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Membrane-assisted propane partial oxidation for solid oxide fuel cell applications

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HIGHLIGHTS

- Propane could be converted to syngas via an oxygen-permeable membrane reactor.
- The reactor produced high concentration syngas at a rate 22 mL cm^{-2} min^{-1}.
- SOFC running on the reformed propane exhibited satisfactory performance.
- The membrane reactor is safer and more durable than the fixed bed reactor.

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ABSTRACT

Conversion of condensable fuels to syngas is required for on-site power generation by solid oxide fuel cells. Here, a membrane reactor is investigated to reform propane into syngas. The reactor consists of two chambers separated by an oxygen-permeable ceramic membrane, and propane is fed into one chamber while air is fed into the other. Propane is reformed into syngas by reacting with the permeated oxygen in the presence of Ru-Ni catalyst. The reactor attains a propane throughput conversion over 90%, H_2, CO yield over 80% and syngas is produced at a rate of 22 mL cm^{-2} min^{-1} at 850 °C. The as-reformed fuel is rich in syngas due to the exclusion of nitrogen in air by the membrane. A disk-shaped solid oxide fuel cell, as fuels with the pre-reformed propane by the membrane reactor, exhibits maximum power densities comparable to the one fueled with pure hydrogen. The fuel cell operates stably with the pre-reformed propane, while it fails rapidly with the un-reformed propane. The membrane reactor shows advantages over the conventional fixed bed reactor in terms of reactor safety and fuel concentration, therefore holding a great promise for use as a pre-reformer in solid oxide fuel cell systems.

1. Introduction

Currently, diesel generators are mainly employed to produce electricity in remote regions with no access to the power grid [1,2]. Solid oxide fuel cells (SOFCs) are considered as a promising alternative to diesel generators for on-site power generation [3–6]. Fuel cell systems for residential applications have proven their ability to produce electricity with lower heating value (LHV) efficiencies up to 65% [7]. Additionally, the system does not produce noise pollution since the internal combustion process is avoided [8]. However, limitation arises from the fuel availability as hydrogen or syngas consumed by SOFCs is difficult to restore and transport [9].

For on-site power generations by SOFCs, an easily condensable fuel such as propane is preferred to gaseous fuels. A vapor pressure of 2.2 MPa at 55 °C allows propane to be refilled and transported relatively easily in the liquid phase compared to methane and hydrogen [10]. Propane is also widely viewed as a safe and reliable fuel, with existing guidelines for safe operation. In practice, propane is often converted into syngas via a fuel reformer before feeding into SOFCs [11], because the direct use of propane may lead to the deposition of coke on the anodes, reducing the durability and performance of SOFCs [12–14].

Steam reforming (SR) is the most common process to convert hydrocarbons to syngas [15–17]. For propane, the reaction is:

$$C_3H_8 + 3H_2O = 3CO + 7H_2 \quad \Delta H = 497\ kJ/mol \tag{1}$$

This process has the highest hydrogen yield and the least side reaction [18,19]. But, it is not well suited for the remote on-site applications, because a water tank and a water management system must be

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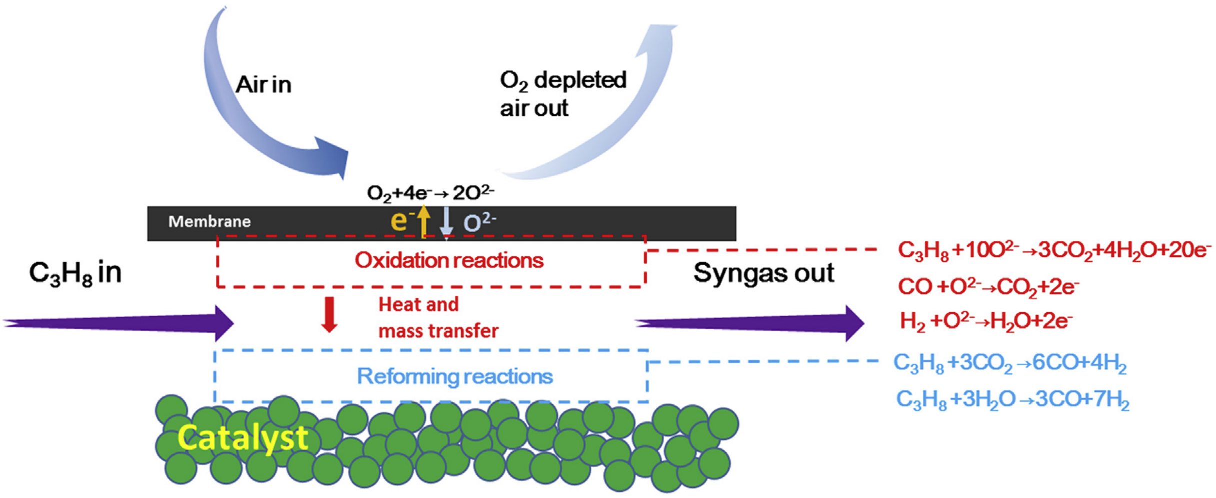

Fig. 1. Illustration of POX membrane reactor.

equipped. Moreover, the process is highly endothermic, thus a powerful burner is needed to balance the heat of the system.

Partial oxidation (POX) is an alternative process to SR [20–23],

$$C_3H_8 + 1.5O_2 = 3CO + 4H_2 \quad \Delta H = -227\ kJ/mol \tag{2}$$

Due to the exothermic nature of the reaction, POX allows for fast start-up, and can be thermally self-sustained. The propane POX is usually carried out in a fixed bed reactor with powder catalysts. In the entrance region of the catalyst bed, complete oxidation occurs, generating a large quantity of heat. Due to the heat transport limitation, the reactor temperature could run away [24]. Moreover, flame and explosion may also occur during vaporization and mixing of propane with air.

The problems with the fixed bed POX reactor could be solved with a membrane reactor. In the membrane reactor, propane is converted into syngas via the oxidation-reforming mechanism as illustrated in Fig. 1. Note that unlike the fixed bed reactor in which oxidant is supplied in form of molecules, the oxidant in the membrane reactor is provided through the membrane in form of lattice oxide ions. As a result, temperature runaway and explosion that might occur to the conventional reactor would be highly unlikely in the membrane reactor [25,26]. The other important feature of the membrane reactor is that nitrogen in air is excluded by the membrane, the reformed fuel is hence rich in CO and H_2 and could be directly used as the fuel for SOFCs [27]. Based on the above considerations, the present study was intended to explore the membrane-based propane POX process targeting the fuel pre-processing application in SOFCs.

2. Experimental

2.1. Preparation and characterization of membranes and catalysts

The membrane was made from a composite of $Zr_{0.84}Y_{0.16}O_{2\text{-}\delta}$ (YSZ) (Shanghai Yiming Materials Tech. Co.) and $La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3\text{-}\delta}$ (LSCrF) (Rare-Chem Hi-Tech Co.). In the present study, the supported composite membrane was prepared using the phase-inversion tape casting/sintering method [28].

The catalyst used in this study was Ru-Ni supported on $Sm_{0.2}Ce_{0.8}O_{2\text{-}\delta}$ (SDC). The SDC support was fabricated by a phase inversion tape casting method. A slurry composed of 43.68 wt % SDC, 14.56 wt % graphite, 34.95 wt % NMP, 5.83 wt % PESF, and 0.97 wt% PVP was milled for 24 h, cast on the glass sheet, and then transferred into the water bath for solidification. After oven-drying, the green tape was calcined at 1200 °C for 4 h in air. The Ru–Ni/SDC (weight ratio, 10:10:80) catalyst was prepared by impregnation using Ni nitrate and Ru chloride as the precursors. After impregnation, the catalyst was dried at 80 °C for 12 h, and reduced for 1.5 h at 800 °C under hydrogen flowing at 50 mL min^{-1}.

The microstructure of the membrane and catalyst was examined by scanning electron microscopy (SEM) (JSM-6390LA, JEOL, Japan) and the phase compositions was analyzed by x-ray diffraction (XRD) (X'Pert Pro, Phillips, Netherlands).

2.2. Construction and testing of membrane reactor

The experimental setup is schematically shown in Fig. 2. YSZ-LSCrF membrane of effective area 4 cm^2 was sealed between two stainless steel moulds (Crofer 22 APU) with the aid of high temperature glass sealants (Shanghai Institute of Ceramics, Chinese Academy of Sciences). Ru-Ni/SDC monolith catalyst was set below the membrane with ~1 mm distance between them. The effluents of the reactor were cooled and dried to remove steam before feeding into GC or fuel cells.

The reaction products were analyzed on-line using GC (1690, KeXiao, China and GC9750, FuLi, China) equipped with TCD and FID detectors, and a column of 5 Å molecular sieve packing material. High-purity helium (15 mL min^{-1}) was added as an internal standard to aid in analysis of the product composition. The propane conversion, CO yield and H_2 yield were calculated according to the following equations:

$$X_{C_3H_8} = \frac{C_3H_8^{in} - C_3H_8^{out}}{C_3H_8^{in}} \tag{3}$$

$$Y_{CO} = \frac{CO^{out}}{3C_3H_8^{in}} \tag{4}$$

$$Y_{H_2} = \frac{H_2^{out}}{4C_3H_8^{in}} \tag{5}$$

2.3. Preparation and testing of SOFC

Disk-shaped SOFCs with NiO-YSZ (40:60 vol) anodes, YSZ electrolytes and YSZ-$(La_{0.8}Sr_{0.2})_{0.95}MnO_{3\text{-}\delta}$(50:50 wt) cathodes were fabricated. The bi-layer of NiO-YSZ/YSZ was prepared by dual-layer tape casting, and the cathode was prepared by screen printing. The electrolyte had a thickness of 12 μm and the cathode had an effective area of 0.237 cm^2 (See Fig. S7). Ag paste was applied as the current collector. The experimental set-up for testing SOFC is given in Fig S8. The syngas converted from propane by the membrane reactor was feed into the fuel cell, and the electrochemical performance was measured using