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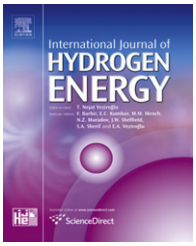

Pt–Co catalyst-coated channel plate reactor for preferential CO oxidation

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ABSTRACT

To achieve preferential CO oxidation, a Pt–Co catalyst-coated channel plate reactor (CCPR) was produced via conventional mechanical milling and catalyst coating. The proposed reactor performed well under a wide range of operating temperatures and provided satisfactory results at low temperatures (CO concentrations of 1–10 ppm at 413–443 K and 1–50 ppm at 413–453 K). In the proposed CCPR, significant deactivation was not observed during continuous operation for 100 h. In addition, the reactor exhibited excellent tolerance to undesirable conditions, including reaction temperature runaway and feeding stream failure. Characterisation results indicated that the catalytic activity of the proposed CCPR was high due to the formation of Pt_3Co intermetallic compounds and nanoscale metal particles. The capacity per channel of the proposed CCPR was approximately 50–100 times greater than those of conventional microchannel reactors; thus, problems associated with excessive reactors were significantly reduced. In general, the results indicated that CCPR has great potential in the small-scale production of hydrogen for fuel cells.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are an eco-friendly and efficient power generator for stationary and portable applications due its high power density, easy scale-down, fast start-up and shutdown, and mild operating temperatures [1]. Although pure H_2 is the ideal fuel for a PEMFC, technical challenges associated with the distribution and storage of H_2 limit its use. To overcome these concerns, reforming systems based on hydrocarbons such as methanol [2], ethanol [3], natural gas [4], and gasoline [5] have been proposed. Although water-gas shift (WGS) reactions are conducted after reformation, H_2-rich gas produced through steam reforming contains approximately 0.5–1% CO [6]. Because Pt-based electro-catalysts are easily poisoned by even low concentrations of CO, CO must be removed to avoid rapid deactivation of Pt-based anode catalysts. To achieve a durability of 20,000 h, the cell must be able to tolerate 10 ppm of CO (target 2005) under steady state conditions; however, in the transient state, the CO tolerance of the cell must be greater than 100 ppm. Alternatively, to achieve a durability of 40,000 h (target 2011), CO concentrations of 1 ppm and 25 ppm must be tolerated under steady and transient conditions, respectively [7]. Thus, several methods for the removal of CO from a H_2-rich

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stream have been developed, including cryogenic separation, pressure swing adsorption, selective diffusion, preferential oxidation of carbon monoxide (PROX) [8], and CO selective methanation (CO-SMET) [9]. Among these methods, CO-SMET and PROX are both effective and promising [10,11].

High activity and selectivity are common challenges in the design of PROX catalysts. To improve PROX catalysts, supported noble metals such as Pt [12,13], Pd [14], Ru [15], Au [16], Rh [17], and Ir [18] have been evaluated. Due to their high activity, selectivity, and stability, supported Pt catalysts are commonly used in PROX. Moreover, promoters such as Co [19], Fe [20], Ce [21], La [22], Nb [23], and alkali metals [24] have been tested for their ability to increase catalytic activity. Among promoters, Co is the most common additive to Pt-based catalysts. For instance, Jain et al. [25] demonstrated that the selectivity and activity of Co- and Fe-promoted Pt/Al_2O_3 catalysts were greater than that of Mn-, Sn-, Cu-, Ni-, and Cr-promoted Pt/Al_2O_3 catalysts. Furthermore, Suh et al. [26] found that the advantages of Co-promoted Pt/Al_2O_3 catalysts are similar to those of Ni- and Mn-promoted catalysts. Similarly, Ko et al. [6] demonstrated that a Pt–Co bimetallic catalyst supported on yttria-stabilised zirconia could achieve high CO conversion at 380–423 K. In other studies, the effects of support materials (CeO_2, MnO_x, or Fe_2O_3) on the performance of PROX have been evaluated [27,28].

PROX is often conducted in a fixed-bed reactor; however, traditional PROX reactors with randomly packed catalytic beds display slow heat and mass transfer and are not able to fulfil the dynamic demands of fuel cell systems. In addition, the highly exothermic oxidation reaction may cause hot spots in the catalyst bed. Besides, large-scale packed-bed reactors are unsuitable for use in mobile and portable devices due to their large volume. To address these issues, several reactors have been developed, including straight-channel monolith reactors [29], microchannel reactors [30,31], and metal foam reactors [32]. Compared to packed-bed reactors, microreactors display rapid heat and mass transfer [33–35], low pressure drop [36–38], high surface to volume ratio [34,37], and fast response, and suppress hot spots [1,34]. Due to their intrinsic safety and easy scale up, micro-structured reactors are ideally suited for PEMFC systems and can be used in low to medium power output applications [39–42]. Despite the potential advantages of micro-structured reactors, only a handful of studies have been conducted on catalyst coatings for PROX. For instance, catalyst coatings based on Pt/Al_2O_3 [1], Rh–K/Al_2O_3 [43], Pt-MIX (1% Pt on 50% 3A zeolite and 50% Al_2O_3) [44], Cu/CeO_{2-x} [30], Pt–Co/Al_2O_3 [45], and Pt–Fe/mordenite [20] have been investigated. However, for most of these catalysts, an outlet CO concentration of less than 10 ppm could only be obtained at high temperatures (>460 K) or with the use of a large amount of precious metals. Thus, further investigations should be conducted to improve the catalytic activity and economy of PROX reactors for mobile or portable fuel processors.

In this study, a Pt–Co/Al_2O_3 catalyst-coated channel plate reactor (CCPR) for PROX was synthesized via conventional mechanical machining and slurry coating. The performance of the CCPR was investigated in detail under realistic conditions, where CO_2 and H_2O were present in the feed. The catalyst coatings were characterised by scanning electron microscopy (SEM), nitrogen adsorption–desorption, X-ray diffraction (XRD) and transmission electron microscopy (TEM). The aim of the present study was to develop a reactor with features such as easy fabrication, low cost, flexible yield and superior activity to meet the requirements of hydrogen production for fuel cells.

2. Experimental

2.1. *Design of the CCPR*

Fig. 1 shows the individual components of the proposed CCPR. A top cover sheet with two holes was used as the inlet and outlet. The active catalyst coating was placed on the upper and lower walls of the straight rectangular channel, which was located in the middle of the sheet. To uniformly distribute the flow throughout the channel, two triangular manifolds were placed on the front and end side of the channel.

For laminar flow over a flat plate, the Sh can be described as follows [46]:

$$\mathrm{Sh} = \frac{kd}{D} = 0.664(\mathrm{Re})^{\frac{1}{2}}(\mathrm{Sc})^{\frac{1}{3}} \tag{1}$$

$$\mathrm{Re} \le 3 \times 10^5$$

$$0.6 < \mathrm{Sc} < 2500$$

where k is the mass transfer coefficient of the length of the channel plate, d is the characteristic length of the flat plate, and D is the CO diffusion coefficient of the reformate. Re and Sc are the Reynolds and Schmidt numbers, respectively.

The pressure drop over the channel length of the CCPR was calculated according to Eq. (2).

$$\Delta p = \frac{c}{\mathrm{Re}} \cdot \frac{l}{d} \cdot \frac{\rho u^2}{2} \tag{2}$$

In the above equation, l is the length of the channel, ρ is the average density of the reformate, and u is the reformate velocity.

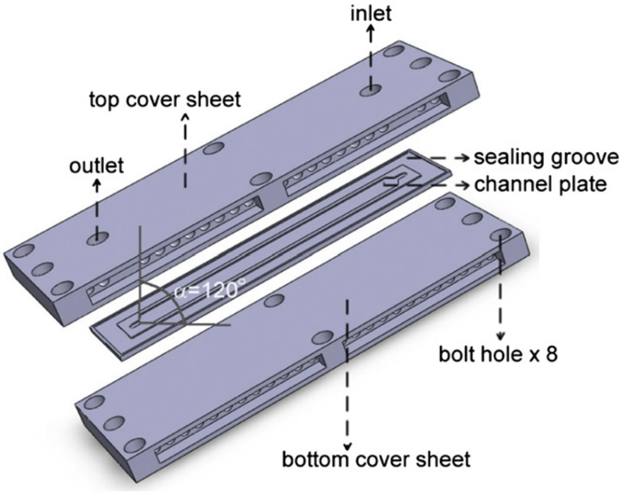

Fig. 1 – Schematic depiction of the channel plate reactor.