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A review on the characterization of hydrogen in hydrogen storage materials

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ABSTRACT

In order to realize a low-carbon hydrogen economy, a continuous search for materials able to store hydrogen in the solid form has been actively carried out globally. The need to accurately characterize the hydrogen storage properties of a variety of materials, including the thermodynamic and kinetic information, is of paramount importance. However owning to the diversity of potential hydrogen storage materials, it is essential to select a proper technique for characterize hydrogen storage properties to avoid faulty results. This paper serves as a critical review on several techniques commonly employed to characterize hydrogen storage materials. In this context, the working principles, advantages and drawbacks, limitations of six categories of techniques – Sieverts method, gravimetric method, secondary ion mass spectrometry, thermal desorption spectroscopy, neutron scattering and electrochemical techniques – are described and reviewed. It can be seen that Sieverts method is a powerful tool for metal hydride samples under normal testing regime. Gravimetric method can be used to investigate the hydrogen storage of porous samples since it normally suffers less from the sample volume uncertainty, however careful buoyancy correction must be applied to avoid faulty results. Secondary ion mass spectroscopy and thermal desorption spectroscopy can be used to study the surface/subsurface hydrogen profile and thermodynamic/kinetic properties of gas desorption of sample, respectively, providing that these samples are stable under vacuum. Neutron scattering is capable of investigating varies types of information including structural, diffusion and hydrogen dynamics of host material under in-stiu environment, although the neutron resources is not always accessible for most researchers. Electrochemical method can be used to study thermodynamic/kinetic properties for both thin film and bulk samples, but it may not be applicable to samples with low corrosion resistance and high plateau pressure.

1. Introduction

Worldwide demand for green energy to replace fossil fuels has risen drastically in the last few decades. Hydrogen is regarded as a promising candidate of energy carrier owing to its high energy density per unit mass, availability and minimum environmental impact when hydrogen can be produced from renewable resources such as photoelectrochemical, biological process, and wind energy [1,2]. Opportunities and challenges in the realization of a hydrogen economy have been identified, and possible strategies to overcome these challenges are proposed [3–5]. One of the challenges is the safety of efficient storage and transport of hydrogen. Compared with gaseous and liquid state hydrogen storage, solid state hydrogen storage is favored because of safety consideration and high volumetric capacity. A large number of researches have been carried out to investigate the ideal materials for hydrogen storage, including intermetallic compounds [6], metal-organic frameworks (MOFs) [7], porous materials [8], complex hydrides [9], and nano-structured carbonaceous materials [10].

In general the hydrogen content of a sample refers to the hydrogen-to-host atomic ratio, H/X, where X represents the number of moles of the host material:

$$\frac{H}{X} = \frac{n_H}{n_X} = \frac{\frac{m_H}{M_H}}{\frac{m_X}{M_X}} \quad (1)$$

Here, n_H and m_H are the number of moles and the mass of hydrogen absorbed in the sample, respectively. M_x and M_H are the molar mass of host material and hydrogen, respectively. Thus the mass fraction of hydrogen f_H in the host material can be written as

$$f_H = \frac{m_H}{m_X + m_H} = \frac{\frac{H}{X}}{\frac{H}{X} + \frac{M_X}{M_H}} \quad (2)$$

Numerous measurable parameters have been proposed for quantifying the performance of potential hydrogen storage materials.

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Table 1
An overview of the 6 common hydrogen characterization techniques.

Method	Detection limit	Advantages	Limitations	Characteristics
Sieverts technique	Depending on the capability and sensitivity of the pressure transducer	• Cost-effective, • Robust • Relatively simple	• Accumulative errors • Less sensitive to low density sample and porous materials with low storage capacity	A technique based on volume or pressure change, and it is widely applied in the characterization of metal hydride
Gravimetric technique	Depending on the capability and sensitivity of the microbalance	• Error is less sensitive to sample density • Direct and continuous measurement of sample weight changes	• Careful buoyancy correction must be applied to avoid faulty result • Required vibration free environment • Sample has to be very clean and free from any volatile species on the surface	Measuring gas absorption/desorption based on gravimetric change, and it is suitable for low density sample such as CNTs and MOFs
Secondary ion mass spectrometry	Down to 3 x 10^{18} atoms/cm^3 (hydrogen)	• Direct-detection of hydrogen, • Able to acquire localized spatial and in-depth hydrogen profile	• Thermodynamic and kinetic information is difficult to acquired • Sample must be stable in vacuum • Destructive method	Acquiring the surface and sub-surface information via destructive ion bombardment; characterization for both bulk and thin film sample are possible
Thermal desorption spectroscopy	Down to ppm and sub-ppm range	• Direct-detection of hydrogen • Tiny amount of sample (down to 1 mg) is required • Short experimental duration for sample with sluggish kinetics	• The capability of TDS is to study the gas desorption only • The interpretation of TDS spectra can be complicated	Facilitating gas desorption based on applying thermal gradient; quantitative analysis is possible if well calibrated standard is provided; the technique is suitable for sample remain stable under vacuum process
Neutron scattering	Limited by the beam flux, thus the scattering vector, and resolution.	• Sensitive to light elements such as hydrogen and deuterium • Little sample preparation is required. • The technique is capable to acquire structural, diffusion and dynamics information of hydrogen in materials, • In-sit environment can be applied	• Less intense beam, thus larger sample is required. • Neutron source is very expensive and not accessible for most researchers	Information such as the structure of hydrides, and hydrogen diffusion dynamics in the host material can be acquired via reaction with neutrons; this technique is suitable for all types of sample
Electrochemical characterizations	Resolution ranging from nano-ampere to several ampere	• Cost-effective, • Less concern on temperature, pressure control and gas safety • Large detection range	• The results may affected by other parts in electric cell such as positive electrode and electrolyte • Not suitable for sample with high corrosion susceptibility • Capacity measured by the electrochemical method only illustrates the capacity up to 1 atm, and the result is highly dependent on activated surface	Acquiring thermodynamic and kinetic information based on voltage and current response, characterization for both thin film and bulk samples are possible