

The future of physical hydrogen storage

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Abstract

Hydrogen is one of the most promising clean energy because it has a much higher energy density than gasoline and emits no carbon dioxide after burning. For the application of hydrogen, hydrogen storage is considered as a key technology. Design and synthesis of porous material with high hydrogen storage capacity should be fully developed at first. However, none of the candidate materials developed so far has meet the DOE target yet. This review aimed to describe the presently major accomplishments and the challenges in the area of hydrogen storage. Copyright © 2018 VBRI Press.

Keywords: Hydrogen storage, porous materials, physisorption, enthalpy of adsorption.

Introduction

Is it amazing that Toyota Mirai runs without petroleum, charging system, and even no carbon emission 1? In fact, this is the basic character of a hydrogen-powered vehicle. Hydrogen, as the most abundant element in the universe and with higher energy density than gasoline, is no doubt one of the green power sources. However, hydrogen source used on Mirai is supplied as a compressed gas at near 700 bar (ambient temperature). Therefore, design and synthesis of novel materials for hydrogen storage under low pressure and near room temperature is highly desirable in terms of safety and cost [2-4].

Two main storage methods are now broadly used as core technology for hydrogen storage: Chemisorption-based or physisorption-based storage without high-pressure tanks. In chemisorption-based materials, such as metal hydrides, complex boron hydrides, metal amides, and amino boranes, dissociated hydrogen was store through chemical bond 5. However, high activation energy barrier make chemisorbents suffer from slower kinetics. Weak-chemisorption materials are an alternative. In contrast, physisorption exhibits fast kinetics of adsorption/desorption and excellent reversibility, due to the weak van der Waals interaction between hydrogen and the pore wall of the sorbents. Such sorbents include porous carbons 6, metal-organic frameworks (MOFs) [7,8], covalent organic frameworks (COFs) 9 and porous organic polymers (POPs) 10. These kinds of materials feature high surface areas and large pore volumes. Notably, the pore size of porous materials can be finely tuned through the design of functional

monomers. Unfortunately, low enthalpy of adsorption for hydrogen results in a low hydrogen density, especially under ambient temperature. The targeted goals proposed by the US Department of Energy (DOE) for onboard hydrogen storage are 4.5wt % and 30g/L (2020 target), 5.5wt % and 40g/L (2025 target), and 6.5wt % and 50 g/L (ultimate target), with the operating temperature from -40-60°C 11. Despite considerable efforts on the design and synthesis of porous materials, none yet meet the DOE targets.

Recently, hydrogen storage based on physisorption has received vast amount of attention. Here, we aim to assemble a review of the representative porous materials in the applications of hydrogen storage. We will discuss the striking developments, the problems encountered in hydrogen storage and the challenges in the future.

Major accomplishments

Hydrogen storage is considered as a key technology in Hydrogen Economy. Physisorption storage relies more on the sorbent's pore size, pore volume, and surface area as well as the hydrogen binding sites decorated in the porous materials. Therefore, numerous work focus on tuning of the pore sizes, optimization of the surface area of porous polymers, and functionalization of the pore wall.

Porous carbon

Different kinds of porous carbon materials have been explored for hydrogen storage, such as active carbon, graphene, nanotube and others [12-14]. Here, a record high hydrogen storage performance achieved by

Cigarette butt-derived carbons was introduced 15. In this work, smoked cigarette filters (SF) was selected as carbon precursor. Hydrochar was first obtained via hydrothermal carbonization of SF. The intrinsic metal additives and added KOH both function as activating agents. Due to the “overactivation” process, the activated carbons exhibited the ultra-high S_{BET} of $4310 \text{ m}^2 \text{ g}^{-1}$, a total pore volume of $2.09 \text{ cm}^3 \text{ g}^{-1}$, and a micropore volume of $1.71 \text{ cm}^3 \text{ g}^{-1}$, respectively. No such excellent results have been reported before. In addition, most proportion of porosity is micropores (<1 nm). More importantly, the excess hydrogen storage capacity was 4 wt% at 1 bar and 77 K. At 20 bar and 77 K, the excess uptake achieved 8.1 wt%. Such superior performance is not only higher than most porous carbons, but also outperforms MOF materials (Fig. 1), such as MOF-210 (6.4 wt%) 16 and NU-100 (6.8 wt%) 17. The high-added-value porous carbon is a promising material to meet the DOE target.

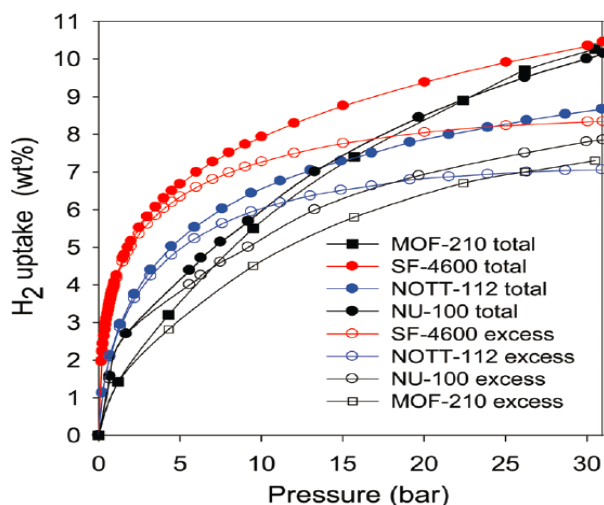


Fig. 1. Excess and total gravimetric hydrogen uptake of activated carbon (SF-4600) derived from smoked cigarette butts compared to the best benchmark high surface area metal organic frameworks (MOFs), namely, NOTT-112, NU-100, and MOF-210 15.

MOFs

MOFs are promising materials for gas adsorption due to the high specific surface areas and interconnected porous structures and channels. Through meticulous selection of metal ions and organic building blocks, the nanostructure of MOFs can be readily tuned. Clearly, it is difficult to imagine the number of possible MOFs. Due to their specific structure character, MOFs have potential utility in gas storage. For example, small pore size can increase the interaction between the pore wall and the hydrogen molecules 18. Furthermore, open metal sites in MOFs can function as binding sites for hydrogen 19. Hydrogen spillover is also positive effect for hydrogen storage 20. Till now, MOF-210 holds the record of total H_2 storage capacity of 176 mg g^{-1} at 77 K and 80 bar 16. This crystalline solid was prepared by Yaghi and co-workers, with S_{BET} of $6240 \text{ m}^2 \text{ g}^{-1}$ and pore volume $3.60 \text{ cm}^3 \text{ g}^{-1}$,

respectively. Besides, NU-100 exhibited the highest excess hydrogen uptake of 99.5 mg g^{-1} for MOFs at 56 bar and 77 K 17. NU-100 also featured ultrahigh S_{BET} of $6143 \text{ m}^2 \text{ g}^{-1}$. There is no doubt that large surface area, proper pore size, and moderate isosteric heat of the hydrogen adsorption contribute to exceptional hydrogen storage capacity.

Very recently, Nayak and coworkers synthesized Zr-based MOF (UBMOF-31 with S_{BET} of $2552 \text{ m}^2 \text{ g}^{-1}$) via mixed-linker approach 21. UBMOF-31 showed a superior hydrogen uptake of 4.9 wt% at 4.6 MPa and 77 K, due to the existence of amino on the linker. This capacity is the highest one among Zr-based MOFs.

COFs

COFs contain light elements of B, C, N, O, Si, etc. with porous and crystalline structures are promising materials for hydrogen storage 22. COF-102 with S_{BET} of $3620 \text{ m}^2 \text{ g}^{-1}$ is one of the best adsorbents in COFs for hydrogen 23. The excess hydrogen uptake of COF-102 was 7.24 wt% (72 mg g^{-1}) at 35 bar and 77 K. Furthermore, it has been studied that the hydrogen storage performance of three-dimensional (3D) COF were significantly better than those of two-dimensional (2D) COF networks. In addition, most works focus on theoretical studies. COF-105 was predicted to have 10 wt% excess hydrogen storage capacity at 77 K and 100 bar 24.

POPs

There are various amorphous POPs, such as conjugated microporous polymers (CMPs), polymers of intrinsic microporosity (PIMs), hypercrosslinked polymers (HCPs), porous aromatic frameworks (PAFs) *et. al.* 25 Li-CMPs 26 and Li@PAF-1 27 showed dramatically high hydrogen storage performance at atmosphere and 77 K, 6.1 wt% and 2.2 wt%, respectively. Frankly to say, hydrogen storage in POPs for practical use is not ideal, due to the low interaction enthalpy between POPs and hydrogen molecule. To enhance the interaction, strong binding sites were introduced in POPs, such as MeLi 28 and Li^+ 29. Fine tune the nanostructure of POPs is another way to enhance the hydrogen uptake. Hydrogen uptake of 2D microporous polymers was 12.4 mmol g^{-1} (2.4 wt%) at 77.3 K and 1.13 bar, the highest hydrogen uptake among HCPs materials 30.

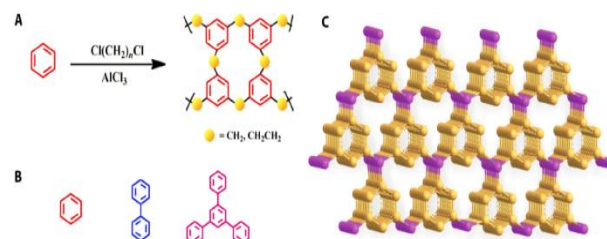


Fig. 2. Synthesis of polymers and building block structures and layered modeled structure of polymers. (A) The synthetic pathway to produce the network structure. (B) Molecular structures of the building blocks for the network. (C) The layered model of benzene-based polymer 29.

Conclusion and future perspectives

Physical hydrogen storage demonstrates great potential in onboard automotive systems. Design and synthesis of novel materials with controllable nanostructures to meet the DOE targets is very essential. Before achieving the final goal, two points should be pay attention to.

With the development of synthetic chemistry, it is difficult to imagine the number of possible porous materials. Therefore, by virtue of computational tools, such as Materials Genome 31 and high-throughput computational methods 32, to screen potential nanoporous adsorbents with optimal hydrogen storage performance is more efficient than experimental synthesis strategy. For example, computational tools analyzed the Nanoporous Materials Genome with more than 850000 materials to explore the optimal features for hydrogen storage 31. Similarly, 137953 hypothetical MOFs were evaluated to predict the hydrogen capacity at cryogenic conditions 32.

To warrant the reproducibility of the experimental results is equally important. In the early 2007, Yaghi and co-workers verified the hydrogen uptake capacity of MOF-177 by three different instruments, aiming to illuminate the importance of calibrating testing instrument 33. Recently, Broom and co-workers once again emphasized the irreproducibility problems 34. In fact, Southwest Research Institute (SwRI) is DOE-approved facility for independent measurements of hydrogen uptake 33. However, it is impossible to send each sample to this facility. Calibrating gas adsorption equipment of ourselves is a feasible way. Systematic error is the main problems, due to the improper null calibration 35. Discrepancies of PCT (pressure-concentration-temperature) curves derived from the same raw data but based on the different null calibration constants are distinct. That's why irreproducibility data occurred.

In all, hydrogen as a clean energy has its brighter future. Developing physisorptive adsorbents with larger binding energy (15-20 kJ mol⁻¹) 33 and with high hydrogen storage capacity under room temperature is researchers' top-priority.

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