INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2015) 1–15

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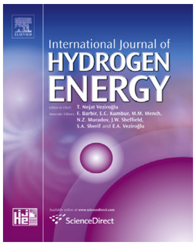

Hydrogen storage at low temperature and high pressure for application in automobile manufacturing

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ARTICLE INFO

Article history:
Received 14 September 2015
Received in revised form
18 November 2015
Accepted 19 November 2015
Available online xxx

Keywords:
Hydrogen energy
Cryogenic storage
High-pressure
Adsorption modeling
Porous carbon

ABSTRACT

A brief review of the different methods of hydrogen storage process for application in automobile manufacturing was presented and discussed. The hydrogen storage by adsorption on super activated carbon AX21 at various thermodynamic conditions was investigated. In order to describe the reality of the system, we planned a brief review, a discussion and modeling of the different EOS equations adapted to a hydrogen gas. Different characterization tools for obtaining the physical property of AX21 were used, among them SEM, BET and Helium displacement method at high temperature. The hydrogen storage capacity of AX21 at different temperature and pressure up to 70 MPa was investigated experimentally. In order to describe the experimental hydrogen gas excess adsorption results, the model of Chilev and a modified potential theory were selected. The comparison of the two models describing adsorption isotherms and a critical discussion of their accuracy was given. Based on the models results the absolute amount adsorbed was obtained. The difference between an absolute and an excess amount adsorbed at 77 K and 293 K was discussed. A comparison between the volumetric tank capacity obtained by pure compression and the adsorption process at both temperatures were studied. The method of hydrogen storage and optimal operating conditions were investigated.

Introduction

The decrease in the global stocks of conventional fuels such as oil, coal and natural gas leads to an increase in their prices. Furthermore, the use of these energy sources is associated with significant environmental pollution which leads to global climate changes of the Earth. Therefore it is a very important research related to finding alternatives of conventional fuels. One of the best candidates for this is hydrogen. There are two primary uses of hydrogen today. In the first case the hydrogen is used in the Haber process to produce ammonia, which is then used directly or indirectly as a fertilizer. In the second case the production of hydrogen is used to convert heavy petroleum sources into lighter fractions suitable for use as fuels. This process is known as hydro-cracking. Recently hydrogen has drawn attention as a next-generation energy carrier for mobile and stationary power sources [1]. It is a carrier of the so-called "clean" energy [2,3] because when hydrogen is used as an

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http://dx.doi.org/10.1016/j.ijhydene.2015.11.099

Please cite this article in press as: Chilev Ch, Lamari FD, Hydrogen storage at low temperature and high pressure for application in automobile manufacturing, International Journal of Hydrogen Energy (2015), http://dx.doi.org/10.1016/j.ijhydene.2015.11.099

energy source there are no released harmful emissions. Problems associated with the use of hydrogen as an alternative of conventional fuel are both its production and safe storage.

The topic our research is related to the modification of the safe storage method of hydrogen.

Most research into hydrogen storage is focused on storing hydrogen for mobile applications. The most important of these applications is related to the use of hydrogen in the automotive manufacturing. The target of the United States Department of Energy [4] (DOE) for the year 2015 is a refueling time of less than 5 min. The requirements defined by the fuel cell propulsion system and by customer demands such as: cost, overall fuel capacity, temperature, min/max delivery pressure, refilling time, the cycle life, and the fuel purity are also crucial to the performance of the storage system. By Felderhoff [5]et al. a critical review about the advantages and disadvantages of such systems and strategy of hydrogen storage methods has been given. One of the most important DOE targets is the storing hydrogen on-board of conventional automobile to enable a 300-mile driving range. The storage of hydrogen on board can be carried out without adding significant weight, volume or price to today's conventional automobile. A minimum of 5 kg of hydrogen [4] would need to be stored on-board to drive even the most fuel-efficient vehicle for three hundred miles. The methods for a mobile hydrogen storage can be divided into a physical storage, where hydrogen molecules are stored (including hydrogen storage via compression and liquefaction), and a chemical storage, where hydrides are stored.

There are many methods for chemical storage of hydrogen into different types of materials such as Metal hydrides [6–10], Carbohydrates [11], Synthesized hydrocarbons, Ammonia [12,13], Liquid organic hydrogen carriers (LOHC) [14], Borane complexes [15,16], Graphene [17,18]. These methods are characterized by a high hydrogen adsorption capacity, but they have a number of disadvantages which prevent practical application. For example, a review for the recent application of metal hydrides to the board of conventional transport is done by B. Sakintuna [10]et al. According to the authors the metal hydrides is no perfect choice of hydrogen store material to meet the set US DOE goals for transport applications. Further research is needed to develop materials satisfying the needs for technical applications. If used Carbohydrates [11], The rate of biochemical reactions is small and it cannot ensure the required amount of hydrogen for vehicle acceleration. In the case of synthesized hydrocarbons, a partial reforming must be done to extract the gas. These reforms are slow to react to changes in demand and add cost to the vehicle. Furthermore, the high temperature and slow startup time of these fuel cells are problematic for on-board applications. The basic difficulty for these applications of Liquid hydrogen carriers [14] is the limited cycles of regeneration and the high costs of LOHC. Borane complexes [15,16] are too expensive or toxic and it is not easily reversible, i.e. not able to be refilled with hydrogen. Ammonia borane would likely have to be removed from the vehicle and be sent to some sort of processing plant and undergo a reaction to be refilled. Graphene [17,18] has a high hydrogen density and it is possible to store hydrogen for hydrogen fuel technologies. However, points out that the discovery of graphane is just one small step because it now exists as little atomic flakes. Hydrogenating a little atomic flake is not creating a hydrogen storage tank [19].

Classical methods for a physical storage of hydrogen are compressed hydrogen, liquid hydrogen and cryo-compressed hydrogen. Compressed hydrogen is the oldest method for hydrogen storage. Hydrogen tanks at 35 and 70 MPa is used for on-board hydrogen storage [20–22]. Using this method, the technology is simple and inexpensive. Limitations of this method are due to the low volumetric density and the risk of accidents. In case of an accident hydrogen is released instantaneously over time, which significantly increases the risk of explosion and is a huge minus for a safe operation. Hydrogen has a high gravimetric energy density (120 MJ/kg) but its volumetric energy density is the lowest of all common fuels. These two density types may correspond either to a materials approach or a systems approach. In the materials approach both densities refer only to the physical object (hydrogen). In the systems approach the energy density levels refer to the all storage system elements, i.e. include all required components and mounts. In the aim of automotive manufacturing, the second approach is preferable [4]. The pure compression hydrogen storage method is highly competitive on a system energy density level [5]. Car manufacturers have been developing this solution, such as Honda [23] or Nissan [24]. High pressure systems up to 70 MPa are the most common solution in light-duty vehicles, whereas 35 MPa systems are used for buses.

Hydrogen can be stored as a liquid at 21.2 K at ambient pressure in cryogenic tanks [22,25]. The cooling and compressing process requires energy, resulting in a net loss of about 30% of the energy stored in the liquid hydrogen [26]. Many other methods for physical storage of hydrogen exist. For example, a mixture of about 50% solid and 50% liquid hydrogen at a triple point temperature (13.8 K) and the corresponding vapor pressure (0.007 MPa) is called *“slu sh”* hydrogen [27,28]. Other methods are hydrogen storage in porous glass [29–33], clathrate hydrate [34], metal-organic frameworks [35], carbon nanotubes [36,37] and activated carbons [38–40]. There are also mixed models representing a combination of those listed earlier such as cryo-compressed hydrogen [41–43]. In 2012 Chilev [44] et al.studies the possibility of hydrogen storage using modified sorbents. Materials are active carbon AC35 [44] in whose structure particles from various metals: Ni, Ni + La and Ni + MM (from German: Mischmetall - “mixed metal” see reference 44) are implanted. The structural study of the activated carbon AC35 is related to the possibility of storing hydrogen by combining physical adsorption on the inner surface of the material and the formation of metal hydrides of these metals in order to increase the total capacity. We can conclude that physical methods for hydrogen storage have more advantages than chemical ones.

The cryo-compressed system has several advantages over liquid hydrogen systems: a dormancy advantage, the option to fill with ambient temperature hydrogen for reduced travel requirements, potentially lower fueling station costs, and a simpler method for monitoring hydrogen in the tank. According to TIAX [45] the cost is estimated to be $14/kWh. This cost is about 50% less than current 70 MPa and 20% less than 35MPa-system, respectively [46]. The cryo-compressed system has approximately twice the volumetric efficiency of 35 MPa

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