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Current Advancement by Membrane Technology: A Review

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ARTICLE INFO	ABSTRACT
Article history: Received 18 March 2019 Received in revised form 26 May 2019 Accepted 26 June 2019 Available online 20 July 2019	In the current years, hydrogen (H2) which is a high quality carrier for clean energy attracts rejuvenated and ever-increasing attention around the world mainly due to the advancement of fuel cells, environmental burdens as well as global climate change issues. Purification and separation technologies are important in the thermochemical processes of H2 production from fossil fuels. The membrane reactors demonstrate reliable assurances in shifting the equilibrium whenever the shift reaction of water–gas is involved in transforming monoxide into H2. Membranes are also crucial in the following purification of H2. In this article, recent developments in each porous ceramic membranes and dense section metal are reviewed while their separation properties and performance in membrane reactor systems are compared. Discussions of this work will focus on the relationship and significance of membrane technology for application in the new generation zero-emission power technologies.
Keywords:	
Membrane technology; hydrogen	
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1. Introduction

Notable significance of separation technology in various sectors of chemical and energy industries is widely acknowledged. Significantly, a major growth will be complete in development of technologies associated with the separation of aerosolized species [1]. This might be due to high fossil fuel demand as well as the demand for various gases for pharmaceutical and industrial applications. [2, 3]. For example, it was calculated that in the fossil fuel sector alone 41 of the verified gas reservoirs within the US are sub-quality which need to be upgraded through the removal of excessive carbonic acid gas, H₂S, N₂ as well as various impurities in order to fulfill the wellhead process or pipeline transmission necessities [4]. Thorough analysis studies are conducted on recent techniques regardless of various established gas separation technologies existed such as pressure swing sorption and liquid absorption in order to identify techniques with capabilities to offer cost-effectives

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operation and management with less complexity [5, 6]. Membranes technology has been a feasible alternative for various applications of gas separation mainly due to its several advantageous such as little footprint, simple scale-up and high energy potency [7, 8]. According to the cited accounts, as of the year 2002, the gas separation membrane technology has become a \$150million/year business with expectation to grow in the coming years [9]. Thus, in depth breakthroughs of R&D for membrane technology maturity is needed in order to overcome the challenges. Aside from high quality, commercially available membranes made of chemical compound, carbon membranes offer an entirely exceptional and appealing membranes category with distinguished selections as well as outstanding gas separation performance. Notable characteristics of carbon membranes are its excellent thermal and chemical stability with the ability to outdo the permeability–selectivity trade-off [10]. Carbon membranes is thought to play an important part in realization and manifestation of morphology in separation performance. This is supported by the porous structure which allows high permeability resulting to high productivity while economical size and discrimination of molecules form resulting to high selectivity are provided by the molecular sieving network [11].

Even though membrane technology has been in the industry for a quite sometimes, there is no commercialization of highly permeable and selective membranes yet for large-scale gas separation operation. Commercialized feasible membranes should have superior separation properties such as highly permeable and selective, also chemically and mechanically stable under the operating environment for a long period. Inorganic membrane is indicated as one of the encouraging candidates for separation and purification of H₂. Inorganic membrane demonstrates rising significance in membrane reactors during the production of H₂. Currently, there is no systematical review focused on the standing of membranes for H₂ applications existed. Therefore, it is the aim of this review to provide a comprehensive evaluation of the current developments in every compact section metal and porous ceramic membranes as well as comparing their performance and separation properties in the membrane reactor systems mainly for the reformation of fossil fuel and the gas shift reactions. Preparation, classification and permeation of the assorted membranes will be provided and mentioned. This work aims to highlight crucial issues existed in these membranes with regards to their economic and technical advantageous and disadvantageous.

2. Materials for Membrane Preparations

Fabrication methods of membranes chosen must be suitable to the polymer precursors used and the membrane structure desired [12]. There are various membrane fabrication methods such as phase inversion, interfacial polymerization, and electrospinning. Fabrication methods that commonly used to fabricate membranes for water and gas separation are phase inversion and electrospinning while the methods used in fabricating membranes for water filtration are stretching and interfacial polymerization [113]. Figure 1 shows the general process of fabricating a membrane. Fabrication of membranes starts with heating the polymer pellets in an oven for 24 hours with the purposes of removing its moisture content. Next, a dope solution is created by adding the dried polymer pellet into a solvent then stirred continuously for more than 24 hours to prevent the transformation of homogeneous dope solution. Removal of bubbles trapped in the dope solution during the fabrication will be done by the process of degassed in the ultrasonic cleaner, then the dope solution is ready to be used in any membrane fabrication methods. The fabricated membrane will be dried to remove its moisture and, other post-treatment processes will be done on the membrane such as surface modification and coating.





Fig. 1. Typical membrane fabrication process

Basically, carbon membranes are formed via the movement of chemical compound precursors. Further studies revealed that the crucial aspects which confirm the transport properties of resultant carbon membranes are shift method parameters, microstructure of the precursor and chemical structure of chemical compound [12-14]. In other words, these parameters are important in producing a masterfully structured membrane containing clearly disseminated pores with vital dimensions as well as preferred surface characteristics. Major attention has been given in producing distinguished precursor type result, therefore various chemical compound materials are studied for fabrication of superior carbon membranes [8, 15]. Essentially, material choice is some basic necessities in preparing membranes specifically for gas separation. Hence, the chosen material need to possess the properties necessary in order to perform the designated practicality with exception for the fabrication technology. Even though equivalent thoughts are applied to the carbon membranes, the candidate materials need to possess more rigorous necessities. For example, good chemical and thermal stability are capable to retain the structure of the molecule as well as network integrity all over the shift method which are assumed to be one of the key conditions. Recently, Zhang et al. (2015) investigated the properties as well as the performance of the gas separation of a totally unique poly (phthalazinone ether sulfone ketone) (PPESK)-based carbon membranes for various gas pairs [12]. According to their observations, carbon membranes produced exhibit good separation performance such as the polyimide-based carbon membranes.

2.1. Porous Ceramic

Porous ceramic is a microporous membranes with high permeability, thermally stable and moderate to high properties [16]. Thus, porous ceramic is attractive for implementations in the reaction of H₂ production. According to the literatures, there are various types of porous membranes analyzed for the purpose of H₂ separation as well as its production. However, these represent carbon molecular sieve membranes for gas separation and H₂ recovery for expert users. Pilot scale studies on carbon molecular sieve membranes are needed focusing on the economical aspect of H₂ separation from gas streams. Chemicals opposition and air merchandise and chemicals opposition utilized the technology for H₂ increment to 56–60% followed by the purification of PSA in order to yield 99% H₂ [17, 18]. Nevertheless, the advanced surface chemistry carbon molecular sieves are not possible candidates for membrane reactor applications such as in steam reforming and water gas shift reactions due to the aerobic nature of its surface. An alternative type of porous ceramic membranes for application in the production of H₂ is based on the corundum mesoporous membranes



[19]. Most of the literatures on separation technology mainly focused on separation of atomic number 2 (He) as well as carbon tetrafluoride instead for H₂. The property is quite low around the order of 1-10 of Knudsen separation. Silicon oxide as well as silicon oxide functionalized ceramic membranes demonstrate good potential for implementation in the separation and production of H₂. In the previous few decades, huge development of silicon oxide membranes is greatly influenced by the involvement of various players from Holland, the USA, Germany, Australia and Japan in leading the analysis efforts in this field.

In the past 30 years, development of synthetic materials with exclusive properties for medical applications had been induced by advances in material science. Metals, ceramics, polymers, and composites are the main classes of synthetic biomaterials. Numerous forms of metals and their alloys had been employed as implants and for hard tissue repair (e.g., dental implants, joint replacement, fracture plates, screws, pins). They are strong, tough and ductile in mechanical structure and can be readily fabricated and sterilized. Nonetheless, corrosion might happen when they are in biological media, causing it to have high densities and mechanical properties that could be mismatched with the bone, which in turn results to the undesirable destruction of the surrounding hard tissues. Currently, due to several fascinating properties for specific applications such as dental implants, hip sockets, joint implants, and heart valves, ceramic biomaterials have received much attention; having the same physical properties to the bone is their main advantage. Also, they possess properties that are inert (e.g., carbon or carbon-coated materials) and can be readily sterilized. Generally, ceramics are hard and strong with high compressive strength. However, they can be brittle with low impact strengths, which causes them to be sensitive to notches or microcracks as they can easily fracture. Also, ceramic materials are difficult to fabricate. Previous researcher stated that when the driving force (pressure ratio) was lower, the selectivity results was higher and the separation process said to be more appropriated; in fact, the operating costs for the separation system also lower [20]. When the permeability was higher, the cost of the system was lowered and the membrane needed was also small. In order to surpass Robeson's upperbound, various researchers have been conducted. Previous membrane researchers mention that membranes which have the potential to exceed such upper bound were inorganic membranes. Therefore, ultramicroporous (0.3-0.5nm) membranes such as carbon membranes have shown their promising performance [21]. Carbon membranes also lack of being damaged in thermal cycles and easily handle at high temperatures when work with supported porous ceramic membrane. High permeation flux and high selectivity are essential requirements for a successful membrane.

2.2. Polyimides

Various literatures in the recent years documents the distinguished characteristics of polyimides as suitable precursors for carbon membranes preparation [20]. This is due to the unique polyimides properties such as rigidity, high glass transition temperature (Tg) and high freezing point while sustaining smart thermal and chemical stability. Therefore, examples of varied polyimides types are those comprising hexafluoroisopropylidene (6FDA) teams [21, 22], pyromellitic dianhydride (PMDA, Kapton) [23, 24], P84 [25, 26], 2,4,6,- trimethyl-1,3-phenylene organic compound and benzophenone tetracarboxylic dianhydride (BTDA)-based [27-29] as well as 3,3,4,4-biphenyltetracarboxylic dianhydride (BTDA)-based [20] polyimides family is tabulated somewhere else [31]. Matrimid is broadly known among them due to its easy accessibility as a poster product [32-34]. The usage of matrimid is mainly as a model chemical compound in order to determine the porousness as well as its effects on gas separation properties of carbon membranes [35]. Various experiences have



undisputable points on the benefits offered by the participation of mixing technology into the chemical compound gas separation membranes field. Nevertheless, limited range of studies extend the idea of mixing in the construction of carbon membranes [36, 37]. In the recent years, various studies reveal results mirroring the positive trend of this method. It is expected that mixing will be utilized as a straightforward method where economical and effective tool is in trade with the properties of the membranes. The primary attention is given to the choice of materials that is suitable in creating homogenised matrix thus satisfies the expectations. Gas separation performance is used in analyzing the membranes. The results revealed interesting gas permeability with perm property can be attained in carbon membranes constructed through mixing with a correct set of parameters chosen.

3. Membrane for H₂ Economy

 H_2 exists in the most plentiful amount in earth. H_2 can be extracted from biomass, water, or hydrocarbons such as fossil fuel or coal. H_2 can also be produced via energy or electricity manufactured from renewable resources such as biomass, star or wind. Typically, H₂ is indicated as 'clean energy' due to its combustion which only produces water compared to the H₂ production from hydrocarbons which yields a greenhouse gas called the carbonic acid gas. At the global scale, H_2 is produced in large amounts which is about five billion blocky meters annually and is mainly utilized to supply ammonia in chemical processes (about 50%), oil processing (37%) and production of alcohol (8%) as well as in the metallurgic and chemical industries (4%). Due to the large pressure lain on energy price, environmental property and security for both transportation and stationary sectors, various efforts are directed at the development of the technologies required in creating the right infrastructure to support the "H₂ economy" [38]. Global investment on H₂ accelerates intensely over the past few years and is currently within the USA billion bucks. For example, \$US1.7 billion are utilized for programs focused in advancing H₂ technologies, mainly, the electric cell vehicles. Japan has announced plans to establish in about 4000 H₂ filling stations by 2020. Meanwhile, European aims for a total adaptation of H_2 by 2050 which is indicated as the most effective example of " H_2 Economy".

 H_2 economy refers to the employment of H_2 as the major energy carrier. In the current few decades, H_2 economy is common among few policy manufacturers as well as futurists. H_2 potential is well-known for almost two centuries. Patriarch de Rivaz in 1805 developed a primary combustion engine consisting of H_2 and oxyacetylene [39]. However, currently it was steam and later is fossil fuel that powered the world's engines, thus some countries around the world are considering the feasibility of shifting towards the H_2 economy. Growing interest of H_2 is mainly driven by its potential to untangle two major challenges in several world's economics which are to achieve energy independence while reducing the environmental effect of economic activity [40]. Four crucial technologies are suggested for development for the purpose of realizing the H_2 economy:

(1) Energy system of H_2 production that is cost-efficient is needed in the carbon affected world. The challenges to be encountered includes the production of H_2 from fossil fuels with considerations of carbon sequestration and rising utilization of renewable sources.

(2) H_2 purification and storage technologies with abilities to separate and purify H_2 streams according to the requirement of the next utilization and storage systems. H_2 storage device that is economic and sensible with capabilities to obtain the USA DOE target.

(3) H_2 distribution and delivery infrastructure that is economical with wide accessibility and is well managed.

(4) Economical fuel cells and various energy transformation technologies that use H₂.



4. Conclusions

Membrane technology has attracted considerable attention in the gas separation industries such as hydrogen recovery, air separation, olefin/paraffin separation, CO₂ capture, nature gas dehydration, and lots more. Carbon membrane is currently being rapidly developed for these purposes. The developed in this research study exhibit a very good resistance toward CO₂-induced plasticization and have viable potentials for various gas separation applications including hydrogen purification and natural gas separation. Within a polymer film, free-volume elements such as pores and channels typically have a wide range of sizes and topologies.

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