Performance and durability evaluation of dry reforming in solid oxide fuel cells

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ABSTRACT

The performance and durability of a single solid oxide fuel cell (SOFC) operating at 1023 K under differing reforming conditions and fed by CH_4, CO_2, and H_2O were investigated. For dry reforming, the CO_2/CH_4 ratio was set to 2.7 to avoid coking in the catalyst and anode support; steam reforming was performed at $H_2O/CH_4 = 2.5$. The current–voltage characteristics of external dry reforming showed lower voltages for low fuel utilization, especially at high current densities, than those observed in steam reforming. The voltages under external dry and steam reforming were 0.880 V and 0.896 V, respectively. However, at fuel utilization values approaching 90%, the voltage under dry reforming was higher than that measured under steam reforming. External dry reforming had short term durability behavior comparable to that of external steam reforming, but the results from internal dry reforming suggested that this condition needs sensitively control regulation relative to the other characterized conditions in order not to cause coking.
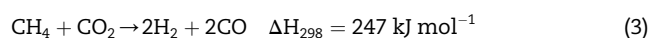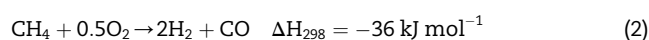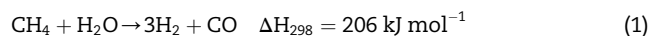
Introduction

Fuel cells are attractive technological solutions for environmental considerations, such as limited fossil fuel sources, because they feature high conversion efficiencies. Solid oxide fuel cells (SOFCs) in particular are well known for high electrical efficiency and fuel flexibility [1], compatible with natural gas, propane, methanol, ethanol, and biogas.

Steam reforming is recognized as the most reliable reforming method for producing a high rate of hydrogen for these prospective fuels, and existing fuel cell systems are equipped to perform this reaction [2,3]. Steam reforming is also attractive because of its low carbon deposition risk compared to other reforming methods such as partial oxidation and dry reforming, especially at low temperatures [4]. However, with steam reforming, water supply systems often cause trouble and complicate the design of the fuel cell system. Partial oxidation reforming is a possible choice for simplifying system configuration. However, an SOFC system utilizing partial oxidation reforming leads to low electrical efficiency because of its low transform ratio of H_2 and CO, and drop in operating voltage caused by residual N_2 [5]. CO_2 reforming (known as dry reforming) is an interesting option for water-free anodic reactions fed by off-gas recirculation, biogas, or CO_2 reutilization from carbon capture and storage systems, maintaining high electrical efficiency [6,7]. The equations for steam reforming, partial oxidation reforming, and CO_2 reforming are respectively given as follows.

$$CH_4 + H_2O \rightarrow 3H_2 + CO \quad \Delta H_{298} = 206 \text{ kJ mol}^{-1} \tag{1}$$

$$CH_4 + 0.5O_2 \rightarrow 2H_2 + CO \quad \Delta H_{298} = -36 \text{ kJ mol}^{-1} \tag{2}$$

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \quad \Delta H_{298} = 247 \text{ kJ mol}^{-1} \tag{3}$$

In the literature, biogas-fueled SOFCs utilizing internal dry reforming have already been reported [8–14]. Internal reforming enables the elimination of the reformer device, simplifying the system while increasing the overall system efficiency by improving the thermal management [15,16]. Therefore, many researchers have focused on internal dry reforming fed by biogas or simulated biogas.

However, rapid degradation is often reported from durability tests of cells utilizing internal dry reforming because coking often occurs in the anode support when the carbon activity is high [8–10,12]. Lanzini et al. evaluated aging behavior on a planar Ni-YSZ anode-supported cell with $CH_4:CO_2 = 1.0:1.0$, current density 0.3 A cm^{-2} at an operating temperature of 1043 K, and reported that the degradation rate was 20% within 300 h. This rate was related to coking because of high carbon activity [8]. In terms of current load effect, loading current will move the operation point to a safer region with respect to carbon deposition. Griona et al. verified the effect of cell polarization on carbon deposition using a cell aged at 1073 K with CH_4/CO_2 with a ratio of 1.5 at OCV and current density 0.12 A cm^{-2} for 120 h [11]. The anode exhibited no carbon precipitation close to the electrolyte interface at loading current, while carbon deposited in the anode at OCV [11].

The C deposited in the coking phenomenon is generated by CH_4 cracking or the Boudouard reaction, as shown in Equations (4) and (5), respectively [17–19].

$$CH_4 \rightarrow C + 2H_2 \quad \Delta H_{298} = 75 \text{ kJ mol}^{-1} \quad (4)$$

$$2CO \rightarrow C + CO_2 \quad \Delta H_{298} = -171 \text{ kJ mol}^{-1} \quad (5)$$
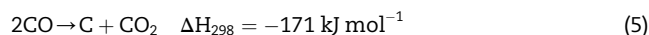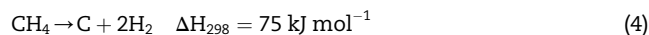
In order to overcome the coking, additional H_2O, CO_2, or O_2 needs to be added to the fuel, decreasing the concentrations of CH_4 or CO from the reforming reaction or water gas shift reaction (Equation (6)).

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H_{298} = -41 \text{ kJ mol}^{-1} \quad (6)$$
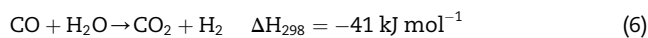
In this study, the performance and short term durability of an SOFC utilizing a non-coking external dry reforming reaction were evaluated and compared to those of a cell using conventional steam reforming.

In addition, to clarify the differences between internal and external dry reforming, the durability of a system operating by internal dry reforming was also determined.

Materials and methods

A commercial anode-supported cell (Elcogen AS Co., Ltd.) was utilized (see Supplementary Fig. 1). The materials were composed of a NiO-yttria-stabilized zirconia (YSZ) anode, YSZ electrolyte, Gd-doped ceria (GDC) barrier, and lanthanum strontium cobalt oxide (LSC) cathode. The thickness and active area of the cell were 550 μm and 81 cm^2, respectively. A NiO-SrTiO$_3$ catalyst (Murata Manufacturing Co., Ltd.) (see Supplementary Fig. 2) was prepared for use in both dry and steam reforming. The loading of the catalyst and the concentration of the NiO were 6.5 cc and 10 wt%, respectively. The grain size of the catalyst was Φ3.8 × 3.8 mm. A schematic diagram of the experiment is shown in Fig. 1, and a photograph of the experimental apparatus is shown in Fig. 2. The catalyst was filled in the catalyst layer (see Supplementary Fig. 3) and was annealed under an atmosphere of $CH_4:H_2O:CO_2 = 1.0:0.3:1.0$ at 1023–1123 K for 3 h to reduce NiO and startup with dry reforming before the anode-supported cell testing using the experimental apparatus shown in Fig. 2. Fig. 3 shows an SEM
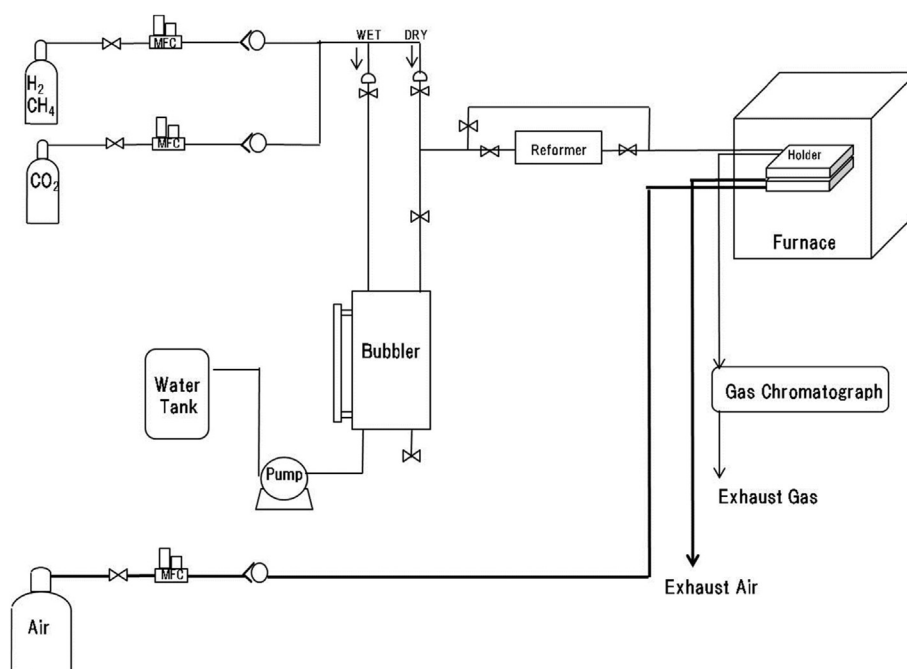

Fig. 1 – Schematic diagram of the experimental apparatus.