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Hydrogen storage in clathrate hydrates: Current state of the art and future directions

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ABSTRACT

Hydrogen is looked upon as the next generation clean energy carrier, search for an efficient material and method for storing hydrogen has been pursued relentlessly. Improving hydrogen storage capacity to meet DOE targets has been challenging and research efforts are continuously put forth to achieve the set targets and to make hydrogen storage a commercially realizable process. This review comprehensively summarizes the state of the art experimental work conducted on the storage of hydrogen as hydrogen clathrates both at the molecular level and macroscopic level. It identifies future directions and challenges for this exciting area of research. Hydrogen storage capacities of different clathrate structures – sI, sII, sH, sVI and semi clathrates have been compiled and presented. In addition, promising new approaches for increasing hydrogen storage capacity have been described. Future directions for achieving increased hydrogen storage and process scale up have been outlined. Despite few limitations in storing hydrogen in the form of clathrates, this domain receives prominent attention due to more environmental-friendly method of synthesis, easy recovery of molecular hydrogen with minimum energy requirement, and improved safety of the process.

Contents

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1. Introduction

Hydrogen is the lightest, simplest and the most abundant element on earth. Hydrogen is termed as 'green fuel' and the 'fuel of the future' as it is a 'clean energy' carrier which on combustion yields only water vapor contributing to near zero emission. Despite numerous benefits of hydrogen, the storage and delivery of hydrogen has been a severe bottleneck and there have been considerable efforts in finding novel materials for developing new processes to increase the hydrogen storage capacity.

Hydrogen being the lightest element in nature has a very low density; hence creates huge problems during storage, as it requires more volume for a given amount of energy. Conventional methods of hydrogen gas storage include compression and liquefaction. Compressing hydrogen gas to high pressures of around 300 bars poses safety risk during transportation and storage. Compressed gas is able to store 15 g/l at 35 MPa [1]. Cryogenic cooling or liquefying the hydrogen gas to temperature of around 20 K is highly energy intensive and equivalent to 30% of the energy stored is expended in achieving such low temperature. Other storage methods include physical adsorption of hydrogen gas to solid material support; interaction between the host material and smaller H_2 molecule is dominated by weak Van der Waals interactions, which limits the storage capacity under ambient conditions [2–4]. Chemical storage of hydrogen in the form of metal hydrides and nitrides seem to be promising considering relative high hydrogen storage [5–7]. However, release of hydrogen from such compounds requires high temperature which is additional energy requirement. Carbon nanotubes, graphenes and metal organic frameworks are the novel materials being researched for hydrogen storage [8–16]. Relatively new and promising material for hydrogen storage is the cage compound or clathrate hydrate [17–20].

Clathrate hydrates are inclusive compounds where the guest gas molecules are trapped in host water molecules [21–24]. There is no chemical reaction, the gas is held inside the cavities only by physical bonds. Gas hydrate or clathrate hydrate research has progressed over several decades from a mere academic curiosity to being a nuisance to the oil and gas industry for flow assurance. Gas hydrate formation continues to have an impact on flow assurance due to the ever progressing deep offshore oil and gas exploration activities making it more favorable to appear in the pipelines and offshore facilities [21,25]. Later in 1960s after the discovery of naturally occurring hydrate deposits, there has been considerable interest among the research community spanning across disciplines of chemical engineering, mechanical engineering, civil and environmental engineering and chemists to understand the energy and environmental impact of these hydrate deposits [26–33]. Over the recent decades, several researchers have been applying this gas hydrate phenomena to develop innovative novel technologies for natural gas storage and transportation [34,35], carbon dioxide capture, storage & sequestration [36–43], refrigeration [44–46], desalination [47], gas separations [48–50] and hydrogen storage [17–20]. This review will focus on one such technological application, i.e. hydrogen storage in clathrate hydrates.

Despite the recent discovery (in the 90s) there have been considerable research efforts in improving the clathrate process for hydrogen storage. Continued interest in exploring the clathrate hydrates for hydrogen storage is due to its inherent advantages which include – (i) clathrate process is environmentally benign as it uses only water and very low concentration of promoters for improving the operating conditions (ii) hydrogen is stored in its molecular form, for ready utilization just by depressurization or minimal thermal stimulation (iii) Moderate temperature and pressure conditions for storage (in the presence of low concentration of promoters) (iv) Relative high hydrogen content per unit mass/volume [1] and (v) it is non-explosive in nature. However, there are few challenges encountered in storing hydrogen as clathrates such as (i) slower formation kinetics of hydrogen hydrates (ii) stability of hydrogen hydrates at ambient conditions (iii) low hydrogen storage capacity when used along with promoters (the promoters occupy hydrate cages preventing hydrogen gas from occupying the cages). Research efforts in overcoming the above challenges and making hydrogen clathrates as a storage medium are on-going. Struzhkin et al. [1] were the first to present a comprehensive review on hydrogen clathrates, they had discussed the history of hydrogen hydrates, different clathrate structures of hydrogen hydrates, explained the characterization techniques for studying the hydrogen clathrates, theoretical models and calculations available for studying the hydrogen clathrates along with the challenges encountered in theoretical studies.

Strobel et al. [51] evaluated the hydrogen storage properties of different clathrate hydrate structures including sII formed by hydrogen/THF mixed hydrates, semi-clathrates formed using TBAB and Jeffrey's structures. Evaluation was based on theoretical calculations as well as experimental volumetric gas release measurements and Raman spectroscopy. Maximum hydrogen storage in the available clathrate hydrate structures and Jeffrey's structures were calculated by using suitable assumptions and valid correlations. One representative compound for each hydrate structure was considered and the hydrogen storage capacity was worked out. Maximum of around 7.2 wt% was predicted for sVI hydrogen hydrate with six molecules of hydrogen occupying the large cages in sVI structure [51]. However, extreme conditions of pressure and temperature are required for achieving high hydrogen storage which may not be feasible at large scale considering the associated energy requirement. It is possible to bring the temperature and pressure requirements to a milder condition if a co-guest is used for hydrate formation along with hydrogen. However, it is very