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Hydrogen production from methanol steam reforming using porous copper fiber sintered felt with gradient porosity

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ABSTRACT

A novel porous copper fiber sintered felt (PCFSF) with gradient porosity is fabricated with the multi-step mold pressing and solid-phase sintering method using the cutting copper fibers. Using the impregnation method, the PCFSF as catalyst support is loaded with Cu/Zn/Al/Zr catalyst, and then is embedded into the laminated-sheet methanol steam reforming microreactor for hydrogen production. Based on the SEM results, the microstructures and surface morphology of PCFSF are analyzed. The reaction characteristics of PCFSF with gradient porosity loaded with Cu/Zn/Al/Zr catalyst for methanol steam reforming are experimental investigated under different gas hourly space velocities (GHSVs) and reaction temperatures. Our results indicate that the gradient porosity in the PCFSF has a significant influence on the reaction performance. The PCFSF with three-grade porosity (70%–80%–90%) exhibits better methanol conversion and H_2 flow rate when the reactant is fed from 90% to 70% porosity portion.

Introduction

Hydrogen has attracted increasing attention as a promising new energy due to its clean, renewable and non-polluting nature, which is widely used in the chemical industry, military equipment as well as electric and electronic devices [1,2]. With the increasing global energy crisis and environmental pollution, hydrogen has been considered as a significant clean fuel in the near future. During the past two decades, the polymer electrolyte membrane fuel cell (PEMFC) with the hydrogen or hydrogen-rich gas as fuel currently appears to be the preferred fuel cell, which providing high energy efficiency, relatively low operating temperature as well as reduced environmental impact [3,4]. Therefore, the PEMFC has been offered as an alternative to conventional batteries, especially for the mobile applications. Up to now, the world-widely research efforts have been made to develop many novel PEMFCs with different structural design, fabrication method, material selection, performance evaluation and so on [5–7].

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The potential applications of PEMFC are also explored such as the stationary power plants, mobile power sources in vehicles and portable power generators [8–10].

As we know, the ideal fuel for the PEMFC is hydrogen gas. To obtain the reliable hydrogen source, there is an effective way to produce hydrogen via catalytic reaction in microreactors from many kinds of fuels such as methanol, natural gas, gasoline, alcohol and methane [11–15]. Among these fuels, methanol exhibits several obvious advantages of high energy density, low reforming temperature, safe handling/storage, good miscibility with water and low content of sulfur compounds, which can be easily converted into the hydrogen via reforming reaction in microreactors for fuel cell applications [16–18]. Typical microreactors usually are composed of fluid channels with an equivalent diameter in the range of 10–500 μm or porous material with larger specific surface area as catalyst support. These catalyst supports provide much lower pressure drop, greatly avoid the heat and mass transfer limitations and exhibit better catalyst loading performance. These advantages also allow optimizing the contact time of the reactants and avoid the formation of unwanted by-products to get better reaction performance [19,20].

To explore much more economical, clean and safe ways to produce hydrogen, intensive research work on different microreactors has been recently developed to produce the hydrogen source. Liu et al. [21] proposed a promising method of solar thermochemical hydrogen production integrating solar thermal energy at 150–300 °C with methanol steam reforming. The influence of two important factors of solar radiation and mole ratio of water/methanol on the chemical reactivity and hydrogen yield was investigated. Fidalgo et al. [22] investigated the performance of the dry reforming reaction under microwave heating using an activated carbon as catalyst and microwave receptor. The influence of operating conditions on the CH_4 and CO_2 conversions, the proportion of CO_2 employed and volumetric hourly space velocity was also studied. Perry et al. [23] also used the microwave technology to provide the heating source for endothermic catalytic reactions of methanol steam reforming. Both theoretical and experimental results in a microwave-heated reactor verified that productivity could be significantly improved. Moreno et al. [24] developed a new class of integrated ceramic microchannel reactors for all-in-one reforming of hydrocarbon fuels. The stable reforming of methanol to hydrogen at conversions >90% and hydrogen yields >70% was achieved at a maximum reaction temperature of 400 °C. However, the production cost of these novel microreactors for hydrogen source is increased due to the addition of heating device or the use of ceramic microchannel structure.

In recent years, more attentions were transferred to develop new catalyst support structure to improve the reaction performance of microreactor for hydrogen production. Pan et al. [25] proposed an oriented linear cutting fiber sintered felt as a catalyst support for methanol steam reforming microreactor for hydrogen production. The catalytic reaction characteristic of oriented linear cutting fiber sintered felt and oriented linear copper wire sintered felts were experimental investigated and compared under different GHSVs and reaction temperatures. The better performance of methanol steam reforming in the oriented linear cutting fiber sintered was obtained. Mei et al. [26,27] designed and fabricated a novel microreactor with micro-pin-fin arrays as catalyst support using the micro thixo-forming technology. Both the numerical simulation and methanol steam reforming experiments were adopted to investigate the heat and mass transfer characteristic of microreactor for hydrogen production. Wang et al. [28] developed a plate-type reactor to investigate the influence of catalyst activity distribution on methanol steam reforming reaction. An optimized catalyst distribution has been proposed for a superior temperature profile for methanol steam reforming. Therefore, the development of these new catalyst support structures plays an important role in improving the reaction performance of microreactor for hydrogen production.

Nowadays, gradient pore structure in porous metal material is attracting more attentions because of its increasing application in high temperature dust remove, biochemistries and food industry, replacement implants, fuel cells as well as ultrafiltration media owing to their outstanding structural and functional properties [29]. Interestingly, several novel fabrication processes to generate different porous materials with a gradient pore structure have been developed. Li et al. [30] developed selective laser melting technique (SLM) to fabricate 316L stainless steel part with a pore gradient structure, investigated the scan tracks feature, densification, and tensile property of SLM produced samples prepared via different scan speeds. Zhang et al. [31] investigated bi-layer composite components with gradient porosity made by powder injection molding method. The shrinkage stress caused by sintering of different materials was also discussed. Suk et al. [32] developed a pulsed electric current sintering process to fabricate a porous material with a gradient porosity. This method presented several outstanding advantages such as very short processing time and easy porosity control. Zhang et al. [33] used a temporary space-holder (NH_4HCO_3) and a conventional sintering method successfully fabricated the porous NiTi alloys with gradient porosity and large pore size. The fabricated samples with radial gradient porosity exhibited excellent superelasticity (higher than 4%). Jung et al. [34] reported a novel method for producing porous Ti scaffolds with a gradient in porosity and pore size using the freeze casting method. The fabricated sample consisted of three distinctive regions with different porosities of 75%, 53% and 35% could be formed using initial TiH_2 contents of 10%, 25% and 40%, respectively. Oh et al. [35] fabricated the porosity graded compacts using the Ti powders with three different particle sizes which were prepared by the plasma rotating electrode process and the gas atomization process, and investigated the microstructures and mechanical properties of porosity-graded Ti compacts.

From above reported literatures, it is found that a majority of research works focus on the fabrication methods and mechanical properties of different gradient pore structures, the information about the PCFSF with gradient porosity as catalyst support for microreactor for hydrogen production is not reported. In the present study, both the multi-step mold pressing and solid-phase sintering method were proposed to fabricate a novel PCFSF with two-grade and three-grade porosity. Based on the SEM results, the microstructures and