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Review

Sodium alanate system for efficient hydrogen storage



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ABSTRACT

Hydrogen is a promising energy carrier in future energy systems. However, hydrogen storage is facing increasing challenges within the development of more environmentally friendly energy systems with high capacity, fast kinetics, favorable thermodynamics, controllable reversibility, especially for applications in vehicles with fuel cells that use proton-exchange membranes (PEMs). In this report, we present a critical review on catalyst modified and nanoconfined NaAlH₄, focusing on their thermodynamics and kinetics behaviors. Catalyst is of increasing interest and may lead to significantly enhanced kinetics, higher degree of stability and/or more favorable thermodynamic properties. Thus, catalyst-doped NaAlH₄ is expected to strongly contribute by the development of novel catalysts and synthesis methods. Additionally, nanoconfined NaAlH₄ may also have a wide range of applications in the PEM fuel cells. Selected catalyst materials, porous scaffold materials, methods for preparation of NaAlH₄ systems and their hydrogen storage properties are reviewed. This is the first review report on catalyst modified and nanoconfined NaAlH₄.

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1. Introduction

In modern society, we are facing tremendous challenges focusing on our energy systems, including increasing energy demands and simultaneously an urgent need for environmentally friendly technologies, due to reducing fossil fuel resources. Hydrogen is regarded as one of the most promising energy candidates for on-board fuel cell applications owing to its high energy density and free of pollutants [1–4]. Nevertheless, the lack of a safe, economical and efficient on-board hydrogen storage method may even pose the major obstacles for practical application of hydrogen storage. Thus,

developing a kind of reliable media and method to efficiently store hydrogen has been the focus of attention for researchers in several decades [5–20].

In general, hydrogen storage technologies can be generally categorized into physical and chemical hydrogen storage strategies (as shown in Fig. 1). The physical storage strategies are most mature, and most prototypes of fuel-cell-powered cars use the physical hydrogen storage. In this case, no strong chemical bonds (covalent or ionic interactions) between hydrogen and a host compound are involved. Currently, the most developed physical storage strategies are compressed hydrogen gas and cryogenically generated liquid hydrogen,

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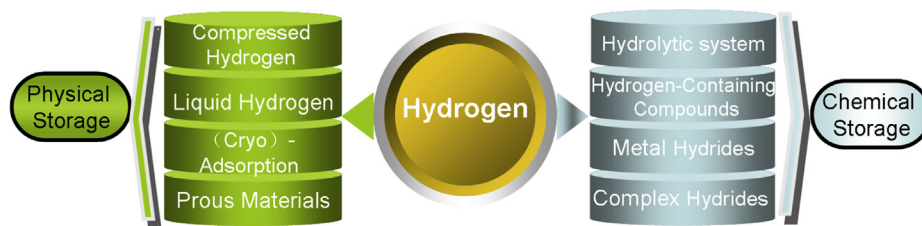


Fig. 1 – Schematic illustration for hydrogen storage technologies.

which can technically fulfill the US Department of Energy (DOE) targets set in 2010. However, high-pressure and cryogenic hydrogen storage systems are unlikely to reach the purpose for vehicular applications due to safety concerns and volumetric constraints [21]. For the tank systems, the main cost drivers are the heat exchanger, the processing and tank system costs. In addition, high pressure level has to be increased to obtain a viable tank system. Thus, liquid hydrogen seems an interesting alternative to directly storage hydrogen. However, hydrogen is difficult to liquefy and it can be produced only by complex and expensive multistage cooling procedures. In addition, liquid hydrogen tanks are usually expensive and delicate and liquid hydrogen storage systems lose hydrogen gas over time by evaporation [22]. For the tank system and the pressure tank vessel, the main cost drivers are the heat exchanger and the storage material vessels. However, these costs are neglected in the present calculations. On the other hand, the permanent evaporation inside the liquid hydrogen tank leads to what we call additional technically required cost [23]. Thus, the tank design and operating strategies have to be improved. More importantly, owing to the very low phase-change enthalpy of about 0.45 MJ per kg of H_2 between the liquid and gaseous state, even advanced engineering concepts have so far not been able to address the challenges of minimizing the heat input into the system adequately. Activated carbons and MOFs are also promising materials for physical sorption of hydrogen, however, the relatively low storage capacities and low operational temperature (about 77 K) hamper its practical applications [24–26]. In addition, carbon-based materials develop into a storage capacity reaching technically relevant values that is highly unlikely because the synthesis procedures of activated carbon are complex. On the other hand, thermal cycling is also a problem, because that cooling down the whole hydrogen storage system for loading the storage material with hydrogen is a very energy-intensive process, even if the material can store hydrogen at ambient temperature. Meanwhile, the interaction between most of the adsorbents and hydrogen of physical hydrogen storage is relatively weak. And hydrogen is adsorbed in the form of molecules. Although the technologies maturity are high, the energy density (energy conversion efficiency), unavoidable hydrogen and energy losses are still immense challenges.

Chemical hydrogen storage, wherein hydrogen is stored in a chemical compound and released via a chemical reaction, is a promising strategy. The mechanism of chemical hydrogen storage in hydrides is different to physical sorption of hydrogen. With regard to chemical hydrogen storage,

hydrogen is dissociated into protons, diffuses into metal and is absorbed. From the application point of view, hydrogen must be stored in a safe, economical and efficient way. Solid-state materials do have the potential to outperform physical methods of storage. In contrast to the existing physical methods, chemical hydrogen storage techniques have high volumetric and gravimetric hydrogen capacities and can reversibly store hydrogen near ambient temperatures. And chemical hydrogen storage is highly desirable to quickly store or liberate hydrogen from solid hydrogen storage materials. Furthermore, thermodynamics must be suitable during the reaction. In summary, chemical hydrogen storage seem to be appropriate for practical large scale application. Thus, chemical hydrogen storage, i. e. hydrogen stored in solid state, has the potential to become an ideal hydrogen storage strategy. Chemical hydrogen storage routes mainly include that hydrogen stores in hydrolytic systems, hydrogen-containing compounds, metals hydrides and complex hydrides. The storage capacity of chemistry hydrogen storage depends on the weight of the metal atoms and the number of possible bound hydrogen atoms in the complex anion. Recently, substantial developments have been made in exploiting the applications of irreversible hydrolytic systems to hydrogen storage [22,27]. For example, hydrides, such as $NaBH_4$ and NH_3BH_3 [28–31], have in general high storage capacities (7.3 wt. % and 19.6 wt. %), since the released hydrogen come from both the hydride and the water. However, considering the costs and irreversibility of the materials, hydrolytic storage systems seem to be not suitable for practical applications. For thermolysis of hydrogen-containing compounds (e.g. hydrocarbons), the technical problems for higher hydrocarbon steam reforming or autothermal reforming seem so severe that they appear almost insurmountable. In addition, hydrogen storage capacities of the intermetallic hydrides, such as $LaNi_5H_6$, $FeTiH$ and $K_2[ReH_9]$ [32–35], are too low to meet the requirements for an on-board storage systems. This is due to the fact that most of the typical metal hydrides are intermetallic transition metal compounds and atomic weight of associated metal atom is high. Thus, hydrogen capacity is considerable low even if several hydrogen atoms can be bound by each metal atom. Namely, in order to store 5 kg of hydrogen, the storing system needs to weight several hundreds kg. Besides, the use of light metal hydrides for practical applications as fuel-cell-powered cars is often hampered by unfavorable thermodynamics [36–38]. For example, magnesium hydride, MgH_2 , is interesting light metal hydrides due to their high theoretical hydrogen density (7.6 wt%) [38,39]. However, the thermodynamic properties of the MgH_2 material

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