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Chapter 1

Introductory Chapter

Jianjun Liu

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1. Introduction

1.1. Importance of developing hydrogen energy

As the global consumption of fossil fuels is growing at an alarming and unsustainable rate, the associated emissions of greenhouse gases and other toxic pollutions are reaching levels that are environmentally unacceptable. A large challenge of world economic development requires meeting the demand of energy consumption while reducing emissions of greenhouse gases and pollutants. Since the sun is our largest and cheapest energy resource, the utilization of solar energy is considered as the ultimate strategy for solving this problem. It continuously bombards our planet with solar energy, with 1 h of solar energy equating to more than all of our annual energy consumption [1]. Among the limited methods for solar energy conversion and utilization, solar water splitting to make hydrogen has been considered as one of the most effective and cleanest ways. Hydrogen, as an energy carrier, is widely regarded as a potential cost-effective, renewable, and clean energy alternative to petroleum, especially in the various transportation tools [2]. The hydrogen produced by solar energy can then be used by fuel cells to generate electricity with zero-emission of water. Figure 1 displays the scheme of renewable energy based on some selected technologies including hydrogen production, storage, and utilization.

Although a great deal of efforts have been made to develop a sustainable hydrogen economy, many challenges still exist in many research fields such as hydrogen generation, storage, and fuel cells in the cyclic system. In order for solar energy to be the major contributor to generate clean hydrogen, the conversion efficiencies of solar water-splitting devices need to be improved, for example, developing highly active catalysts for hydrogen/oxygen evolution reactions. One significant barrier that prevents the widespread use of hydrogen as an energy source is the lack of efficient hydrogen storage systems. For on-board application, the hydrogen storage system is required to provide the needed quantity of hydrogen with accepted

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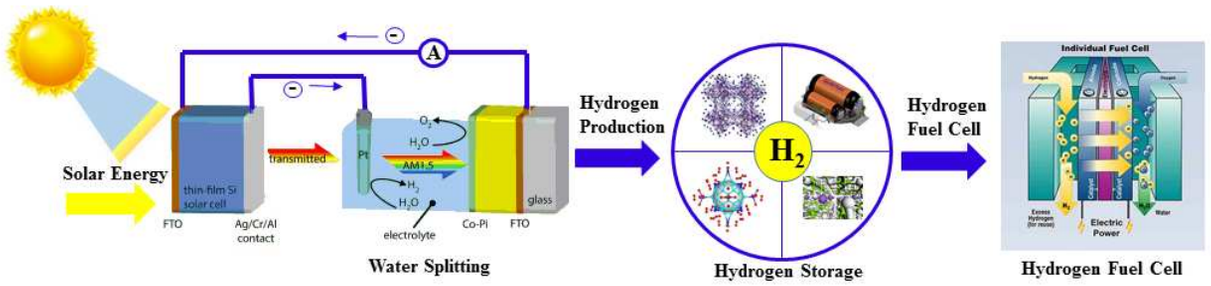


Figure 1. A scheme of renewable energy (solar energy to hydrogen) based on some selected technologies including hydrogen production, storage, and utilization.

engine. The currently available hydrogen storage systems include compressed hydrogen, nanomaterials, metal hydrides, and complex metal hydrides. Each can meet some of the requirements but none of them meets all the requirements for critical applications. Therefore, developing a compact and efficient hydrogen storage technology is the most technically challenging for achieving hydrogen economy. Hydrogen fuel cells are a pathway to convert hydrogen-carried energy into electricity. The development of high-performance fuel cells is leading to higher efficiencies and cleaner energy utilization than the other conventional technologies. Costs vary over a wide range, and future cost projections depend on mass production estimates, driven by the automobile market, in volumes and quantities that do not represent the volumes of trucks, buses, and trains.

Advances of materials science have generated a significant impact on many technology fields [3]. Scientists always think, work, and interact to develop and optimize advanced materials and process in different time and space scales. Developing high-performance materials is playing an important role in creating new fields of fundamental sciences and promoting practical technologies. In order to achieve a technological breakthrough in effective renewable energy conversion from solar energy to hydrogen energy, we need to develop advanced materials which can be applied in some technologies of hydrogen production, storage, and utilization. To this end, the potential capabilities of advanced high-performance materials must be extensively discovered at a more fundamental level.

The specific aim of this book is to provide a fundamental study and in-depth understanding of mechanisms involved in hydrogen applications. In the past years, there are a few review books to discuss development of advanced materials in hydrogen production, or hydrogen storage, or hydrogen fuel cells. However, a comprehensive review in these three aspects is not found so far. Herein, we intend to provide a complete review in the present and previous research progresses including discovered materials and research methods in experiment and computation.

2. Advanced materials in hydrogen production, storage, and utilization

Nano-photocatalysts for hydrogen production plays an important role in enhancing conversion efficiency from solar energy to hydrogen chemical energy [4]. The highly active catalysts

should have suitable band gaps which are favorable to improve the absorbance of abundant solar light to drive hydrogen and oxygen evolution reactions. In addition, good charge-transfer ability for electrons and holes and high surface catalytic reactivity for half-reaction are very important for this kind of photocatalysts.

Loading cocatalysts onto photocatalysts to form hydrogen or oxygen evolution sites have been considered as an effective method to enhance photocatalytic activity for water splitting. In the past decades, different kinds of materials such as transition metals and transition metal compounds (oxides, carbides, nitrides, and sulfides) have been developed as effective cocatalysts for photocatalytic water splitting [4, 5] Some noble metals such as Pt, Ru, Au, Rh, etc., and metal oxides such as NiO_x, Cr_2O_3, etc., perform well for water reduction cocatalysts by entrapping electrons from semiconductor. In addition, some noble metal oxides such as IrO_2 and RuO_2 as well as spinel and layer materials such as Co_3O_4 and $LiCoO_2$ have been found to have effective water oxidation by entrapping holes [6].

Solid-state nanomaterials for hydrogen storage perhaps offer the best opportunity for meeting the requirements of on-board applications. Nanoscience and nanotechnology involve studying and working with matter on a nanometer scale. Nanomaterials with at least one dimension <100 nm can be in the form of thin films or surface coatings, nanowires and nanotubes, or nanoparticles. The unique properties of nanomaterials originate from the increased surface area and quantum effects, both of which relate to the small size. Therefore, reactivity, strength, and electrical characteristics of nanomaterials may be significantly different from those of conventional materials. For example, a particle 30 nm in size has only 5% of its atoms on its surface. When the size is reduced to 3 nm, the particle has 50% of its atoms exposed on the surface. This makes nanoparticles have a much greater surface area per unit mass than bulk structures. Both surface area and exposed atoms on the surface could be useful for storing hydrogen. Therefore, nanotechnology is expected to play a key role in designing high-capacity solid-state hydrogen storage materials. In fact, the concept of nanoscience and nanoengineering has been actively exploited in improving existing hydrogen storage materials and searching for new hydrogen storage candidates. For example, nanocatalysts have been used to improve kinetics of hydrogen uptake and release or to improve hydrogen storage capacity through spillover [7]. Novel building blocks have been proposed to maximize the hydrogen capacity and optimize the strength of hydrogen binding. Large-surface-area nanomaterials which offer more host atoms/sites for hydrogen and allow easy access of these sites have been synthesized, as in materials such as molecular organic frameworks (MOFs) and covalent organic frameworks (COFs), and show promise as hydrogen storage media [8, 9].

The photoelectrochemical (PEC) water splitting has been considered as the most attractive method over other hydrogen production approaches. The pioneering work of solar-driven water splitting in PEC frame consisted of TiO_2 anode and Pt cathodes for oxygen and hydrogen evolution reaction [10]. In fact, TiO_2 represents one of the most important semiconductor materials for PEC water splitting. However, due to its wide band gap, TiO_2 cannot absorb visible and infrared light for solar water splitting. Doping of many metals and non-metals has been widely adopted to narrow the band gap [11]. In the past decades, many different

nanoengineering methods such as tailoring morphology and composition and interface have been applied to improve the performance of light absorption of TiO_2.

ZnO, another widely used semiconductor, has also been widely investigated as a photoanode of PEC water splitting. In the past years, different approaches including ion doping and visible light sensitization with narrow band gap semiconductors have been used to expand the light absorption region and hence improve the PEC water-splitting performance [12, 13]. Hematite (α-Fe_2O_3) is an increasing promising material for solar-driven PEC water-splitting applications due to its relatively narrow band gap (2.1 eV). However, the poor charge-transfer property of α-Fe_2O_3 greatly prevents its efficiency as a photoanode material for splitting water. Similarly, ion doping and nanocomposition have been extensively applied to improve its charge transfer property [14].

Nanostructured electrocatalysts for hydrogen fuel cells can harness the chemical energy of hydrogen to convert electricity at a high-energy conversion efficiency of >70% without combustion and pollution, owing to the slow kinetics of oxygen reduction reaction on the cathode, which is primarily responsible for reduced voltage and low conversion efficiency. The noble metal Pt has been regarded as the most active electrocatalyst for this reaction. However, the high cost and scarcity of Pt greatly limit the development and widespread commercial application. In the past two decades, many different catalysts such CrN, WC, and Mo_2C have been studied to replace Pt [15]. Although none of them has a comparative catalytic activity as Pt, their resource is abundant and available at low cost.

3. Outline of the book

The primary focus of the book is on developing advanced materials for hydrogen production, storage, and utilization. Unravelling structure-related chemical/physical properties of these materials plays an important role in designing high-performance materials. The chapter is concluded with a descriptor of chemical and physical properties of materials.

Chapter 2 presents electron-microscopic, energy-dispersion, and optical (IR-absorption and low-temperature (4.5 K) photoluminescence) investigations of InSe- and GaSe-layered crystals intercalated using the below considered methods with various concentrations of hydrogen or hydrogen-containing molecules such as water, toluene, and alcohol. These materials have promising applications of these layered matrices (and powders from them) when creating operation elements of solid hydrogen accumulators. At the same time, these InSe- and GaSe-layered crystals themselves with different types of conductivity and their thin-layer intercalates as well as other similar compounds can be considered as promising candidates for creation of various hybrid-layered structures for flat flexible displays. Chapter 3 presents the extensive studies for understanding hydrogen bonding interaction mechanism in biomolecules, which is favorable to develop hydrogen production technology by biomass approach.

As an example for hydrogen storage, hydrogen desorption/adsorption processes in a metal hydride bed reactor are simulated using the software COMSOL Multiphysics to study the

diffusion and heating of hydrogen and metal hydride powder in both radial and axial directions. They are presented in Chapter 4. The model consists of a system of partial differential equations (PDE) describing two-dimensional heat and mass transfer of hydrogen in a porous matrix. The influence of the operating parameters such as temperature, pressure, concentration, permeability, and thermal conductivity on the rate of absorption/desorption of hydrogen in metal hydride will be fully discussed. The simulation results obtained could be applied to the on-board hydrogen storage technology, in particular for the hydrogen supply of a fuel cell for powering of a hydrogen fuel cell vehicle.

Chapter 5 reports a research progress on hydrogen storage based on metal amidoboranes and their derivatives. Extended from ammonia borane as high-capacity hydrogen storage materials, thermodynamic tailing of dehydrogenation of metal amidoboranes, metal borohydride–ammonia borane complexes, and metal amidoboranes ammoniate as well as their derivatives was studied with emphasis on syntheses, crystal structures, and dehydrogenation properties. These studies clearly are greatly important to further design novel high-capacity hydrogen storage materials. In addition, the authors also summarize nanoconfinement and nanocatalysis of ammonia borane and metal amidoboranes, and their derivatives.

Author details

Jianjun Liu*

Address all correspondence to: jliu@mail.sic.ac.cn

State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China

References

[1] L. Vayssieries, *On Solar Hydrogen and Technology*, John Wiley and Sons, Singapore, 2009.

[2] S. S. Mao, S. Chen, *International Journal of Energy Research* 31 (2007) 619–636.

[3] F. D. S. Marquis, *Journal of the Minerals Metals and Materials Society* 63 (2011) 43.

[4] X. Chen, S. Shen, L. Guo, S. S. Mao, *Chemical Reviews* 110 (2010) 6503–6570.

[5] S. Shen, J. Shi, P. Guo, L. Uo, *International Journal of Nanotechnology* 8 (2011) 523–591.

[6] S. Shen, S. S. Mao, *Nanophotonics* 1 (2012) 31–50.

[7] Y. W. Li, R. T. Yang, *Journal of the American Chemical Society* 128 (2006) 726–727.

[8] N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe, O. M. Yaghi, *Science* 3 (2003) 1127–1129.

[9] S. S. Han, H. Furukawa, O. M. Yaghi, W. A. Goddard, *Journal of the American Chemical Society* 130 (2008) 11580–11583.

[10] A. Fujishima, K. Honda, *Nature* 238 (1972) 37–38.

[11] S. U. M. Khan, M. Al-Shahry, W. B. Ingler Jr., *Science* 297 (2002) 2243–2245.

[12] A. I. Hochbaum, P. Yang, *Chemical Reviews* 110 (2010) 527–546.

[13] Y. J. Lin, G. B. Yuan, R. Liu, S. Zhou, S. W. Sheeha, D. W. Wang, *Chemical Physics Letters* 507 (2011) 209–216.

[14] K. Sivula, F. Le Formal, M. Gratzel, *ChemSusChem* 4 (2011) 432–449.

[15] H. Zhong, X. Chen, H. Zhang, M. Wang, S. S. Mao, *Appllied Physics L*etters 91 (2007) 163103.

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