

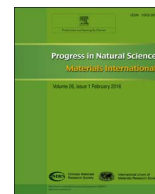
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Review

Synchrotron radiation X-ray powder diffraction techniques applied in hydrogen storage materials - A review[☆]Honghui Cheng^{a,*}, Chen Lu^a, Jingjing Liu^a, Yongke Yan^a, Xingbo Han^{b,*}, Huiming Jin^a, Yu Wang^b, Yi Liu^b, Changle Wu^c^a College of Mechanical Engineering, Yangzhou University, Yangzhou 225127, China^b Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China^c Test Center, Yangzhou University, Yangzhou 225009, China

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ABSTRACT

Synchrotron radiation is an advanced collimated light source with high intensity. It has particular advantages in structural characterization of materials on the atomic or molecular scale. Synchrotron radiation X-ray powder diffraction (SR-XRPD) has been successfully exploited to various areas of hydrogen storage materials. In the paper, we will give a brief introduction on hydrogen storage materials, X-ray powder diffraction (XRPD), and synchrotron radiation light source. The applications of ex situ and in situ time-resolved SR-XRPD in hydrogen storage materials, are reviewed in detail. Future trends and proposals in the applications of the advanced XRPD techniques in hydrogen storage materials are also discussed.

1. Introduction

Hydrogen is very advantageous in the sense that (i) it is a clean burnable fuel, (ii) it possesses a high energy density, and (iii) it is widely distributed all over the globe. In spite of all these advantages, a dependable economic system based on H₂ fuel could not be easily established due to many technical challenges, such as hydrogen production, storage and application. Among these, hydrogen storage presents a huge challenge. It was proposed by U.S. Department of Energy (USDOE) that a hydrogen storage media with 5.5 wt% reversible hydrogen capacity under affordable conditions should be established for commercial onboard applications [1]. Both high compression storage and cryogenic storage modes are considered ineffective due to high cost and safety concerns [2]. Accordingly, the effective means of hydrogen storage system appears to be reversible hydrogen storage materials. A lot of these materials have been investigated but none of them offers the required performances of USDOE. After decades of extensive investigation, it is now concluded that the USDOE aim can be achieved only through light weight materials, particularly with elements having atomic number < 20. In fact, many high capacity materials are known with capacity even more than double the USDOE target. But these hydrides are either too stable or unstable and not reversible under moderate conditions. Hence, research efforts like catalyzing high capacity hydrides, decorating/doping particular

sites for tuning the properties, and chemical modifications for enhancing the thermodynamic features and tailoring of new light weight composite systems have been attempted to develop a new material capable of reversibly storing hydrogen under moderate conditions, and meanwhile exhibiting high capacity and quick reaction kinetics.

The properties and performances of materials are strongly correlated to their microstructures. Synchrotron radiation X-ray powder diffraction (SR-XRPD) is a puissant and special characterization technique that exploits the interaction between synchrotron radiation (SR) X-ray and matter to investigate the microstructures of materials. SR-XRPD is more accurate to evaluate phase composition, crystallite size, strain and defect and allows time-resolved studies. Although hydrogen storage materials are a big family consisting of thousands of members, we limit our discussion scope to those materials widely concerned in the present review. We initially address the basic aspects of hydrogen storage materials, X-ray powder diffraction (XRPD), and SR light source. A detailed introduction of recent advances in a variety of SR-XRPD applications in hydrogen storage materials is sequentially indicated. The future trends of the research field are finally discussed.

2. Hydrogen storage materials

The interaction mechanisms between hydrogen and host material can be categorized to physisorptive binding of molecular hydrogen and

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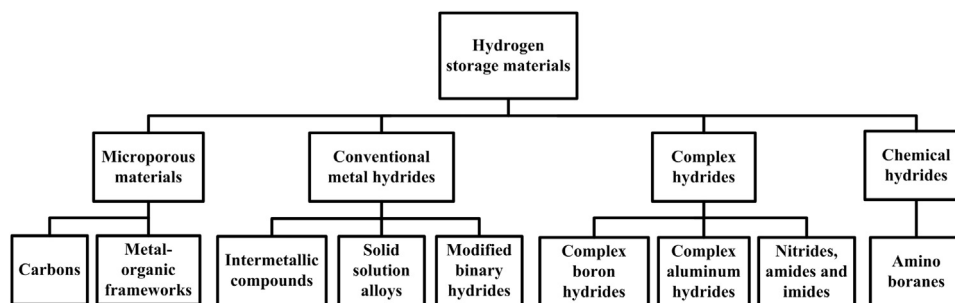


Fig. 1. Family tree of hydrogen storage materials.

chemisorptive binding of atomic hydrogen [3]. The forces involved in physisorption are weak Van der Waals forces. This process usually occurs with fast kinetics because no activation energy barrier is involved. Chemisorption requires energy of $> 436 \text{ kJ mol}^{-1}$ to break the bond of H_2 . Therefore, this interaction exhibits slower kinetics. If the barrier is large, the reactants are required to be activated, by either carrying out the reaction at high temperature or introducing catalysts. The catalytic component does not change the basic reaction thermodynamics, but enhance the reaction rate. It is desirable that the employed catalyst is in nano-sized and disperses throughout the system to increase catalyzing efficiency. Hydrogen storage materials are usually classified into four broad categories using a combination of two criteria: (i) the nature of their sorption mechanism, and (ii) the identity of the material itself [4]. As shown in Fig. 1, these four categories are microporous materials, conventional metal hydrides, complex hydrides and chemical hydrides.

Microporous materials have pore dimensions of $< 2 \text{ nm}$ and extraordinarily large surface areas. The amount of adsorbed hydrogen and the surface area are generally in the direct ratio. These materials adsorb H_2 through physisorption. Materials in this category mainly include carbons [5] and metal-organic frameworks (MOFs) [6]. Carbons can be differentiated into a variety of forms such as activated carbons, fullerenes, and carbon nanotubes. MOFs are crystal materials constituted of metal ions or clusters linked by organic bridges. Both carbons and MOFs are striking materials for hydrogen storage, as they have the potential to be reversible and low-cost with facile hydrogen absorption/desorption kinetics and favorable gravimetric capacity. However, the problem is that the materials tend to possess high storage capacities only at low temperatures near the boiling point of liquid N_2 . Therefore, one big research challenge for these materials is to increase the hydrogen binding strength to above $15 \text{ kJ mol}^{-1} \text{ H}_2$.

Conventional metal hydrides store atomic H in the bulk of the materials and have been studied for more than half a century [7,8]. H_2 is split into atomic H on the material surface and then diffuses into its bulk. However, the gravimetric capacity of these materials is mostly too low, or the thermodynamics of H bonding is either too weak or too strong for automotive applications. For example, AlH_3 has fantastic gravimetric capacity (10.07 wt%). Whereas, due to a low formation enthalpy of -6.0 – $-7.6 \text{ kJ mol}^{-1} \text{ H}_2$ [9] for AlH_3 directly from Al and H_2 , it is unattainable to directly regenerate AlH_3 from H_2 and Al under modest pressure. MgH_2 has a comparatively high gravimetric capacity (7.66 wt%) too, but suffers from too strong binding energy ($\Delta H = -66$ – $-75 \text{ kJ mol}^{-1} \text{ H}_2$), demanding about $290 \text{ }^\circ\text{C}$ to desorb H_2 at 0.1 MPa [10]. Besides, metal hydrides with reasonable cohesive energies, e.g. LaNi_5H_6 , have good thermodynamics ($\Delta H = -30$ – $-43 \text{ kJ mol}^{-1} \text{ H}_2$), but are comprised of heavy transition and rare earth metals, and therefore have low gravimetric densities (1–4 wt%).

Complex hydrides are a kind of ionic compounds which are constituted by metal cations (e.g. often Li^+ , Na^+ , Mg^{2+} , and Ca^{2+}) and H-containing “complex” anions (e.g. often BH_4^- , AlH_4^- , and NH_2^-). Hydrogen atoms and central atoms are covalently bonded in the complex. Thus, complex hydrides are classified as chemisorptive

mechanism. Examples of distinguished complex hydrides include LiBH_4 , NaAlH_4 and LiNH_2 . The strong interest in the hydrides is the result of their uncharacteristically high possible storage capacities (e.g. 18.36 wt% for LiBH_4). Nevertheless, there are serious limitations to their practical use, which include high hydrogenation/dehydrogenation temperatures (100–300 $^\circ\text{C}$ or even higher), slow kinetics, and high sensitivity to air and moisture. Especially for Li–N–H system, NH_3 liberation during the dehydrogenation reaction is also an issue, because NH_3 is a very strong poison for membranes of polymer electrolyte membrane fuel cell (PEMFC). To this kind of hydrides, the research aim is often to avoid byproducts and lower the hydrogen cohesive energy [11–14].

Chemical hydrides are non-reversible storage materials that require an off-board regeneration process [15]. However, some chemical hydrides have high gravimetric and volumetric capacities, and moderate operating conditions which are often less than $80 \text{ }^\circ\text{C}$ at 0.1 MPa hydrogen pressure. NH_3BH_3 is a hopeful solid-state chemical hydride with hydrogen content of 19.6 wt%. Hydrogen desorption from NH_3BH_3 is mostly carried out via thermolysis, because it has good storage capacity for automotive applications. The thermolysis of NH_3BH_3 involves three sequential steps occurring at 70–112, 110–200 and 500–1100 $^\circ\text{C}$, with 6.5 wt% H_2 liberated in each step. A primary challenge for NH_3BH_3 is to improve the dehydrogenation rate at low temperatures about $85 \text{ }^\circ\text{C}$ which is the PEMFC functioning temperature and simultaneously prevent the generation of harmful byproducts (e.g. $(\text{BH})_3(\text{NH})_3$) to electrodes. In addition, avoiding the formation of very stable dehydrogenated products is also a big challenge. [16].

As we know, materials are constructed by atoms. Knowledge of how atoms are arranged into crystalline structures and microstructures is important for understanding of the structure, synthesis and properties of materials. Since hydrides normally exist in powder state, powder diffraction with X-rays or neutrons are the main techniques for finding the atomic arrangements. Because neutrons are sensitive to low atomic number elements, such as hydrogen and boron, and skilled in distinguishing elements with adjacent atomic numbers, such as Fe and Co, isotopes of the same element, or element groups whose atomic numbers are wide apart, such as Pd and H, the extracted information of neutron powder diffraction (NPD) is unique compared to that obtained from XRPD. However, many disadvantages, such as need of large sample, small neutron flux, and low availability, make that NPD is only a supplementary technique to XRPD in the field of hydrogen storage materials.

3. X-ray powder diffraction

X-rays going through a crystal will be scattered by the electron clouds of atoms and bent at different angles. The process is called diffraction. Thanks to its advantages of rapid, non-destructive analysis without troublesome sample preparation, XRPD is extensively used to obtain the structural information of hydrides. In addition, the XRPD instrumentation is flexible, allowing both Bragg-Brentano (flat-plate)

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