ni, etc., BH$_4^-$ has serious hydrolysis reactions on it. It is called "catalytic" electrode; while electrode materials such as Au and Ag have high hydrogen overpotential, the hydrolysis reaction of BH$_4^-$ on Au and Ag electrodes is considered to be very small, so it is called "non-catalytic" electrode.

In short, on the DBFC anode, while BH$_4^-$ undergoes electrochemical oxidation, there is also a hydrolysis reaction [3]. The hydrolysis reaction includes heterogeneous "catalysed" hydrolysis reactions and homogeneous hydrolysis reactions. Since the homogeneous hydrolysis reaction rate in strong alkaline medium is very small, it can usually be ignored. The hydrolysis reaction mentioned in this article refers to the "catalysed" hydrolysis reaction of BH$_4^-$ on the metal electrode. It can be seen that the BH$_4^-$ anodic oxidation reaction actually involves a complex electrode reaction system that converts the valence state between $H^- - H^\circ - H^+$.

3. **LiBH$_4$ hydrogen storage and release performance improvement**

Different from the traditional metal alloy hydride, which realizes the absorption and release of hydrogen through the reversible entry and exit of hydrogen atoms into and out of the matrix metal alloy lattice, the hydrogen absorption and release reaction of coordination metal hydrides is accompanied by the complete destruction and reconstruction of the hydride lattice. The essential difference in the hydrogen storage and release reaction of materials determines the difference in the technical approaches used to improve the hydrogen storage performance of materials. This is fully reflected in LiBH$_4$, a representative study of coordination metal hydrides [4]. Through research efforts in recent years, scholars from various countries have revealed several effective ways to improve the thermodynamic and kinetic properties of hydrogen storage and release of LiBH$_4$.

3.1. Reactant instability method

According to the "reverse stability" criterion, the academic community almost simultaneously proposed a new method to improve the hydrogen storage and release performance of LiBH$_4$. By adding appropriate reactants to participate in the hydrogen desorption process, a more stable hydrogen desorption product can be generated, which effectively reduces the thermodynamic stability of LiBH$_4$.

Taking system $2\text{LiBH}_4 + \text{MgH}_2$ as an example, the hydrogen absorption and desorption reaction is shown in formula (6).

\[
2\text{LiBH}_4 + \text{MgH}_2 \rightarrow 2\text{LiH} + \text{MgB}_2 + 4\text{H}_2
\]  

(6)

Compared with the reaction enthalpy change of each single-phase system (LiBH$_4$: 67 kJmol; MgH$_2$: 76 kJmol), the Li-Mg-B-H system hydrogen release reaction enthalpy change is significantly lower, about 46 kJmol, as shown in Figure 1. The reason is: MgB$_2$ is more stable than the corresponding hydrogen-releasing product (elemental B or Mg) of each single-phase system, which leads to a reduction in the energy difference between the hydrogen-absorbing and hydrogen-releasing materials.
Figure 1. Schematic diagram of enthalpy changes of \( \text{LiBH}_4 \), \( \text{MgH}_2 \) and \( 2\text{LiBH}_4 + \text{MgH}_2 \) systems

Compared with \( \text{LiBH}_4 \), Li-Mg-B-H system has significantly improved thermodynamic properties. However, the study found that the important prerequisite for achieving good cycle stability of the system is to effectively control the hydrogen released products. The paper uses hydrogen-releasing material \( (2\text{LiH} + \text{MgB}_2) \) as the starting material and maintaining a certain hydrogen pressure (>3bar) in the system during the hydrogen-releasing process to obtain good cycle capacity stability; on the contrary, such as in vacuum or low hydrogen pressure When hydrogen is released under the conditions, the system will have the same degree of capacity decay as pure \( \text{LiBH}_4 \) material during the cycle of hydrogen absorption and release. X-ray diffraction analysis results show that the former generates \( 2\text{MgB}_2 \) during the hydrogen desorption process; while the latter mainly generates elemental Mg. The above research shows that controlling the generation of hydrogen desorption product \( 2\text{MgB}_2 \) helps \( \text{LiBH}_4 \) regeneration [5]. During the hydrogen release process of the system, applying a certain hydrogen pressure can effectively inhibit the rapid decomposition of \( \text{LiBH}_4 \) in the molten state. Compared with the solid-state reaction of MgB, the solid-liquid reaction of \( \text{MgLiBH}_4 \) is obviously more conducive to the formation of \( \text{MgB}_2 \).

3.2. Nanostructure modulation

Nanomaterials structure is an important technical way to improve the hydrogen storage performance of materials. Hydrogen storage materials are mostly crystalline powders at near room temperature, and the nanostructure of its structure includes two meanings: one refers to reducing the crystal grain size to the nanometre level; the other refers to nanoparticle size. The former can be easily obtained by methods such as ball milling. In the process of ball milling, the powder of the ground material is repeatedly cold welded and broken, and the crystal structure of the material is gradually destroyed. When structural defects accumulate to a certain extent, nanocrystalline materials will be formed. Compared with microcrystalline or coarse-grained materials, the ratio of grain boundary disordered regions to grain ordered regions in nanocrystalline materials is significantly increased. The disordered regions of grain boundaries provide fast diffusion channels for hydrogen atoms, so nanocrystalline hydrogen storage materials have excellent hydrogen storage and release dynamics. However, the development of practical hydrogen storage materials requires the synergistic improvement of hydrogen storage and release kinetics and thermodynamic properties. For the latter, nanocrystalline hydrogen storage materials usually appear powerless and need to be realized by nanomaterials or composition adjustments.
In the thesis, \( \text{LiBH}_4 \) is filled into the nanopores of the carbon aerogel by melt impregnation method (the pore diameter is about 25nm, and the loading is 45wt%). Compared with bulk materials, the hydrogen release temperature of the prepared \( \text{LiBH}_4 \) nanoparticles are reduced by about 70°C, and the attenuation of the circulating hydrogen capacity has also been significantly improved. Recently, the research group used chemical impregnation technology to fill \( \text{LiBH}_4 \) into commercial activated carbon (AC, average pore diameter is about 2nm, loading is 30wt%), and obtained more excellent hydrogen storage and desorption performance, as shown in Figure 2. Compared with bulk \( \text{LiBH}_4 \cdot \text{LiBH}_4 \cdot \text{LiBH}_4 \), the hydrogen desorption temperature of nanocomposites is reduced by about 150°C, and the hydrogen desorption rate is increased by about an order of magnitude. At the same time, nano-particles have also led to a substantial improvement in the hydrogen absorption performance of the material. After bulk \( \text{LiBH}_4 \) is decomposed, reversible hydrogen charging can be partially completed under the harsh conditions of 600°C and 15.5-35MPa; \( \text{H}_2 \) for \( \text{LiBH}_4 \) nanoparticles filled in AC, the decomposition products can be achieved at 300°C and 5MPa \( \text{H}_2 \). The hydride is partially reversible. Experimental studies have found that nano-materials can significantly improve the thermodynamic properties of hydrides while improving the dynamic performance.

![Figure 2. Thermogravimetric mass spectrum (\( \text{H}_2 \)) curve of \( \text{LiBH}_4 \cdot \text{AC} \) nanocomposite material and bulk \( \text{LiBH}_4 \).](image)

3.3. Anion substitution

In addition to cation substitution, anion substitution can also be used to adjust the properties of the borohydride, which is achieved by reactant ball milling to achieve partial substitution of \( [\text{BH}_4^-] \) or \( \text{H}^- \) by anions of the same charge and approximate size to obtain the corresponding solid solution. Studies have shown that the coordination anion \( [\text{BH}_4^-] \) as a whole can be replaced by heavy halogen elements, such as \( \text{Cl}^- \), \( \text{Br}^- \) or \( \text{I}^- \), and \( \text{F}^- \) can only replace the \( \text{H}^- \) in \( [\text{BH}_4^-] \). Thermal analysis shows that the hexagonal phase \( \text{Li}[\text{BH}_4]\cdot\text{Cl}_2 \) obtained by anion substitution has higher stability, and its hydrogen release temperature is slightly higher than that of pure \( \text{LiBH}_4 \). Similarly, the addition of \( \text{LiBr} \) or \( \text{LiI} \) will also make \( \text{LiBH}_4 \) more stable. Theoretical calculations show that the introduction of more electronegative \( \text{F}^- \) can significantly reduce the thermodynamic stability of the original system. For
example, in the $3\text{LiBH}_4 - \text{LiBF}_4$ sand $9\text{LiBH}_4 - \text{LiBF}_3$ system, the temperature of hydrogen separation is as low as 80°C, which is more than 3 times lower than that of a single component, but a large amount of borane will be released when hydrogen is released. Based on $\text{Li}[[\text{BH}_4]_4]\text{Cl}$, the researchers extended the anion substitution to the $\text{NaBH}_4,\text{Ca(BH}_4)_2,\text{Mg(BH}_4)_2$ system. A stable $\text{Na(BH}_4)_n,\text{Cl}_n$ solid solution was formed by $\text{NaBH}_4$ and $\text{NaCl}$ ball milling, and its stability increased with the increase of chloride substitution. The introduction of $\text{CaX}_2 (X = F, Cl)$ reduces the hydrogen release temperature of $\text{Ca(BH}_4)_2$ by about 10°C, which is mainly due to the formation of $\text{CaH}_2 - \text{CaF}_2$ and $\text{CaHCl}$ solid solutions during the hydrogen release. It is worth noting that the decrease in the hydrogen release temperature of the $\text{Ca(BH}_4)_2$ anion substitution system is due to the optimization of the hydrogen release pathway rather than the thermodynamic improvement of the entire system. Similarly, the hydrogen release temperature of the $\alpha-\text{Mg (BH}_4)_2$ system has also decreased. However, the introduction of $\text{CaI}$ will lead to an increase in the temperature of $\alpha-\text{Ca (BH}_4)_2$ for hydrogen release. The specific reason is not yet clear.

4. Conclusions
The side reaction of hydrogen evolution on the anode of the direct borohydride fuel cell not only reduces the Faraday efficiency of the battery, but also involves the safety of use, so it is the biggest obstacle to the development and application of DBFC. $\text{BH}_4^-$ lot of research has been done on the mechanism of A anodic oxidation. It can be seen that the oxidation mechanism of $\text{BH}_4^-$ on the anode involves a complex electrode reaction system that converts the valence state between $H^+ - H_{\text{gas}} - H^+$. It contains a number of non-electrochemical and electrochemical elementary steps. The sequence, series or Parallel, reaction rate and rate control will all have a decisive influence on the electrode reaction behaviour, such as the apparent number of released electrons, whether there is adsorption or catalytic current limitation, etc. At present, the catalytic reaction mechanism of $\text{BH}_4^-$ anodic oxidation has not been concluded, especially the lack of quantitative reaction kinetics research.

References
[1] Nabid, M. R., Bide, Y., & Kamali, B. Hydrogen release from sodium borohydride by Fe2O3@ nitrogen-doped carbon core-shell nanosheets as reasonable heterogeneous catalyst. International Journal of Hydrogen Energy, 44(47) (2019) 25662-25670.
[2] Dao, A. H., López-Aranguren, P., Zhang, J., Cuevas, F., & Latroche, M. Solid-state Li-ion batteries operating at room temperature using new borohydride argyrodite electrolytes. Materials, 13(18) (2020) 4028.
[3] Liu, H., Ren, Z., Zhang, X., Hu, J., Gao, M., Pan, H., & Liu, Y. Incorporation of Ammonia Borane Groups in the Lithium Borohydride Structure Enables Ultrafast Lithium Ion Conductivity at Room Temperature for Solid-State Batteries. Chemistry of Materials, 32(2) (2019) 671-678.
[4] Bozkurt, G., Özer, A., & Yurtcan, A. B. Hydrogen generation from sodium borohydride with Ni and Co based catalysts supported on Co3O4. International Journal of Hydrogen Energy, 43(49) (2018) 22205-22214.
[5] DEMİRCİ, Ü. B. Sodium borohydride for the near-future energy: a"rough diamond"for Turkey. Turkish Journal of Chemistry, 42(2) (2018) 193-220.