Pre-reforming of propane for low-temperature SOFCs

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Abstract

Lowering the operation temperature and effectively utilizing practical fuels are two critical issues facing the development of economically competitive solid oxide fuel cell (SOFC) systems. Although steam reforming or partial oxidation is effective in avoiding carbon deposition of hydrocarbon fuels, it increases the operating cost and reduces the energy efficiency. In this communication, we report our preliminary findings in developing catalyst (1 wt.% Pt dispersed on porous Gd-doped ceria) for pre-reforming of propane with relatively low steam to carbon (S/C) ratio ($\sim$ 0.5), coupled with direct utilization of the reformate in low-temperature SOFCs. Propane was converted to smaller molecules during pre-reforming, including H_2, CH_4, CO and CO_2. A peak power density of 247 mW/cm^2 was observed when pre-reformed propane was directly fed to an SOFC operated at 600 °C. No carbon deposition was observed in the fuel cell for a continuous operation of 10 h at 600 °C. These results imply that pre-reforming could greatly enhance the performance of low-temperature SOFCs that run on higher hydrocarbon fuels.
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Keywords: Pre-reforming; Low-temperature SOFC; Propane; Pt-GDC

Fuel flexibility is one of the significant advantages of solid oxide fuel cells (SOFCs) over other types of fuel cells [1–5]. Nickel-based anodes have been very efficient when H_2 or CH_4 is used as the fuel. However, direct utilization of higher hydrocarbons (e.g. propane and butane) as the fuel in SOFCs has caused severe carbon deposition and hence rapid deactivation of nickel catalysts [6,7]. Thus, avoiding carbon deposition is one of the key issues in the development of SOFCs that run on carbon-containing fuels. Hydrocarbon-fueled SOFC systems will therefore require a fuel processing system, such as steam reforming and partial oxidation [8], which will convert hydrocarbons to a mixture of hydrogen and carbon monoxide before feeding to SOFC stacks. While steam reforming or partial oxidation is effective in avoiding carbon deposition, it increases the operating cost and reduces the energy efficiency. For example, a

steam-to-carbon (S/C) ratio of >3 is needed to avoid coking for steam reforming propane.

On the other hand, pre-reforming, which is often an additional process step for steam reforming, can convert heavier hydrocarbons to a mixture of smaller molecules such as CH_4, H_2 and carbon oxides at low temperatures [9,10]. Therefore, it is possible to reduce the steam/carbon ratio dramatically by applying a pre-reforming process, compared with a general steam reforming process. Moreover, previous results [11] demonstrated that methane can be directly used as fuel for Ni-GDC anode-based SOFCs at low temperatures (< 650 °C) without carbon deposition. Thus, pre-reforming could be a crucial step towards effective utilization of carbon-containing fuels in low-temperature SOFCs. However, little is reported in the literature on the combined use of catalytic chambers and fuel cells [12]. In this communication, we report our initial findings in developing novel catalysts for pre-reforming of propane, coupled with direct utilization of the reformate in low-temperature SOFCs.

Gadolinium-doped ceria ($Ce_{0.9}Gd_{0.1}O_{1.95}$, GDC) with 1 wt.% Pt was applied as the catalyst for the pre-reforming of propane in this study. GDC with 1% Pt was also studied by Krumpelt et al. [7] for partial oxidation and autothermal

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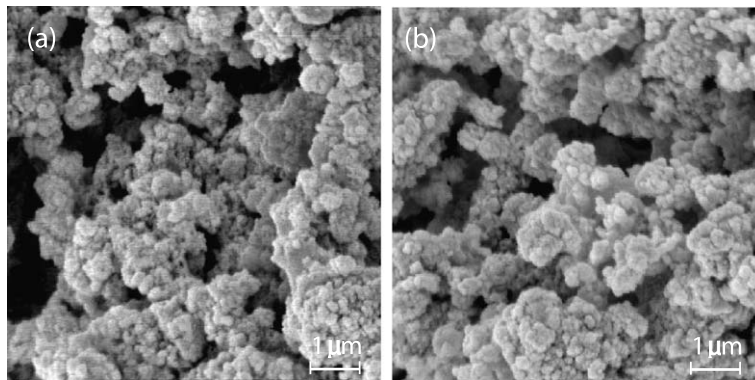
Fig. 1. Surface view (SEM micrograph) of the Pt-GDC catalyst (a) before and (b) after exposure to propane for 10 h at 650 °C.
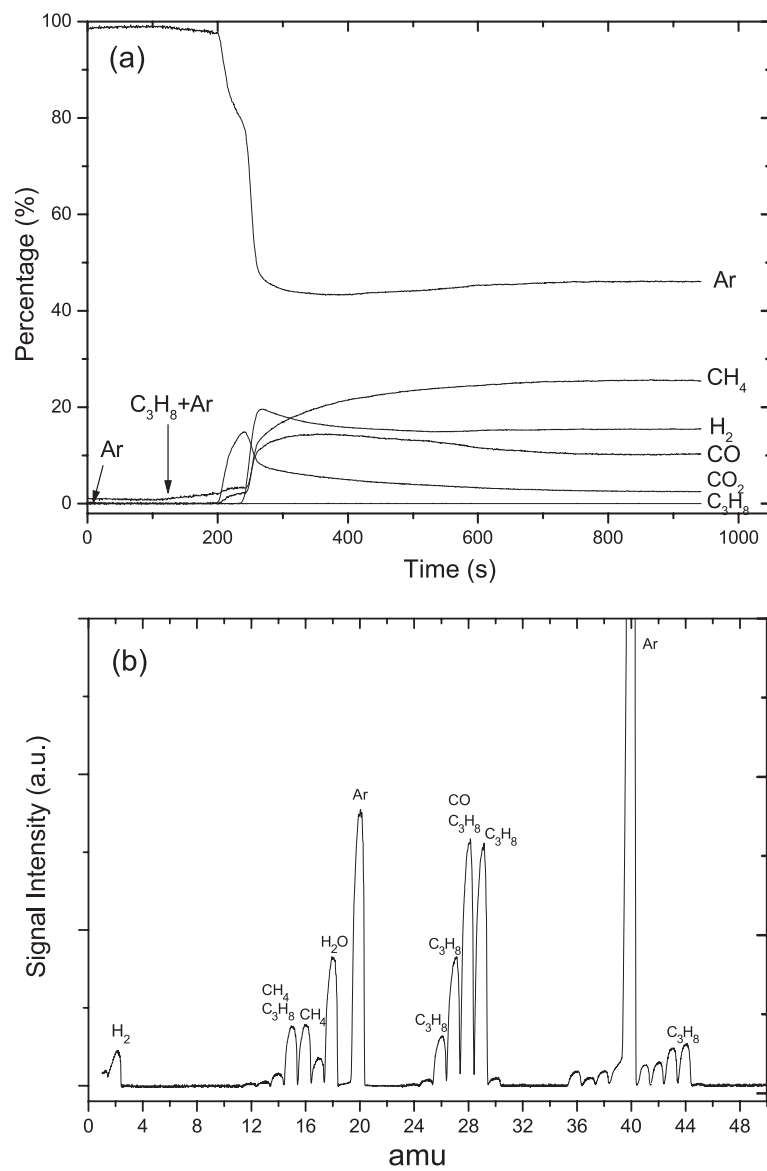

Fig. 2. (a) A typical mass spectrum of the reformed propane on catalyst Pt-GDC at 650 °C (S/C = 0.5), and (b) mass spectrum of the outlet gas of propane and steam flowing through a heated alumina tube (650 °C) without catalyst.

reforming previously. The GDC powder (5 g) prepared by a glycine/nitrate process [13] was mixed thoroughly with appropriate amount of $Pt(NH_3)_4(NO_3)_2$. Then a Heraeous binder (V006) and acetone were added and ball-milled to form uniform slurry. The slurry was coated on the surface of small pieces of thin YSZ substrate (~ 0.15 mm in thickness). After fired at 900 °C for 2 h, the porous catalyst of Pt-GDC was filled in an alumina tube as a reactor. The inlet gas stream was composed of propane and argon with flowing rate of 5 and 20 ml/min, respectively. Here, argon was used as a diluent gas. The pre-reforming process was taken place at 650 °C in a tube furnace by keeping S/C ratio at 0.5. The outlet gas stream was fed directly into the fuel chamber of a Ni-GDC anode-supported SOFC. The fabrication process and set-up of the SOFC were as described elsewhere [14].

The microstructure of the Pt-GDC catalyst was observed using a scanning electron microscope (SEM, Hitachi S-800). X-ray diffraction (Philips, PW-1800) and Raman scattering (Renishaw, Raman System 2000) were used to analyze the catalyst phases before and after the pre-reforming process. The composition of the outlet gas stream was monitored on-line by a mass spectroscopy (MS, Hiden HPR 20) at room temperature. Fuel cell performances were measured with an EG&G potentiostat/galvanostat (model 273 A) interfaced with a computer. The impedances of the cell under open-circuit conditions were measured using an EG&G impedance system consisting of a lock-in amplifier (model 5210) and an EG&G potentiostat/galvanostat (model 273 A).

Shown in Fig. 1(a) is the morphology (SEM micrograph) of the as-prepared Pt-GDC catalyst to be used for pre-reforming propane. The catalyst has good porous microstructure with an average particle size of about 0.2 μm and

BET surface area of 5 m^2/g. After the running of pre-reforming, there were no observable changes in morphology from the as-prepared sample, as shown in Fig. 1(b). Shown in Fig. 2(a) are the mass spectra of the outlet gas when C_3H_8 and steam (at S/C = 0.5), diluted by argon were fed to the catalyst bed with 1 wt.% Pt-GDC as the catalyst at 650 °C for pre-reforming. In order to examine the background of the pre-reforming process due to thermal cracking, the same inlet gas stream was also fed to the alumina tube without catalyst. The corresponding mass spectra were shown in Fig. 2(b). It can be clearly seen that only a small amount of propane was converted to smaller molecules (e.g., H_2, CH_4 and CO) in the blank runs. In contrast, when 1 wt.% Pt-GDC was used as the catalyst at 650 °C, nearly all propane was converted to H_2, CH_4, CO and CO_2. The composition ratios of CH_4, H_2, CO and CO_2 were 2.5:1.5:1:0.25, as estimated from the mass spectra shown in Fig. 2(a). It is also noted that the S/C ratio was very low (~ 0.5), which shows that the pre-reforming process using 1 wt.% Pt-GDC as the catalyst can result in energy savings. It is believed that both Pt and GDC are activated to be excellent catalysts for the pre-reforming of propane at elevated temperatures. Additionally, it is believed that the catalytic performance of platinum is enhanced by the ionic conduction of doped ceria in a humidified atmosphere. Because of the combined effect of ceria and platinum, propane dissociates on platinum and reacts with oxygen ions adsorbed on doped ceria [15,16]. After operation for 6 h, a small amount of carbon deposition was observed only in the area close to the entrance of the gas inlet. There are no observable differences in the XRD patterns of the Pt-GDC catalyst before and after pre-reforming operation. Shown in Fig. 3 are Raman spectra of the catalyst samples before and after the pre-reforming opera-
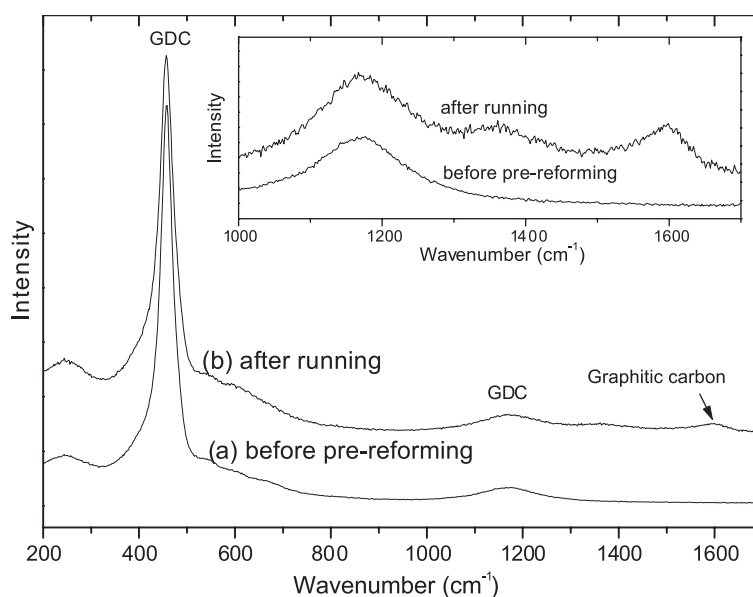

Fig. 3. Room temperature Raman spectra of Pt-GDC catalyst (a) before pre-reforming and (b) after pre-reforming operation (in the gas entrance area). Insert shows the intensity for wavenumber from 1000 to 1700 cm^{-1}.
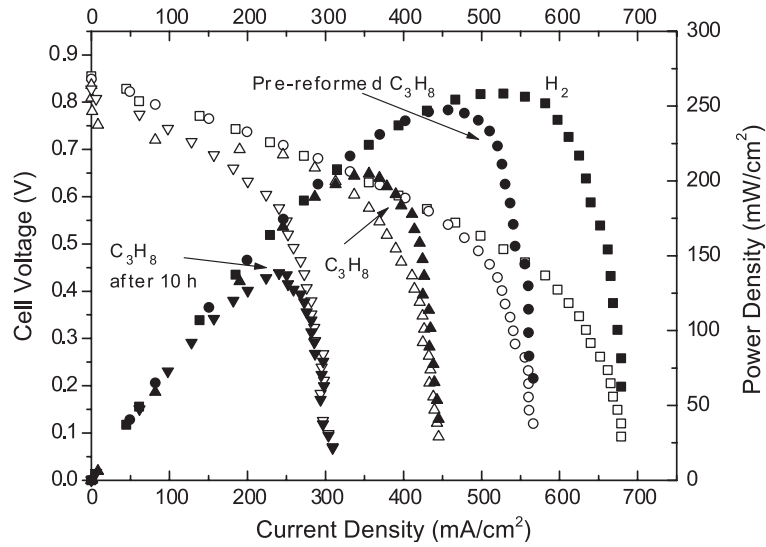
Fig. 4. Cell voltages (open symbols) and power densities (solid symbols) as a function of current densities for a fuel cell, Ni-GDC (anode)/GDC/ $Sm_{0.5}Sr_{0.5}CoO_3$-GDC (cathode), at 600 °C (measured after operating for 0.5 h). The data are shown for the following fuels: ($\square$) 10 ml/min H_2 in 10 ml/min Ar, ($\bigcirc$) pre-reformed propane in 20 ml/min Ar and ($\triangle$) 5 ml/min propane in 20 ml/min Ar. (The cell performances after running for 10 h are also shown.)

tion. While a weak and broad carbon peak is observed for the catalyst sample taken from the area where the gas (propane and steam) enters the reactor after the pre-reforming operation, there was no observable carbon peak for the catalyst

taken from other parts of the reactor after the pre-reforming operation.

Fig. 4 shows the cell voltages and power densities versus current density for a typical anode-supported fuel
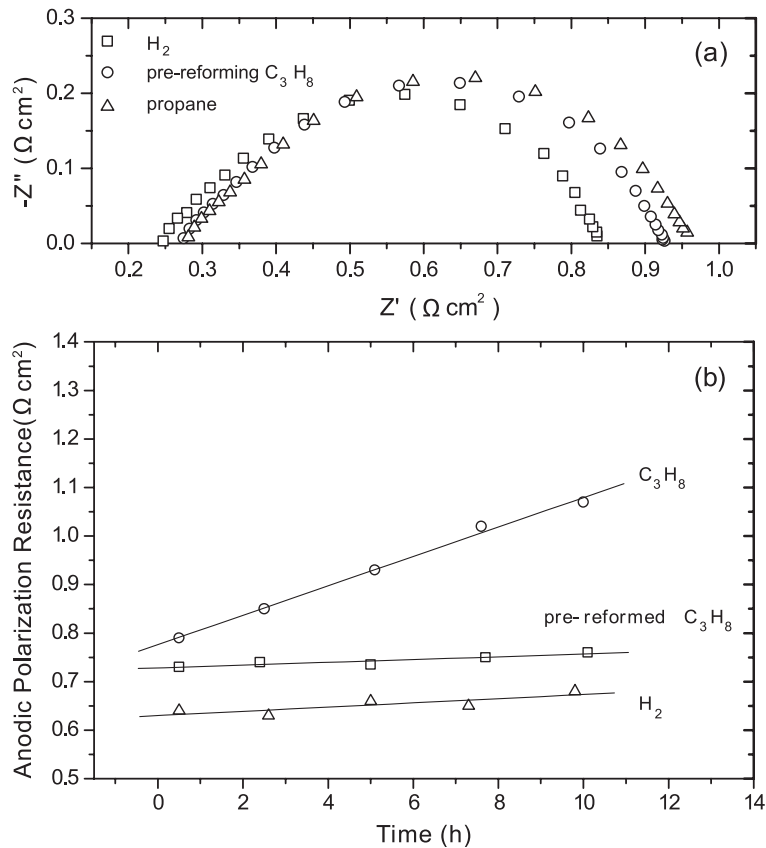

Fig. 5. (a) Impedance spectra for the fuel cell measured under open-circuit conditions at 600 °C using a two-electrode configuration. (b) The time dependence of anodic polarization of the fuel cells running on different fuels.

cell operated at 600 °C, with a cell configuration of Ni-GDC (anode)/GDC/$Sm_{0.5}Sr_{0.5}CoO_3$-GDC (cathode). While the cathode was exposed to stationary air, the anode was fed with different fuels: hydrogen (10 ml/min H_2 + 10 ml/min Ar), propane (5 ml/min C_3H_8 + 20 ml/min Ar) and pre-reformed propane. Each datum point was recorded about 30 min after the cell reached the steady state. As shown in Fig. 4, open-circuit voltages (OCVs) of 0.855, 0.849 and 0.836 V were observed at 600 °C for H_2, pre-reformed gas and propane, respectively. The lower OCV values compared to Nernst potentials were due to the partial electronic conduction of GDC electrolyte, which became more severe when thin electrolyte membrane was used [17]. In this study, the thickness of the electrolyte was about 20 μm. The maximum power densities were 258, 247 and 205 mW/cm^2 for the cell using three kinds of fuels, respectively. These results show that when the pre-reformed gas was used directly as fuel, the fuel cell performances were similar to those using hydrogen as fuel. Moreover, no carbon deposit was observed after continuous operation for more than 10 h using the pre-reformed propane as the fuel, which was consistent with our previous result when methane was fed directly as fuel to the fuel cells [11]. In contrast, when propane was directly used as the fuel, the fuel cell performance was relatively low and degraded quickly due to carbon deposition. For example, the peak power density reduced to only 140 mW/cm^2 after running on propane for 10 h, while the values for fuel cells running on diluted H_2 and pre-reformed propane remained stable during the 10-h operation. Fig. 5(a) shows the impedance spectra for the fuel cell measured under open-circuit conditions at 600 °C using a two-electrode configuration. After excluding the cathodic contribution [11,18], the anodic polarization resistances were 0.64, 0.73 and 0.79 Ω cm^2 when the anode was fed with H_2, pre-reformed propane and propane, respectively. As can be seen from Fig. 5(b), the anodic polarization resistance for pre-reformed propane remained relatively constant during the entire period of measurements. However, it increased about 35% after 10-h operation due to carbon deposition when propane was directly used as the fuel.

Acknowledgements

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