

Effects of low hydrocarbons on the solid oxide fuel cell anode

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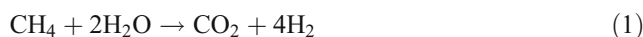
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Abstract In this work, the effects of ethylene on the solid oxide fuel cell (SOFC) anode were investigated both for an SOFC single cell and an SOFC stack. Two fuels were used to observe the effects that low hydrocarbons (over C1-hydrocarbons) in the reformat gas stream have on the SOFC anode. Methane or ethylene was supplied to the electrolyte-supported SOFC anode. Using ethylene as a fuel, catastrophic degradation of SOFC performance was observed due to ethylene-induced carbon deposition onto the SOFC anode. Thus, a new methodology, termed “post-reforming,” is introduced for the removal of low hydrocarbons (over C1-hydrocarbons) from the reformat gas stream. The CGO-Ru catalyst was selected as the post-reforming catalyst because of its high selectivity for removing low hydrocarbons (over C1-hydrocarbons) and for its long-term stability. The diesel reformer and post-reformer were continuously operated for ~250 h in coupled-operation mode. The reforming performance was not degraded, and low hydrocarbons (over C1-hydrocarbons) in the diesel reformat were completely removed.

Keywords Solid oxide fuel cell (SOFC) · Carbon deposition · Diesel reformat · Ethylene (C₂H₄) · Post-reforming

Introduction

Fuel cells are devices that directly convert chemical energy into electrical energy at relatively high efficiencies. Fuel cells can be classified with respect to electrolyte types, feed reactants, electrolytic ions, and operating temperatures. Solid oxide fuel cells (SOFCs) are high-temperature fuel cells that are made of ceramic materials and that use oxygen ions (O²⁻) as the electrolytic ions [1, 2]. The high operating temperatures of SOFCs provide various advantages, including high efficiency and much greater fuel flexibility, than low-temperature fuel cells (e.g., proton exchange membrane fuel cells and phosphoric acid fuel cells). With sufficient steam feeds, SOFCs can directly use CH₄ or CO as fuels; therefore, SOFCs do not require a CO clean-up processor such as a water-gas shift (WGS) reactor or a preferential oxidation reactor. The use of CO or CH₄ is possible because the anode material of SOFCs is active in steam reforming (SR) [Eq. 1] and in the WGS [Eq. 2] reactions [1, 3].

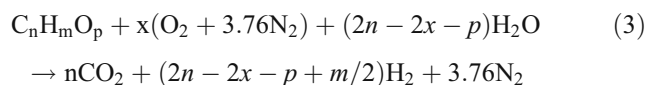


Because of this capability, hydrogen-rich syngas produced from a hydrocarbon fuel-reforming process can be used as the fuel for SOFCs. Among several fuels, liquid fuel reforming is useful to an SOFC system because liquid fuels have several advantages including high hydrogen density and a well-distributed infrastructure. Of the reforming methods, autothermal reforming (ATR) is suitable for liquid hydrocarbon fuel reforming because oxygen-aided reactions can break the aromatics in the liquid fuel and

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because the steam can suppress carbon deposition during reforming reactions. Many research groups have investigated the ATR process for liquid fuels because of its potential in applications requiring compact, lightweight hardware [4–7]. The idealized ATR reaction for the conversion of a hydrocarbon or oxygenate fuel is shown in Eq. 3 [7].



In a deviation from the idealized ATR reaction, the compounds CO, CH₄, H₂O, and low hydrocarbons are also formed from the ATR reaction. In particular, reformates of liquid fuels contain higher concentrations of low hydrocarbons (over C1-hydrocarbons) than gaseous reformates. Hence, the hydrogen/syngas produced from most liquid hydrocarbon fuel reforming is unfit for SOFC operation because reformates of these liquid hydrocarbon fuels (i.e., gasoline, kerosene, and diesel) contain higher concentrations of low hydrocarbons (over C1-hydrocarbons; e.g., ethylene, ethane, propane, and propylene) than other hydrocarbon fuels (e.g., methane, NG, and LPG) reformates. It is important to note that the concentration of ethylene (C₂H₄) is usually higher than that of other low hydrocarbons (over C1-hydrocarbons) in the reformat [4, 5]. Ethylene is well-known as a carbon deposit precursor on Ni-based catalysts during steam reforming. Rostrup-Nielsen et al. identified ethylene as a severe carbon precursor contributing to rapid coke formation during the reforming process [8]. Figure 1 shows the rate of carbon deposition for several hydrocarbons. The carbon deposition induced by ethylene is the fastest reaction in comparison to the other

hydrocarbons presented, including the aromatics. If a liquid fuel reformat including C₂H₄ is supplied directly to the SOFC anode, the C₂H₄ in the reformat may readily induce carbon deposition on the Ni-based anode.

Because of their high operating temperatures, SOFCs theoretically can use any hydrocarbon as a fuel. This study investigates the effect of ethylene on the SOFC anode. Three fuels were used to observe the effects of low hydrocarbons (over C1-hydrocarbons) in the reformat gas stream on the SOFC anode. Hydrogen, methane, and ethylene were supplied either to an electrolyte-supported SOFC anode or to a seven-cell SOFC short stack. When using ethylene as a fuel, catastrophic degradation of SOFC performance was observed. This result was caused by carbon deposition on the SOFC anode. Thus, the removal of low hydrocarbons larger than C₂—especially ethylene—from the reformat gasses is important for the stable operation of a SOFC. A new methodology for removing low hydrocarbons (over C1-hydrocarbons) from the reformat gas stream was investigated, and the term “post-reforming” is introduced in this paper.

Experimental

Single-cell operation

Electrolyte-supported SOFC single cells were prepared to investigate the effects of ethylene on the SOFC anode. Yttria-stabilized zirconia (YSZ) electrolyte-powder (Tosoh TZ-8Y) was pressed and sintered at 1,500°C to make dense YSZ pellets with a thickness of 1.5 mm and a diameter of 25 mm. Using a screen-printing method, an anode consisting of NiO (Sumitomo), YSZ, and poly-methylmethacrylate (Aldrich) was coated onto one side of the YSZ to a thickness of 15 μm and was then sintered at 1,300°C. A cathode consisting of a 60:40 weight ratio LSM (La_{0.8}Sr_{0.2}MnO_{3±δ}) and YSZ at was coated onto the other side of the YSZ pellet by screen printing to a thickness of 15 μm and was then sintered at 1,100°C. A single-cell test setup was prepared (Fig. 2) and the performance measurement was conducted at 750°C. Electrical contact with the cell was achieved using a Pt wire with a Pt paste at the cathode and using a Ni paste at the anode. The cell was then attached to an alumina tube by using a ceramic adhesive (Aremco ceramic sealant 516). A gaseous mixture of C₂H₄, H₂, H₂O, and N₂, designed to simulate the reformat gas from a diesel reformer, was fed into the anode side. Air was supplied to the cathode side. To study the effect of ethylene alone, other C-containing gasses such as CO, CO₂, and CH₄, were excluded from the anode feed gas. The current-voltage characteristics and impedance spectra were measured as functions of time.

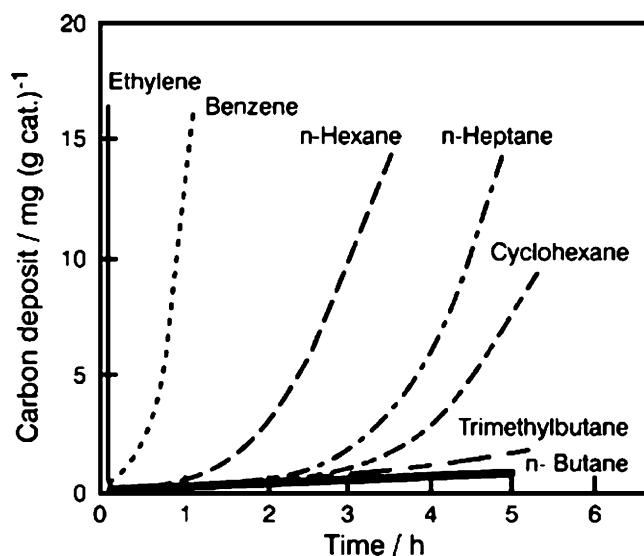


Fig. 1 Rate of carbon formation for different hydrocarbons [8]

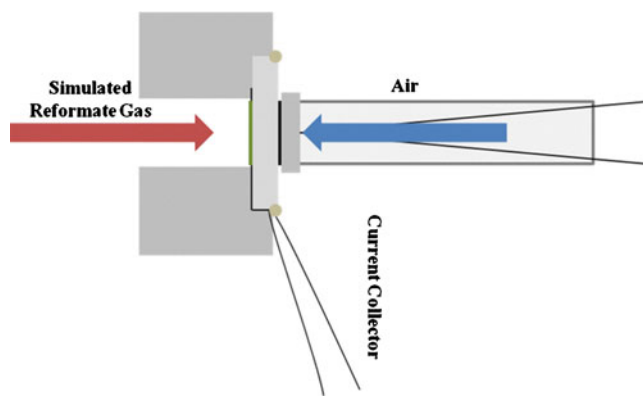


Fig. 2 The schematic of the single-cell test setup

Electrical conductivity test of the Ni-YSZ anode

A mixture of NiO (Sumitomo), YSZ (Tosoh TZ-8Y) and Poly-methyl-methacrylate (Aldrich) in the ratio of 60:40:15 (wt.%) for use as a pore former was ball-milled for 24 h and then dried. The powder was uni-axially pressed (784 MPa) into rectangular bars ($5 \times 5 \times 18$ mm) and sintered at $1,500^\circ\text{C}$ for 5 h. Next, the NiO-YSZ cermet specimens were reduced for 5 h at 750°C under a 4% H_2 (balance Ar) atmosphere. After reduction, the open porosity and the pore size distribution of the sample were measured by a mercury porosimeter (Micromeritics Autopore IV 9500). The porosity was 42.1%, and the pore diameter was $2.91 \mu\text{m}$. Therefore, reactants can easily penetrate into the sample.

SOFC short stack (seven cells)

The seven-cell SOFC stack was installed in an electric furnace because the SOFC stack was too small to operate in a self-sustaining mode. The SOFC stack was supplied by Korea Electric Power Research Institute. The components of the cell were layered in the following order: lanthanum strontium cobalt ferrite (LSCF) (cathode, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$), CGO buffer layer (the protective layer of $\text{CeO}_2\text{-Gd}_2\text{O}_3$ was deposited between the LSCF and YSZ), YSZ (electrolyte), Ni-YSZ (anode). The cell was operated at 720°C . The planar stack was based on an internal manifold and cross-flow-type structure. Low-melting temperature borosilicate was used to seal the stack. For current collection, nickel felts were located between the cells and interconnect on the

anode side. Flexibility of the nickel felts may also relieve undesired mechanical stress, which can be produced as the stack heats. Voltages at the stacks were measured for each layer. The size of the cell was 10×10 cm, and STS 430 interconnects were used. Details of the fabrication process, along with performance data for the single cells and the small stacks, were presented in our previous paper [9]. Here, two types of gasses were supplied to the SOFC anode. The degradation of the SOFC stack, driven by syngas containing CH_4 or C_2H_4 , was investigated, and the effects were compared. The SOFC short stack was operated for 10 h at 20 A for each experiment. The syngas compositions of the anode inlet gas are shown in Table 1. The system configuration for operation of the short stack is shown in Fig. 3.

Diesel reforming

An experimental micro-reactor was prepared for studying diesel ATR and post-reforming. A Pipe & Instrumentation Diagram of the micro-reactor system is shown in Fig. 4. Each diesel reforming and post-reforming reactor was made from 0.5 in STS tube and was placed inside an electrical furnace. The reactants for ATR were fuel, water, and air. The reformate product of the diesel ATR was then supplied directly to the post-reformer. For the post-reforming catalyst test, the diesel ATR reactions were carried out using an O_2/C ratio of 0.5 and an $\text{H}_2\text{O}/\text{C}$ ratio of 2 and using a synthetic fuel feed, a mixture of $\text{C}_{12}\text{H}_{26}$ and $\text{C}_{11}\text{H}_{10}$ [10]. For the long-term performance test, the reaction was carried out at an O_2/C ratio of 0.8 and an $\text{H}_2\text{O}/\text{C}$ ratio of 3 and using a commercial diesel feed (GS-Caltex, Korea). This set of conditions was used for comparison with previous research results [4]. The fuel and de-ionized water ($>15 \text{ M}\Omega$) were supplied by high performance liquid chromatography pumps (MOLEH Co. Ltd.). The air and N_2 were metered using mass flow controllers (MKS Co. Ltd.). The ATR reforming catalyst used in this study was a noble metal-based catalyst of Pt on Gd-doped CeO_2 (CGO-Pt (0.5 wt.%)). For the ATR reaction, a gas hourly space velocity of $12,500 \text{ h}^{-1}$ was selected, and the temperature of the electrical furnace was set at 800°C . The post-reforming test was performed at a variety of reaction temperatures with various catalysts. The reaction conditions of each experiment are indicated in the corresponding figure caption.

Table 1 Compositions of the anode inlet gas supplying the SOFC short stack

Case	$\text{LHV}_{\text{HC}}/\text{LHV}_{\text{H}_2+\text{HC}}$ (%)	H_2 (mol.%)	CH_4 (mol.%)	C_2H_4 (mol.%)	H_2O (mol.%)	N_2 (mol.%)
I	10.0	40.7	1.6	-	45.4	Balance
II	10.0	40.5	-	1.0	45.2	Balance

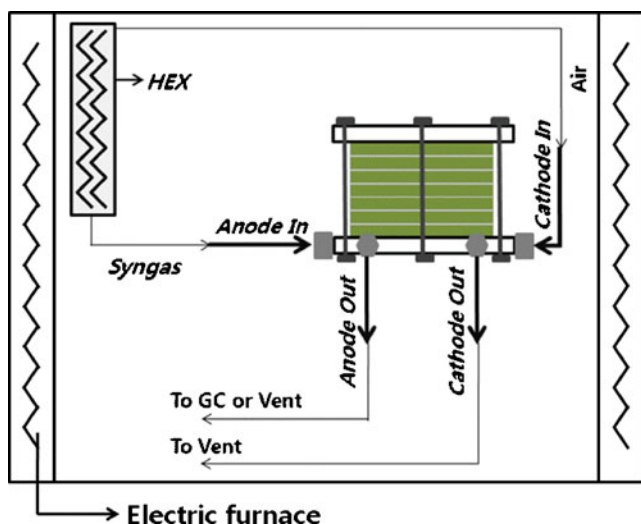


Fig. 3 Schematic of the SOFC short stack (seven cells, 10×10 cm)

Analysis

Using a frequency resonance analyzer and a potentiostat (Solartron 1260 and 1287), the current-voltage characteristics of the single cell were measured, and electrochemical impedance spectroscopy was performed with the cell in the open-circuit voltage state. To calculate the electrical conductivity, the conductance of the anode material was measured by using the four-probe method and then multiplied by a geometric factor, defined as the length between the second and third probes divided by the cross-sectional area. The electrical load was applied to the SOFC stack using a DC loader (DAEGIL EL-1000P).

After the complete removal of moisture, the diesel reformate was analyzed by an Agilent 6890 gas chromatograph equipped with a thermal conductivity detector (TCD) and a

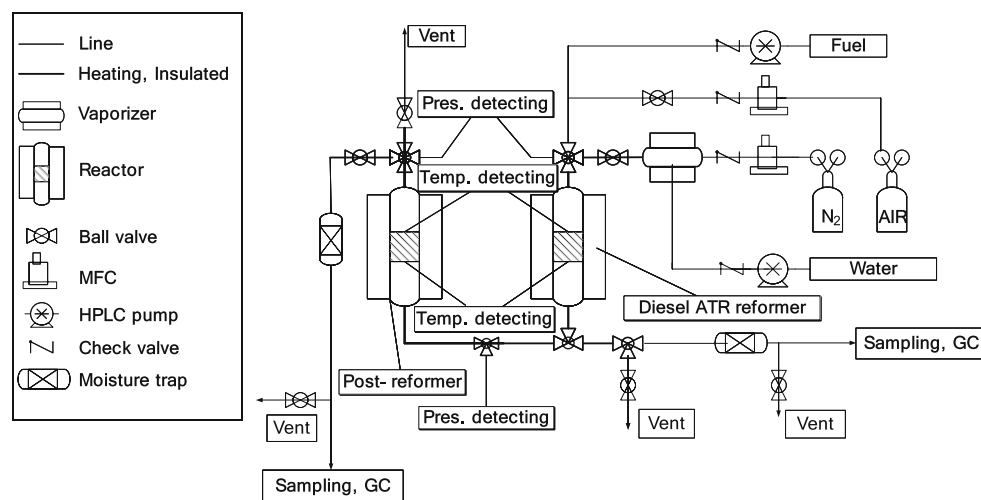
flame ionization detector (FID). The compounds H_2 , CO , CO_2 , N_2 , and O_2 were analyzed by TCD with Ar as the carrier gas, and all hydrocarbons from the C_1 -level to the C_4 -level (i.e., CH_4 , C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8 , $n-C_4H_{10}$, $i-C_4H_{10}$, and C_2H_2) were analyzed by FID with He as the carrier gas.

Results and discussion

Ethylene effects on the SOFC single cell

Cell deactivation via carbon deposition occurred more rapidly in the electrolyte-supported cell with a smaller anode thickness than in the anode-supported cell. The performance of the SOFC decreased during its operation. The addition of ethylene (2 mol%) caused a severe voltage drop (Fig. 5), although carbon formation is not thermodynamically favored at these concentrations of H_2 and H_2O . The impedance spectra of the SOFC single cell exhibited semi-circle behavior. The high frequency intersection of the intersection with the x -axis corresponds to the Ohmic resistance, and the diameter of the semi-circle corresponds to Faradaic resistance (Fig. 6). The Ohmic and Faradaic resistances increased as the exposure time increased, and those increases caused the voltage drop shown in Fig. 5. The increase of these two resistances can be explained by the detachment of the anode from the YSZ pellet (Fig. 7). It appears that carbon formed by ethylene weakened the bonding between the Ni particles, and consequently, the structure of anode was completely broken down. It has been reported that the bulk electrical conductivity, related to the intrinsic contiguity of the nickel particles, can decrease due to infiltration of carbon into the anode [11]. Therefore, the rate of carbon deposition by a hydrocarbon can be inferred from the rate of decrease in the

Fig. 4 Schematic diagram of the micro-reactor system



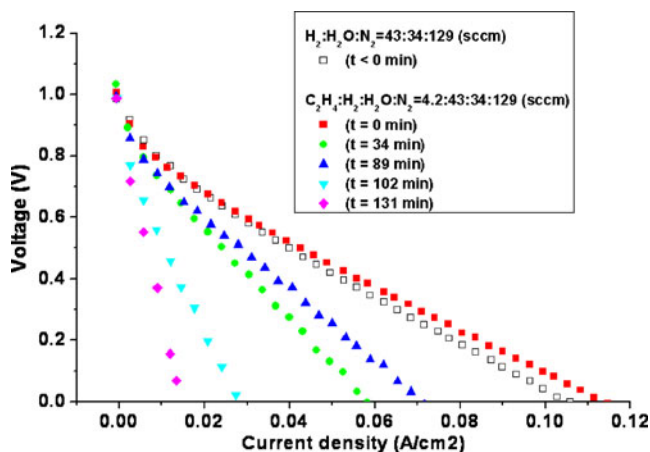


Fig. 5 I-V characteristics of a single cell when using fuel containing 2 mol% ethylene

bulk electrical conductivity. To compare the rate of carbon formation by ethylene and methane, the changes in bulk electrical conductivity of the Ni/YSZ-cermet anode was measured using a four-probe DC technique. Compared to the methane-fed case, the electrical conductivity decreased rapidly when using ethylene diluted with nitrogen (Fig. 8). Therefore, during operation under ethylene, the vigorous carbon formation and its consequent infiltration into the anode lead to the fatal breakdown of the anode structure and the single-cell performance severely deteriorates. However, there is not yet a quantitative relationship between the ethylene concentration and the rate of the performance deterioration.

Ethylene effect on the SOFC short stack

The performance of the SOFC short stack with different syngas mixtures containing either CH₄ or C₂H₄ in the anode inlet gas was studied. The SOFC short stack operated for 10 h for each experiment. Figure 9a shows the performance

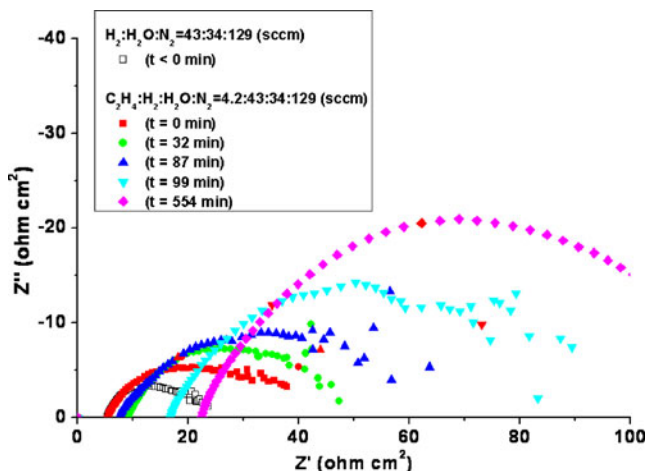


Fig. 6 Impedance spectra obtained with the single cell at open circuit using a fuel with 2 mol% ethylene

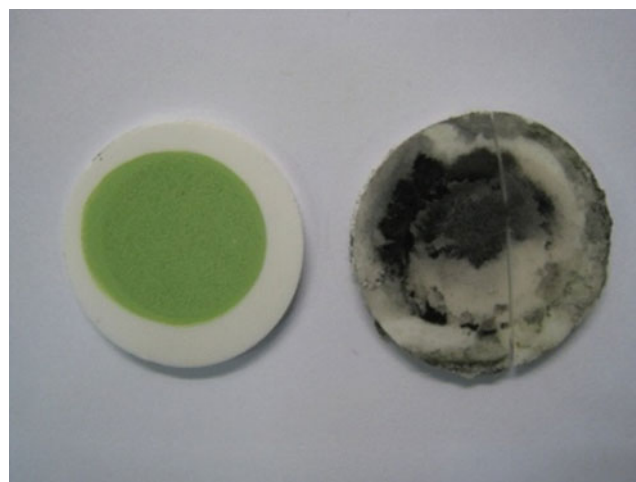


Fig. 7 The electrolyte-supported single cell before and after exposure to fuel containing 2 mol% ethylene

change in the SOFC short stack using the CH₄-syngas. There is no significant performance change when the fraction of CH₄ was 10% in the LHV base (case I). However, a catastrophic decrease in performance was observed when the fraction of C₂H₄ was 100% in the LHV (case II; Fig. 9b). The performance of the SOFC short stack decreased slowly over the first 4 h, and then the stack voltage dropped suddenly, with a decrement of about 15% of the total voltage. This experiment was performed twice and the result was reproducible. The phenomenon of stack degradation is similar to that seen in the single cell experiment with a C₂H₄ feed. The difference in power output between case I and case II was small, but stable operation of the SOFC does not guarantee the ability to use diesel reformat containing ethylene, a carbon precursor.

Additionally, our previous research on ethylene steam reforming showed that hydrogen yield suddenly decreased

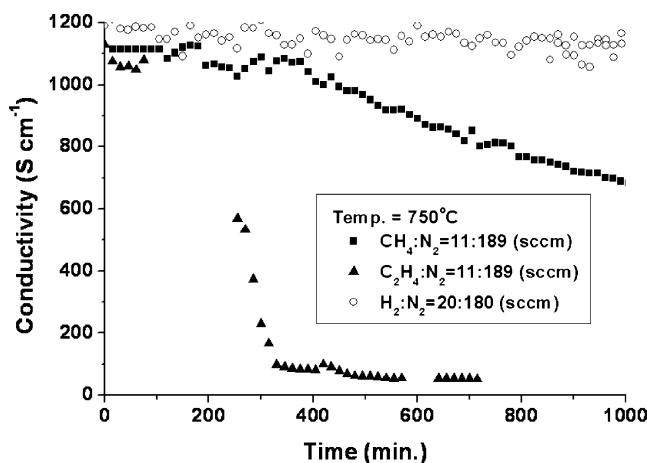


Fig. 8 Time-course comparison of the electrical conductivities of a Ni-YSZ single cell under a H₂-N₂, CH₄-N₂ and C₂H₄-N₂ atmosphere at 750°C

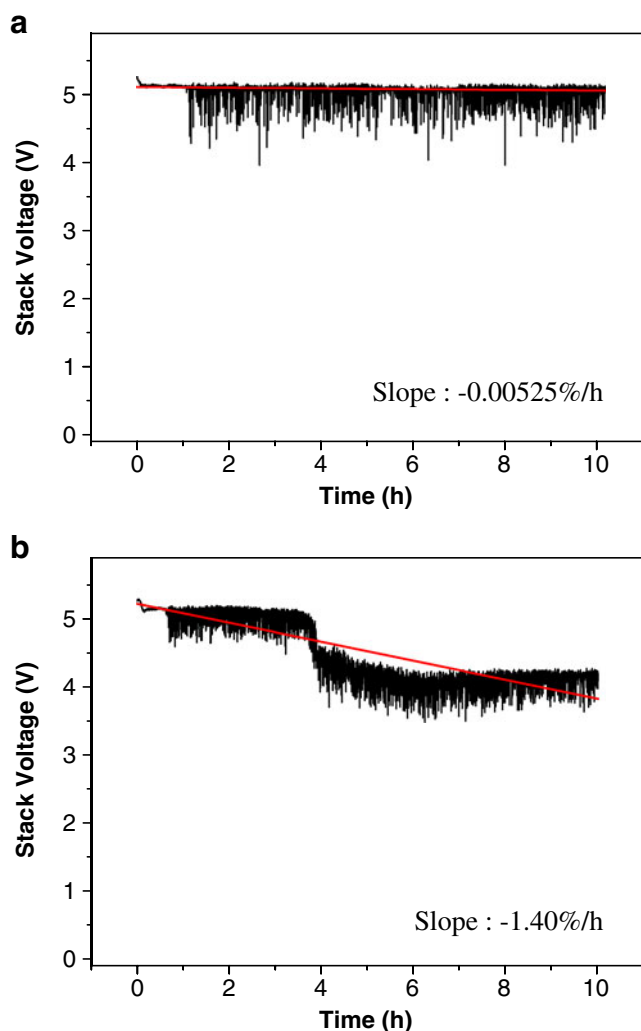


Fig. 9 Degradation of SOFC short stack performance for **a** $LHV_{CH_4}/LHV_{H_2+CH_4} = 10\%$ and **b** $LHV_{C_2H_4}/LHV_{H_2+C_2H_4} = 10\%$

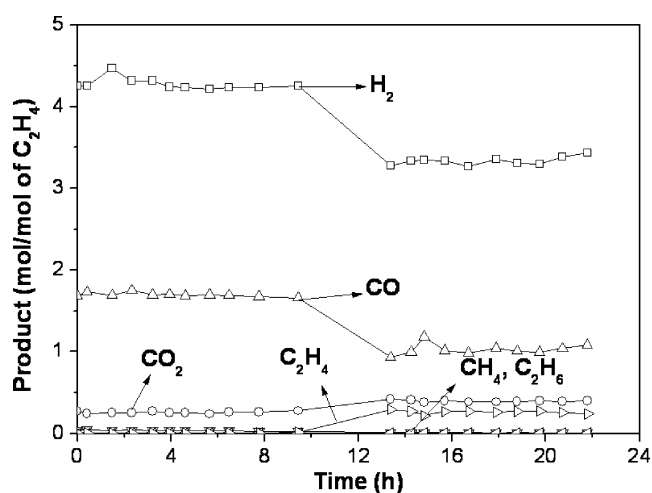


Fig. 10 C_2H_4 steam reforming ($H_2O/C=1.25$) [4]

during the C_2H_4 SR reaction [4]. Ethylene SR was performed for 22 h with a H_2O/C ratio of 1:25. After about 12 h of operation, there was a sudden decrease in H_2 yield (Fig. 10). Ethylene may induce carbon deposition on the SOFC anode. It is difficult to predict the reliability of a SOFC with C_2H_4 in the feed, even though the concentration of C_2H_4 is very low. Therefore, low hydrocarbons (over C1-hydrocarbons) in the reformat, especially ethylene, should be completely removed for the stable operation of SOFCs.

Low hydrocarbons removal from diesel reformat for stable operation of SOFC

Several research results have shown that it is difficult to remove ethylene from liquid fuel reformat. Compounding this difficulty, the ethylene concentration in diesel or kerosene reformat is dramatically increased as the reforming operation time increases [4, 6, 12, 13]. Hence, a new method for removing low hydrocarbons (over C1-hydrocarbons) in a liquid fuel-reforming process was developed as a part of this work. This process has been termed “post-reforming.” The objective of post-reforming is to complete the conversion of low hydrocarbons (over C1-hydrocarbons) in the liquid fuel reformat. Here, a synthetic diesel reformat was used for testing the post-reformer and the catalysts for post-reforming. The product distribution of the diesel reformat is shown in Table 2; this reformat was directly supplied to the post-reforming reactors. Several catalysts were used for the post-reforming reaction. After the post-reforming reaction, low hydrocarbons (over C1-hydrocarbons) amounts were detected (Fig. 11). Commercial pre-reforming catalyst (C11-PR from Süd-Chemie) and CGO-Ru (3.0 wt.%) catalyst showed high activity for low hydrocarbons (over C1-hydrocarbons) removal. Although low hydrocarbons (over C1-hydrocarbons) in the ATR reformat are effectively converted by the C11-PR catalyst, this catalyst has a drawback for post-reforming because a hydrogen pre-reduction process is required when using Ni-based catalysts. On the other hand, the Ru-based catalyst does not need a hydrogen pre-reduction protocol. Several research results indicate that if Ni-based catalyst was not reduced appreciably with H_2 , then it was inactive in reforming reaction. Therefore, a pre-reduction treatment with H_2 is important to achieve high activation and deactivation resistance in a catalyst [14, 15]. For the hydrogen pre-reduction system, the

Table 2 Composition of the synthetic diesel reformat

Species	H_2	CO_2	CO	N_2	H_2O	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
(mol%)	17.7	9.6	4.91	37.2	29.0	0.65	0.73	0.06	0.17	0.01

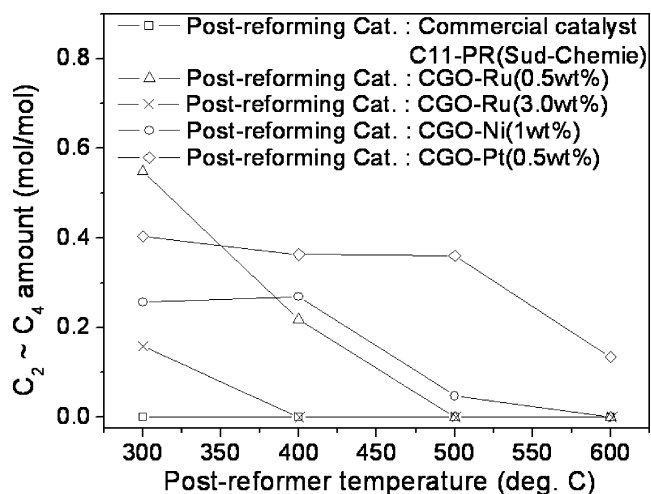


Fig. 11 Low hydrocarbons (over C1-hydrocarbons) amounts in post-reforming reformat when using different post-reforming catalysts. ATR catalyst (CGO-Pt (0.5 wt.%)) vol=2 mL, GHSV=12,500/h, $H_2O/C=2$, $O_2/C=0.7$, ATR temp=800°C, post-reforming catalyst vol.=3.5 mL

diesel reforming processor in an SOFC system should be larger. Additionally, the Ni-based catalysts have lower coke tolerance than noble metal-based catalysts.

Finally, the long-term performance of commercial diesel fuel reforming was investigated using post-reforming, and the CGO-Ru (3.0 wt.%) catalyst was selected for post-reforming. The product distribution of the reformat product after post-reforming at a temperature of 600°C is shown in Fig. 12. The ATR temperature was fixed at 800°C. The low hydrocarbon species (over C1-hydrocarbons) present in the product gas were not detected for about 250 h.

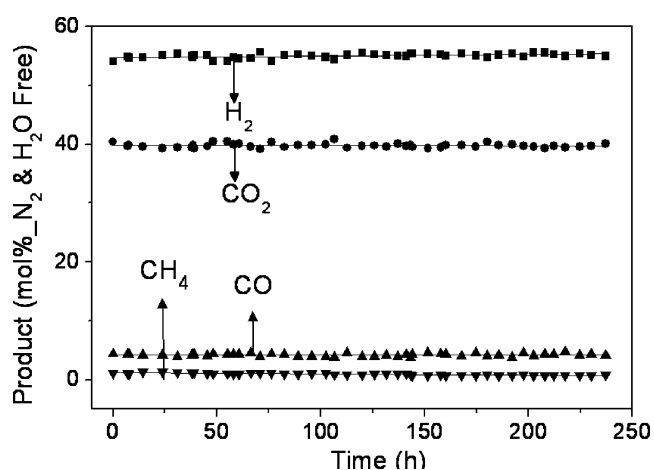


Fig. 12 Product distribution of post-reforming product operating in integrated mode with ATR; ATR catalyst (CGO-Pt (0.5 wt.%)) vol=1 mL, GHSV=12,500/h, $H_2O/C=3$, $O_2/C=0.8$, ATR temp=800°C, post-reforming catalyst (CGO-Ru (3.0 wt.%)) vol.=1.75 mL, post-reforming temp=600°C

Conclusion

Here, we report the effects of using low hydrocarbon species (over C1-hydrocarbons) to drive SOFCs with Ni-based anodes. Ethylene is closely related to carbon deposition on the SOFC anode. The performance of both the SOFC single cell and the SOFC short stack were dramatically decreased by ethylene-induced carbon deposition. Therefore, the presence of ethylene in the reformat gas at the anode inlet is fatal to the long-term reliability of SOFCs. The development of a high-tolerance anode and a method for the removal of low hydrocarbons (over C1-hydrocarbons) from the reformat are both necessary to guarantee stability in SOFC operation. In this study, a post-reforming method was introduced to remove low hydrocarbons (over C1-hydrocarbons) in a liquid fuel reformat. Using a CGO-Ru (3.0 wt.%) as a post-reforming catalyst, a diesel-reforming system including a post-reformer was continuously operated for ~250 h, and low hydrocarbons (over C1-hydrocarbons) were completely removed. When applying the post-reforming methodology to diesel reforming, stable operation of a diesel-driven SOFC system is expected.

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