Review

Solid State Hydrogen Storage in Polymeric Materials: A Review

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Abstract: Hydrogen storage is one of the major obstacles to overcoming so that hydrogen becomes next fuel and/or energy carrier of the future. The hydrogen storage materials are one of the principal challenges that must be met before the development of a hydrogen economy. Among all materials studied an important class that could have a future, in particular in portable applications, is the polymers class. Here are reported some results obtained using different polymeric matrices in different operative conditions.

Keywords: Review on Polymers, Chemical-Physical Characterizations, H_2 Storage

Introduction

Hydrogen is presently considered as one of promising ecologically clean energy carriers for transport of the future. Therewith, the use of a combination of a hydrogen air fuel cell and electric engine, rather that substitution of fossil fuels in Internal Combustion Engines (ICEs) by hydrogen is considered to hold the greatest promise.

Hydrogen fuel cell produce energy with environmentally friendly burning byproducts; however, the low H_2 density obliges that it can be stored in tank sat high pressure (70 MPa) having specifics characteristics in terms of safety, system mass, volume and its cost.

The aim is to have a cheap material, easy to synthetized with good properties in terms of H_2 sorption capability, comparable to H_2 compressed (about 5 wt%), at room conditions. As a consequence, the United States Department of Energy (US-DOE) and the United States Council for Automotive Research (US-CAR), promoted the first targets for the materials to be used in automotive application. These targets are changed successively, 2009, reducing the storage capacity until 5 wt% (FCHJU, 2014). Since in this field there is a lot number of materials that are used both in portable and stationary applications, it can be useful to consider them by two kind of mechanisms: (1) Hydrogen chemisorption; atomic hydrogen interacts with the material sites by chemical bonds. The most common materials belonging to this category are metal hydrides, complex hydrides and chemical hydrides. Their good capability to store H_2occurs, after activation steps, by using drastic condition of temperature and pressure. The main drawback of these materials is of thermodynamic nature. A lot papers are carried out to overcome these problems and to achieve fast reaction kinetics (Schüth *et al.*, 2004). (2) Physisorption, molecular H_2interacts on the surface of the material with weak bonds, such as Van der Waals forces, that do not give any alteration in the material. In this class can be considered Metal-Organic Frameworks (MOFs) (Rowsell *et al.*, 2004), nanoporous carbon (Ting *et al.*, 2015), Carbon Nanotubes (CNTs) (Barghi *et al.*, 2014).

The incorporation of nanoparticles or nanoporous structures in polymeric materials may be an alternative to obtain materials with promising properties for hydrogen storage. Different polymers are studied, including: Polyaniline (PANI) (Naresh *et al.*, 2015), Polypyrrole (PPY) (Nour *et al.*, 2014), polythiophene used as activation material for porous carbon (Sevilla *et al.*, 2011), hyperbranchedpolyurea (P-Urea) (Rehim *et al.*, 2011), hyperbranched Poly (Amide-Amine) (PAMAM), Polymer Dispersed Metal Hydrides (PDMH) (Schmidt, 2001). Another big class of polymers is represented by Microporous Poymers (Wood *et al.*, 2007; Li *et al.*, 2010).

Other interesting class is composed by composite polymers were metal oxide, such as Mn oxide, is synthesized in situ (Pedicini *et al.*, 2011; 2014; 2017).

Hydrogen Storage Measurements

To know the real H_2 storage capabilities of solid materials different methodology are used, among all, gravimetric and volumetric methods are more common. These characterizations give lot information not only in term of H_2 sorption/desorption properties, but in

addition, the energy and the thermodynamics aspect of the reactions. Each of these measurement methods has different characteristics; in this way to determine whether it is more suitable it is important to know what type of reaction occurs, chemisorption or physisorption. Gravimetric method is a direct way to know H_2 storage capacity as the final result gives a H_2 % of sorption. On the contrary, a drawback of this apparatus is determined at the start of the measurement in which the Buoyancy effect can condition the final value. Volumetric measurement is a indirect method were the H_2 wt% it is possible calculate knowing the volume, H_2 moles and pressure value. The main drawback of this technic is the H_2 leak can be occur during the measure; this no real value could be considered as H_2 adsorption.

Volumetric Method

This method, named Sievert apparatus also, gives the H_2 storage value through temperature-pressure-volume correction. As before described, this kind of measure is an indirect method so volumes and temperatures of tank and sample must be known in advance. A thermocouple is located close to sample holder and the T must maintain constant during the measure; the calibrate volume must be chosen carefully. The pressures of the tank and the sample holder can be measured using pressure transducers.

Normally, H_2 tank is set at a specific pressure (measurement pressure) and, after some minute that it is necessary to reach the thermic equilibrium, it can be recorded the H_2 storage value (Blach *et al.*, 2007; Webb *et al.*, 2013).

Gravimetric Method

This methodology uses a microbalance to know in real time the changing of the sample mass during the measurement. Generally, before the test, it must be known the sample mass, in this way it is possible, by the difference of two values, the real percentage of H_2 adsorbed. The sample holder is designed to minimize the Buoyancy effect, that can give and important error in the first step of the measurement. The chamber containing the sample holder is filled with hydrogen at a certain pressure, with a temperature and volume known. During the measurements, if there is a sorption of gas there will be an increase in sample mass and a decrease of pressure (Ansòn *et al.*, 2004).

Comparison Results

One of the most widely used materials in hydrogen storage is the Polyaniline (PANI). Some years ago first studies was carried out on treated PANI and PPY. The authors confirm that the HCL treatment for both polymer promote the H_2 sorption properties, in fact, they report an H_2 storage value in a range of 6-8 wt%

at 298 K and 90 bar (Cho *et al.*, 2002). This result, although the same materials and the same procedure have been used, the same results have never been achieved (Panella *et al.*, 2005).

The possible explanation of this increased H_2 sorption capacity was in the formation of microporous in the structure after the acid treatment (Deb *et al.*, 2007). This possible PANI characteristic has increased the interest of the researcher for this polymer; so, PANI having different morphology such as Fibers and Nano-Fibers (PANI-NF) had produced several interesting results with very easy synthesis and controlled porous (Long *et al.*, 2011).

Some PANI-NF mixed to surfactant and sucrose were obtained. The hydrogen uptake using a surfactant, at 298 K and 80 bar, was about 3 wt% (Jurczyk *et al.*, 2009). A higher value, at room temperature and 20 bar, than previous sample was obtained using sucrose in the synthesis; this kind of materials adsorbed 4,3 wt% of H_2 (Rahy *et al.*, 2011).

Another approach, using PANI as a matrix, was utilising different nanomaterials having different characteristics. These nanofillers, thought as catalysts, can be improve the H_2 storage properties of the modified PANI. Some of these, such as MWNTs, SnO_2 and Al powder, were found interesting H_2 storage value in a T range of 298-398 K. In fact PANI with Al powder at 398 K improve the H_2 sorption of pristine PANI from 0,35 to 0,5 wt% at 60 bar (Jurczyk *et al.*, 2007).

This kind of materials, due to their good adsorption kinetic reaction, better than metal hydrides, have obtained very attention, in particular in the last years (Germain *et al.*, 2009). The modified PANI, utilising different cross-linking agent, showed a high surface area reaching a value up to 632 $m^2 g^{-1}$.

The hydrogen storage values, operating at 77 K and 60 bar, were about 2,5 wt% (Germain *et al.*, 2007).

Another kind of polymer, Polythiophene activated with KOH solution, produces porous carbons having a surface area up to 3000 $m^2 g^{-1}$ (Sevilla *et al.*, 2011). A very high hydrogen storage value, 5,71 wt%, was found at 77 K and 20 bar, while at 1 bar hydrogen uptake decreases at 2,33 wt%.

Hyperbranched Polyurea (P-Urea) was characterized in cryogenic condition up to 20 bar. These isotherm test reveala linear correlation between the hydrogen storage percentage and the pressure test, in-fact, the trends shows at 5 bar, 0,3 wt% of H_2 sorption, increasing the pressure at 15 bar its H_2 storage capability increases until 1 wt%. At the end of the test, over than 20 bar, it stores about 1,4 wt%.

Pure Hyperbranched poly (amide-amine) (PAMAM) and PAMAM composite with Vanadium Oxide (VO_x) were studied in cryogenic conditions. Pure PAMAM is able to adsorbs 0,9 wt% at 25 bar while pure VO_x adsorbs about 0,6 wt% at 20 bar. Both H_2 adsorption trend are linear thus, their H_2 storage capacity have a direct proportionality.

To increase the H_2 storage capacity of PAMAM, VO_x was incorporate in the polymeric matrix to develop PAMAM/VO_x nanocomposite. A new composite material shows an increase of H_2 sorption reaching 2 wt% under the same measuring conditions (25 bar). Due to a layered structure, VO_x should increase the interlayer distance leading a more high hydrogen uptake.

Other interesting classes of materials are Polymer Dispersed Metal Hydrides (PDMH). The aim is to disperse metal hydrides in a particular polymeric matrix with a final product having a high H_2 storage capacity, due to metal alloy presence and low density since polymeric matrix gives this properties to the hybrid material. The dispersion of the metal hydride in a polymeric matrix gives an increase of the metal alloy stability, in particular during H_2 charge/discharge cycles; in addition, a possible little quantity of hydrogen could be stored in the polymeric layers.

Polymers with Intrinsic Micro porosity (PIMs) having lately very importance due to their important morphological characteristics.

PIMs are amorphous organic micro porous materials that have the pores size less than 2 nm diameter. PIM micro porosity derives from the fused ring structures, which prevent free rotation along the polymer backbone, resulting in a highly rigid and contorted fixed shape. Therefore, the final product will have a several number of free volumes, as a consequence of a surface area up to 2000 m^2 g^{-1}. PIMs couple the advantages of polymers with the advantages of conventional micro porous materials. In this kind of materials there is a direct correlation between surface area and hydrogen storage capability. Considering, for example, a PIM obtained by mixing Catechol and Aryl alide, has a surface area ranging between 760-850 m^2 g^{-1} with a H_2 sorption capacity of about 1 wt% at 77 K and 1 bar. Another network polymer demonstrating a large surface area of 960 m^2 g^{-1} is composed by Porphyrin and PIM. This kind of material shows a more high surface area, of about 960 m^2 g^{-1}, adsorbing 1,9 wt% of H_2 in the same measurement conditions. A very high surface area of a mixed PIM with Tripticene was found, about 1159 m^2 g^{-1}, the relative H2 sorption test, at 77 K and 1bar reveal a H_2 sorption value of 1,83 wt% that increases until 3,2 wt% at 10 bar.

Another innovative class of hydrogen storage materials consists of composites polymer using a metal oxide (Manganese Oxide) as adsorbent material anchored to a polymeric matrix (Polyetheretherketone, PEEK). Functionalised PEEK, using Chlorosulfonic acid, shows a higher sulphonation degree (over that 100%) (Pedicini et al., 2011). Manganese oxide was inserted using a Mn precursor such as $KMnO_4$ solution at different concentration (from 0,02 M to 0,1 M). This reaction can occurs changing the experimental parameters as temperature and time of reaction. In this way, different Mn oxide content was obtained (starting from 15 wt% until 82 wt%). XRD analyses reveal the anchorage of the oxide with a probable crystalline structure based on Birnessite (lamellar structure). This kind of oxide, confirmed XPS analyses, was MnO_2. H_2 sorption measurements in cryogenic conditions showed interesting values of sorption: 1,1 wt% at 1bar after different H_2 sorption desorption tests Fig. 1.

More high H_2 storage values were obtained in a T range between 323-383 K using Sievert apparatus. As reported in Table 1, increasing MnO_2 content increases the H_2 storage capacity. It was found that the T of the synthesis cannot overcome 323 K since, a more drastic condition, an irreversible H_2 sorption trend was recorded (Wood et al., 2007) (15).

Limiting the T of the synthesis at 323 K and testing these samples in the same T condition were obtained very promising results, as reported in Fig. 2a and 2b.

The final H_2 sorption value obtained was about 3,5 wt%, even if the kinetic reaction was very slow. The reversibility was verified by H_2 sorption/desorption cycles Fig. 2b in which a very short time it is necessary to desorb H_2.
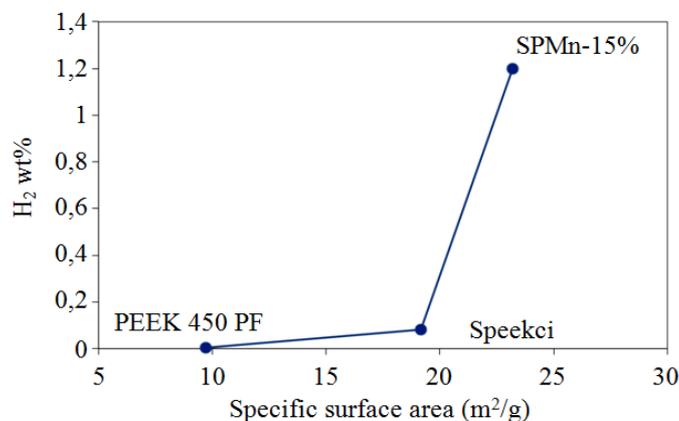
Fig. 1. H_2 sorption trend at 77 K/1 bar
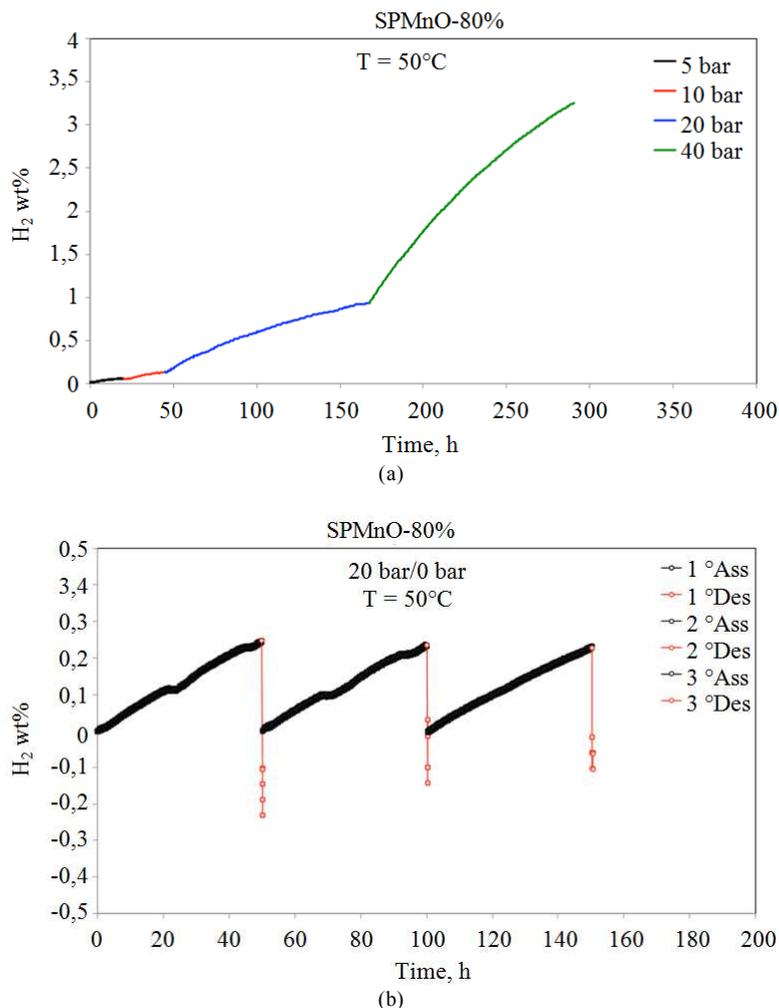
Fig. 2. (a) H_2 sorption test and (b) short H_2 sorption/desorption test. It reproduced with permission of Elsevier

Table 1. H_2 sorption values of synthetized materials

MnO_2 wt%	T/K	P/bar	H_2 wt%
15	383	40	0,1
20	383	60	0,2
78	383	60	1,2
80	323	40	3

Conclusion

The hydrogen storage properties of some materials based on polymeric matrix were discussed. In these last years, this kind of materials have been mostly studied since they have interesting characteristics to promote a fuel cell portable applications and, consequently, the H_2 use as a fuel. A lot of papers focus their effort considering common polymers such as PANI, PIM, PEEK etc., modifying their morphology and/or structure mixing them with metals, metal oxides or other porous polymers. The mainly of the polymeric materials have the best H_2 storage performances in cryogenic conditions. Lately, these new classes of functionalized polymer act over than room temperature in not drastic condition in term of P. The aim, as well as other types of materials, is to be able to approach the DOE targets, over than 5 wt% of H_2 sorption.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and there are no ethical issues involved.

Conflict of interest

The author declare that have no conflict of interest.

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