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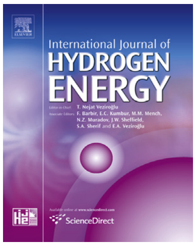

Carbon membrane performance on hydrogen separation in H_2–H_2O–HI gaseous mixture system in the sulfur-iodine thermochemical cycle

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ABSTRACT

Sulfur-iodine thermochemical cycle is considered as a promising route for hydrogen production without CO_2 emission. In this cycle, the hydrogen iodide conversion rate plays an important role in the total thermal efficiency to some extent. To improve the efficiency of HI decomposition, the homemade carbon membranes supported by α-alumina porous tubes were well-designed in a specific way and evaluated aiming at removing H_2 from HI decomposition reaction side. Permeability, selectivity and stability of self-designed carbon membranes are investigated in some gaseous components in the present work. Firstly, single-component (H_2/Ar) permeance was observed with differential pressure ranging from 0.05 to 0.2 Mpa. The result shows that differential pressure has little effect on H_2 and Ar permeance. Secondly, the hydrogen and argon permeance through carbon membrane is 3.1×10^{-8} mol m^{-2} s^{-1} Pa^{-1} and 5.7×10^{-10} mol m^{-2} s^{-1} Pa^{-1} respectively at 300 °C. The separation factor of H_2 and Ar is 54, which is greater than the theoretical value calculated by Knudsen diffusion equation. Thirdly, hydrogen permeability in the H_2–HI–H_2O gaseous mixture system owns nearly the same as that of the single-component (H_2) at 300–500 °C. Due to the large molecule diameter, most of HI are stopped by carbon membrane. However, H_2O molecules could pass through the carbon membrane obviously. The permselectivity of H_2/HI is over 310 at 500 °C. Last, after 10 h of stability tests, some slight damage are observed on the surface of carbon membrane according to the scanning electron micrograph (SEM). The structure change of carbon membrane gave rise to a little increase of H_2 permeance at 20–100 °C.

Introduction

Vast of air pollution and greenhouse gas (GHG) emission released from fossil fuel, hydrogen, as a clean, efficient and flexible energy carrier, will be the ideal substitute for traditional fuel. Because of the significant advantages of hydrogen, more and more researchers pay their attention to hydrogen production and utilization gradually [1]. As the most promising large scale, high efficient and low cost hydrogen production technology, sulfur-iodine (SI or IS) thermochemical cycle makes it

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possible for hydrogen wide utilization [2]. The SI process proposed by General Atomic contains three essential reactions as shown below:

1. Bunsen reaction: $SO_2 + I_2 + 2H_2O \xrightarrow{290\sim390K} 2HI + H_2SO_4$
2. H_2SO_4 decomposition reaction: $H_2SO_4 \xrightarrow{970\sim1270K} H_2O + SO_2 + 1/2O_2$
3. HI decomposition reaction: $2HI \xrightarrow{570\sim770K} I_2 + H_2$

The process appeals to many researchers for its attractive characteristics that it needs nothing but heat and water as raw material in the closed cycle, it produces only hydrogen and oxygen, and it is suitable for utilizing the solar [3] and nuclear energies [4,5].

By the reason of the low equilibrium decomposition of gaseous HI (about 22%, at 500 °C), the total thermal efficiency of SI cycle cannot be improved further availably to some extent [6]. In order to improve one-pass conversion rate of HI, hydrogen needs to be extracted from the section of HI decomposition reaction continuously. The application of a membrane reactor for HI decomposition reaction seems to be useful to enhance the conversion rate [7,8], and reduce the amounts of recycle materials.

A hydrogen-permselective membrane reactor is a single unit operation including HI decomposition and H_2 separation. Inorganic membranes for hydrogen separation have been reported abundantly in the field of H_2 production, showing respectable H_2 selectivity from hydrogen-rich mixtures. Based on the nonpolymeric materials, inorganic membranes can be classified into metal, molecular sieving carbon, zeolites, and ceramics [9]. Although metal membranes, such as Pd and its alloys, are able to separate hydrogen with a purity of up to 99.99% [10], the susceptibility to the corrosion by hydroiodic acid prevents metal membranes from the application in SI process. Ceramic membranes may be an ideal choice for the membrane reactor, since they own many excellent advantages, such as great mechanical strength, relatively pleasant resistance to corrosion, and high temperature stability [11]. Due to inheriting the characteristics of ceramic membranes, zirconia-silica composite membranes coated on porous ceramic tubes were investigated in the separation experiments for the mixtures of H_2–H_2O–HBr (for the UT-3 cycle) and of HI–H_2O (for the IS cycle) [12]. Although the separation factor of H_2/HI was not studied, it was the first attempt at using ceramic membranes in the SI process and it was found that HI could be concentrated in the permeated gases. Shigeharu Morooka et al. succeeded in plugging pores of α-alumina tubes with silica formed by thermal decomposition of tetraethyl-orthosilicate at 600–650 °C and applied them to separate H_2 from an H_2–H_2O–HBr mixture system at 200–400 °C [13,14]. Silica membranes prepared by chemical vapor deposition (CVD) were investigated systematically to promote HI decomposition rate in SI process [15–17]. In the studies from Gab-Jin Hwang, some different silica membranes produced by CVD were evaluated by its permeability, selectivity and stability. The simulation results demonstrated that hydrogen iodine conversion rate would exceed 0.9 in the silica membrane reactor theoretically [8].

However, because of its no catalytic activity in HI decomposition reaction, silica membrane is only used for packed bed membrane reactor (PBMR), rather than catalytic membrane reactor (CMR) [18]. According to the research and development of carbon materials based catalysts in HI decomposition, carbon materials demonstrated considerable catalytic activity for their different carbon structures [19–22]. It is well-known that carbon membrane could also be used for hydrogen separation from hydrogen-rich mixtures, but there has been no reports about hydrogen separation through carbon membrane in the IS cycle process until now. Consequently, carbon membrane has the potential to separate hydrogen and catalytic decompose HI in the same time, which will simplify the experimental setup of IS process and the membrane reactor. In this paper, carbon membranes coated on α-alumina porous tubes are prepared. The carbon membrane's permeability, selectivity and stability in H_2–H_2O–HI gaseous mixture are investigated, and characterized by XRD and SEM.

Experiments

Preparation of carbon membrane

A type of α-alumina porous tubes (o.d., 12.4 mm; i.d., 7.4 mm; length, 380 mm) with an open end and the other close end from Jiangsu Jiuwu Hi-Tech Co. are used as supports. The α-alumina porous tubes have an average pore size of 191 nm and over 40% porosity. The permeating portion of carbon membrane is 50 mm in length, and the other portion need to be glazed with a SiO_2–BaO–CaO sealant (Nippon Electric Glass, GA-13) calcined at 1200 °C for anti-permeation purpose.

As a thermosetting resin, poly furfuryl alcohol (PFA) is well known as the precursor of carbon membrane [23]. Catalyzed by oxalic acid (Sinopharm Chemical Reagent Co.,Ltd), furfuryl alcohol (Aladdin Reagent Co.,Ltd) readily polymerizes under the condition, stirring for 12 h at 70 °C.The polymerization reaction includes two stages, furfuralcohol monomers' linear condensation and cross-link curing [24].

The support fixed on automatic coating machine is immersed in PFA solution at a speed of 2 cm/min, kept dip-coating for 5 min, and then withdrawn from the coating liquid at the same speed. Prior to carbonization, the polymer needs to be dried at 80 °C for 12 h firstly and then at 120 °C for 12 h later. The dried precursor with support is calcined at 700 °C for 4 h under argon atmosphere. In this process, the pore distribution of carbon membrane is strongly affected by the rate of temperature rise. After several times of tests, 1 °C/min is considered as the appropriate rate of temperature rise. Repeating the above procedure for three times, the proper carbon membrane that shows specified selectivity of H_2/Ar can be obtained.

Membrane characterization

Surface morphology of fresh support and carbon membrane is explored by scanning electron micrograph model Hitachi S-4800 operating at an accelerating voltage of 5 kV. Samples are fixed between two little aluminium blocks, and the surface morphology is showed by secondary electron image. X-ray diffraction (XRD) analysis is performed with a Rigaku K/max2550/PC diffractometer. Cu K-α radiation with a power of

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