



Multi-Fuel Capability of Solid Oxide Fuel Cells

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Abstract. One of the most attractive features of solid oxide fuel cells is their flexibility for fuels so that internal reforming and/or simple external reforming may be possible. In this study, equilibria in various possible fuel gases are considered, and C–H–O diagrams are constructed. Power generation characteristics for these fuels are measured and compared with those for simulated reformed gas in equilibrium compositions. We have succeeded to demonstrate direct-alcohol SOFCs for e.g. methanol, ethanol, and propanol. Mixtures of CH₄ and CO₂ are used as simulated biogas, and iso-octane (C₈H₁₈) and n-dodecane (C₁₂H₂₆) are highlighted as simulated gasoline and kerosene, respectively. Influence of fuel impurities on power generation characteristics is also discussed.

Keywords: SOFC, anode, fuel gas compositions, alcohols, higher hydrocarbons, biogas

1. Introduction

Fuel cells have been increasingly accepted as environmentally compatible, efficient energy conversion systems. In particular, solid oxide fuel cells (SOFC) may be regarded as the most flexible fuel cells in respect to their flexibility in selecting the types of fuels [1–9] able to be supplied directly to the fuel electrodes. Because of their multi-fuel capability, not only hydrogen and carbon monoxide but also various kinds of fuels including hydrocarbons and alcohols could be used via internal reforming and/or via simple external reforming, as illustrated in Fig. 1.

The purpose of this study is therefore to examine and compare power generation characteristics of SOFCs for various types of SOFC fuels. First, we carry out thermochemical calculations to understand chemical equilibria, which is helpful to adjust initial fuel compositions. Power generation characteristics of SOFCs operated with alcohol- and hydrocarbon-based fuels via internal reforming or via external reforming are then measured. Fuel gases containing a small amount of H₂S are also supplied to analyze the influence of fuel impurities on electrochemical performance.

2. Fuel Gas Equilibria

2.1. Thermochemical Calculations

Fuel gases including e.g. hydrocarbons and alcohols are either directly supplied or reformed in a reformer before supplying to fuel cells. In order to apply such fuel gases, it is in particular essential to know the chemical compositions in thermodynamic equilibrium under given operational conditions for any types of fuel cells. In the case that reforming and/or decomposition kinetics are sufficiently fast, compositions of fuel gases are identical to those in thermodynamic equilibrium. Thermochemical calculations will give such information for any kinds of fuel gases if their thermochemical data are available [4–9]. Thermochemical calculations have also been demonstrated to be useful e.g. for fuel cell materials development [10], for studies on interfacial electrochemical properties [11], and for point defect engineering of fuel cell related materials [12]. As possible fuels, following species have been taken into account: natural gas (consisting mainly of CH₄ with a small amount of other hydrocarbons such as C₂H₆), coal gas (consisting mainly of CO and H₂), liquefied petroleum gas (LPG, consisting mainly of C₃H₈ with C₄H₁₀), naphtha (consisting mainly of C₅ and C₆ hydrocarbons), gasoline (consisting mainly of hydrocarbons with carbon numbers around 8), diesel and kerosene

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— For realizing flexible fuel cells —

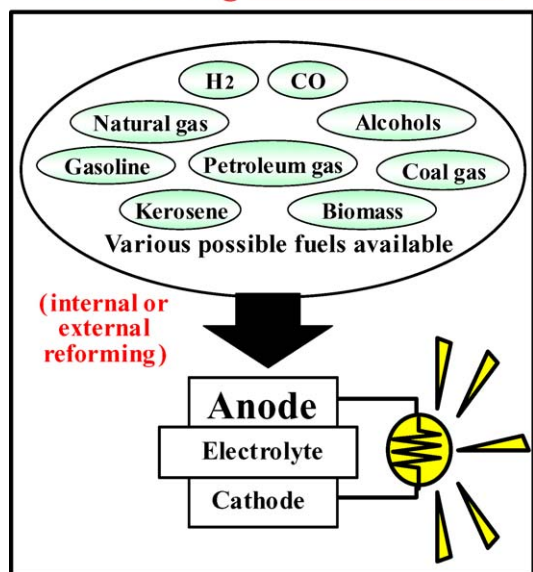


Fig. 1. Multi-fuel capability of solid oxide fuel cells.

(consisting mainly of hydrocarbons with carbon numbers around 12), alcohols, dimethylether, biogas (consisting mainly of CH_4 , CO_2 and H_2O), and coke oven gas [4, 5].

Thermochemical calculations were carried out using a program, HSC chemistry (Version 4.1, Outokumpu Research Oy, Finland) with an extensive thermochemical database. The calculations were performed by assuming a reactor to which a (mixed) fuel gas normalized to 1 kmol carbon was supplied, and the amounts of gas, liquid, or solid products in thermodynamic equilibrium were numerically derived, in the temperature range between 100° and 1000°C with a step of 10°C .

Figure 2 shows equilibrium products for (a) methane- and (b) methanol-based fuels with the steam-to-carbon ratio of 1.5. It can be found that carbon deposition can be neglected within the wide temperature range. The calculation results for other fuels mentioned above have been shown elsewhere [4]. Minimum amounts of H_2O essential to prevent carbon deposition were calculated, and the results are shown in Fig. 3 for hydrocarbons. While S/C of 1.5 is enough for CH_4 , higher S/C is needed with increasing carbon number of hydrocarbons, especially at lower temperatures. We have also made similar calculations for O_2 (partial oxidation) and CO_2 (CO_2 reforming) [4].

2.2. C–H–O ternary diagram: An Atlas for Adjusting Fuel Compositions

It has been found that the major equilibrium constituents in fuel gases are $\text{H}_2(\text{g})$, $\text{H}_2\text{O}(\text{g})$, $\text{CO}(\text{g})$, $\text{CO}_2(\text{g})$, $\text{CH}_4(\text{g})$, and $\text{C}(\text{s})$ [4]. Since their compositions depend solely on the C–H–O ratio, we can plot, on such C–H–O diagrams [5, 6, 9], parameters relevant to optimize operational conditions, including carbon deposition region, gas partial pressures, and electromotive force.

Figure 4 shows the positions of various fuel species for fuel cells [5]. Their positions can be shifted by adding H_2O (steam reforming), O_2 (partial oxidation), and/or CO_2 (CO_2 reforming) as co-reactants. One of the most important issues to be prevented for SOFCs is carbon deposition from the fuels. Figure 5 shows the carbon deposition limit lines, the carbon rich side of which corresponds to the carbon deposition region at each temperature. From Figs. 4 and 5, we can find that an addition of these co-reactants is essential to prevent carbon formation from most of these fuels shown in Fig. 4, at SOFC operational temperatures. More details on the C–H–O ternary diagrams are described elsewhere [5]. Once the C–H–O ratio is specified, C–H–O ternary diagrams are useful to derive relevant operational parameters without any additional thermochemical calculations, and thus useful for adjusting fuel compositions.

3. Electrochemical Performance for Various Fuels

3.1. Experimental Procedure

Planar-type cells were used in this study. Sintered electrolyte plates of 8 mol% Y_2O_3 - ZrO_2 (YSZ) with a thickness of $200\ \mu\text{m}$ and a diameter of 20 mm (supplied by Tosoh Corp.) were used, on which anode layers (80 wt% NiO-YSZ) were deposited via screen-printing [14] and were sintered at 1400°C for 5 hours. The cathode layers ($\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$) were then deposited, followed by sintering at 1150°C for 5 hours. The area of both electrodes was $5 \times 5\ \text{mm}^2$ [15–19, 21–24].

For electrochemical characterizations, air was supplied as oxidant, while various kinds of (evaporated) fuel gases were supplied to the anode. For alcohol-based fuels, the mixture of alcohol and water was supplied using a liquid chromatograph pump to an

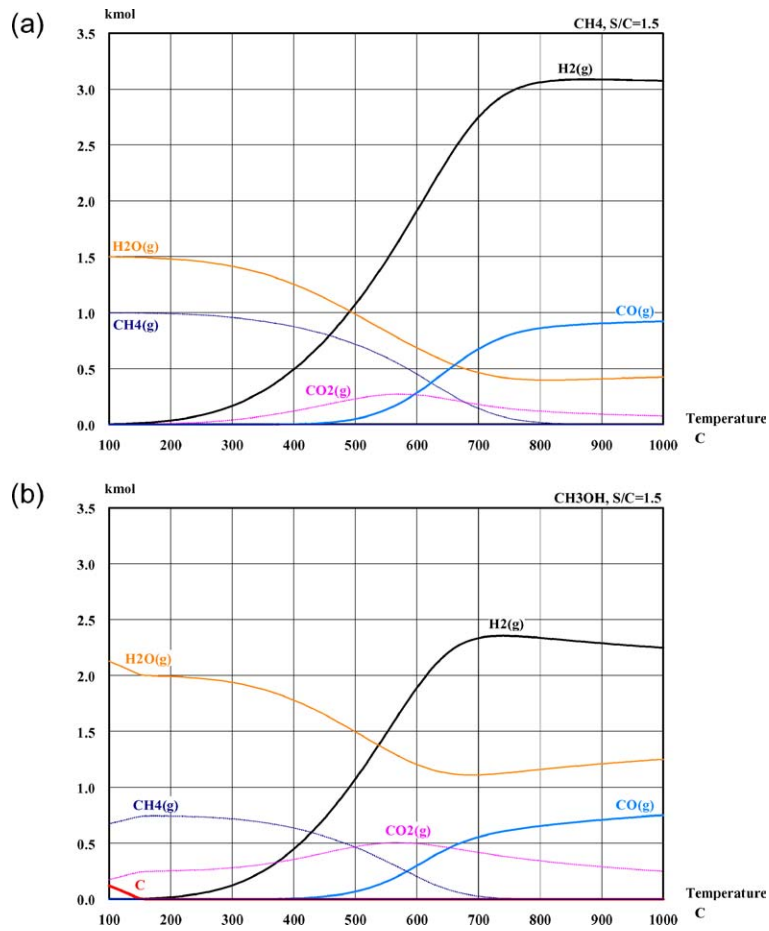


Fig. 2. Equilibrium products from (a) methane- and (b) methanol- based fuels with the steam-to-carbon ratio of 1.5 [4].

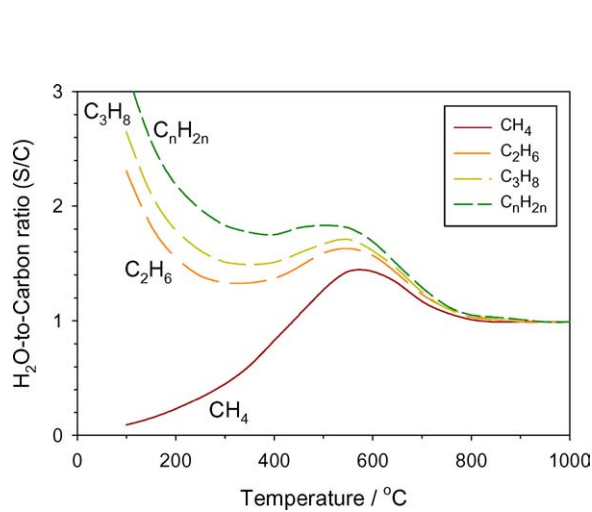


Fig. 3. Minimum steam-to-carbon (S/C) ratio needed to prevent carbon depositions in thermodynamic equilibrium for hydrocarbons [4].

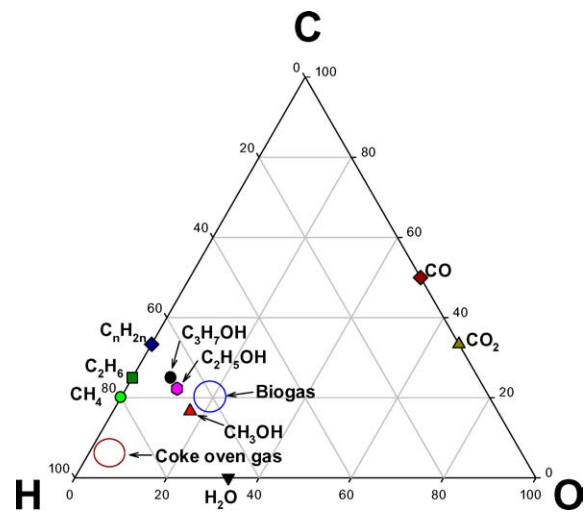


Fig. 4. Various hydrocarbons and related species in the C–H–O diagram [5].

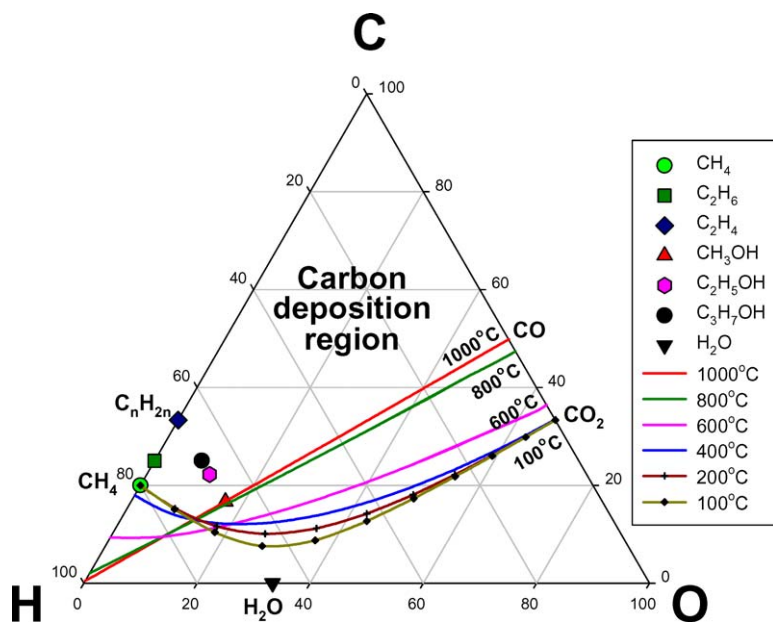


Fig. 5. Carbon deposition limit lines at various temperatures in the C–H–O diagram [5].

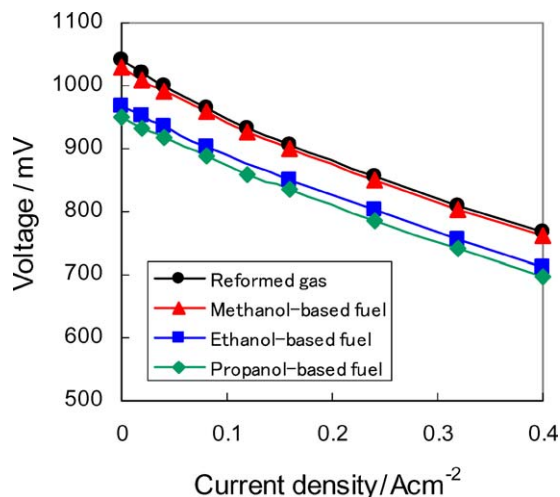


Fig. 6. Current-voltage characteristics of SOFCs for alcohol-based fuels at 1000°C [15, 16].

evaporator connected to the gas supply tube on the anode side. For higher hydrocarbon-based fuels, a corresponding amount of water was supplied to the evaporator in which the vapor of hydrocarbons was mixed with water vapor, and then supplied via reforming catalyst (Ru/Al₂O₃) bed to the anode [15, 19]. Nitrogen gas was used as a carrier gas. Electrochemical performance was examined by measuring current-voltage (I–V) characteristics.

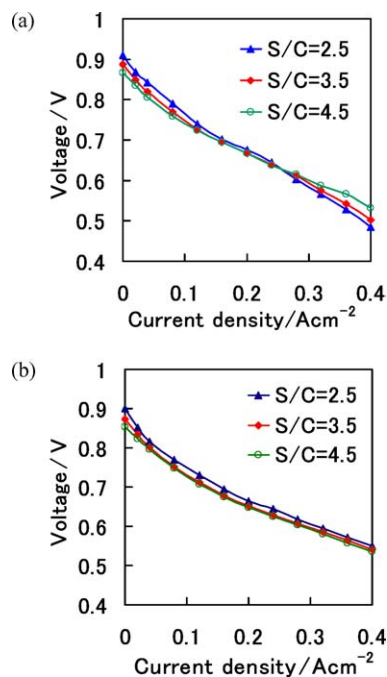


Fig. 7. Current-voltage characteristics of SOFCs for fuels based on (a) iso-octane and (b) n-dodecane at various steam-to-carbon (S/C) ratios at 1000°C [15, 19].

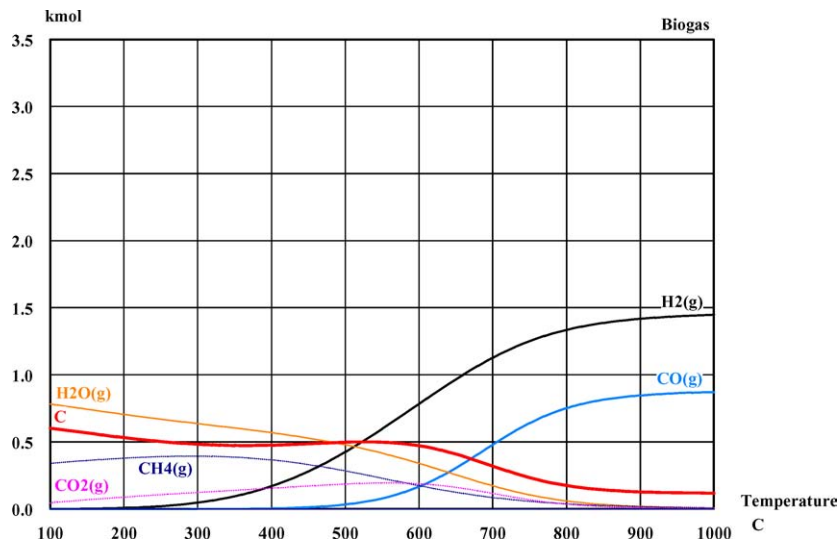


Fig. 8. Equilibrium products from a typical biogas, e.g., CH_4 55%, CO_2 30%, and H_2O 15%. The total amount of carbon is normalized to 1 kmol [4].

3.2. Alcohol-Based Fuels

The use of alcohols as SOFC fuels is of technological interest, as alcohols (bioliquids) can be derived from biomass and can be easily reformed. In addition, direct-alcohol SOFCs could be alternative to direct-methanol fuel cells. Power generation characteristics for alcohol-based fuels and for the simulated reformed gas (consisting mainly of H_2 , CO , and H_2O) are shown in Fig. 6. All these alcohols were premixed with water, so that C–H–O ratio was fixed to the same value for comparison (C:H:O=9:38:10 for all these fuels). It has been demonstrated that direct-alcohol SOFCs can be realized, at least, for alcohols with carbon number up to 4 (butanol) [15, 16]. In case that methanol was directly supplied, the I-V characteristics were similar to those for the simulated reformed gas. However, with increasing carbon number of alcohols, a decrease in cell voltage was observed. From our gas analysis by gas chromatograph, it has been revealed that the compositions of the simulated reformed gas and the methanol-derived fuel gas were almost the same, well explaining the similar I-V characteristics [15, 16]. However, increasing carbon number of alcohols, a decrease in H_2 and CO concentrations was observed, associated with a decrease in cell voltage [15, 16]. Therefore, a higher catalytic activities to reform alcohols at fuel electrodes is desired to optimize direct-alcohol SOFCs.

3.3. Hydrocarbon-Based Fuels

Compared to CH_4 -based fuels mixed with H_2O , internal reforming of C_2H_6 and C_2H_4 has been found to be difficult as carbon deposition can be easily occurred [9]. Therefore, for higher hydrocarbons, external reforming may be needed to prevent carbon deposition. Power generation characteristics for (a) iso-octane (C_8H_{18})-based and (b) n-dodecane ($\text{C}_{12}\text{H}_{26}$)-based fuels with various steam-to-carbon ratios are shown in Fig. 7. We have demonstrated relatively stable power generation, at least within 10 hours, using $\text{Ru}/\text{Al}_2\text{O}_3$ as a reforming catalyst for such simple ex-

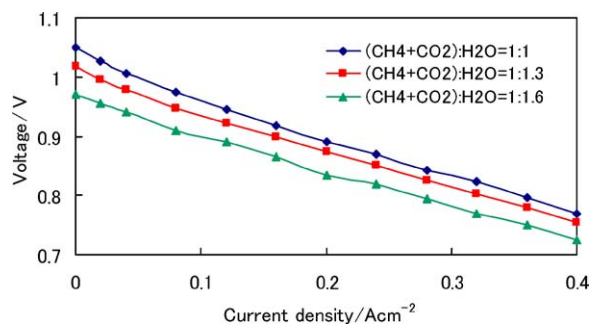


Fig. 9. Current-voltage characteristics of SOFCs for biogas-based fuels at 1000°C .

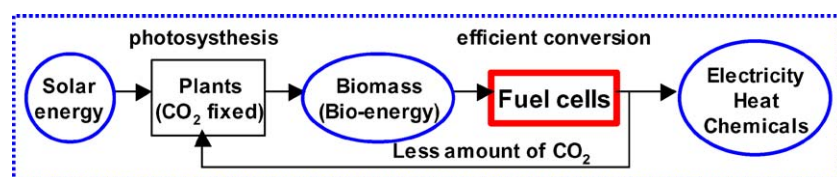


Fig. 10. A carbon-neutral zero-emission renewable energy system based on fuel cells.

ternal reforming with a liquid hourly space velocity (LHSV) of 1.0 h^{-1} [15, 19]. This result suggests that alternative or chemically modified fuel electrodes with a higher catalytic activity to prevent carbon formation may be essential to realize SOFC operated by internal reforming of higher hydrocarbons.

3.4. Biogas

Biogas can be produced from biomass via various procedures such as fermentation and thermal decomposition. Figure 8 shows the equilibrium products from biogas consisting initially of CH_4 , CO_2 , and H_2O . High-temperature equilibrium gas from the biogas consists mainly of H_2 and CO , so that a comparable electrochemical performance with hydrogen-based fuels [20] is expected. This figure also indicates that carbon formation especially at lower temperatures is thermodynamically expected, so that an addition of H_2O and/or O_2 is needed. Figure 9 shows preliminary results of the current-voltage characteristics of SOFCs operated with simulated biogas to which H_2O was added. Similar to the methane-based fuel with steam, the use of fuels consisting of CH_4 , CO_2 , and H_2O led to satisfactory electrochemical performance. We found no carbon deposition after the measurements. Solid oxide fuel cells could be thus a core technology to realize carbon-neutral zero-emission renewable energy systems, illustrated in Fig. 10, as biogas can be efficiently converted to electricity and heat while exhaust CO_2 gas may be reused in photosynthesis of biomass using solar energy.

3.5. Influence of Fuel Impurities

Practical fuel cell fuels contain various impurities. In particular, biogas, coal gas, and various fossile fuels contain sulfur-related impurities, while sulfur-based odorants are also added to commercial LP gas and city gas. In order to simplify fuel cell systems and understand their long-term stability, the influence of sulfur-related impurities on electrochemical perfor-

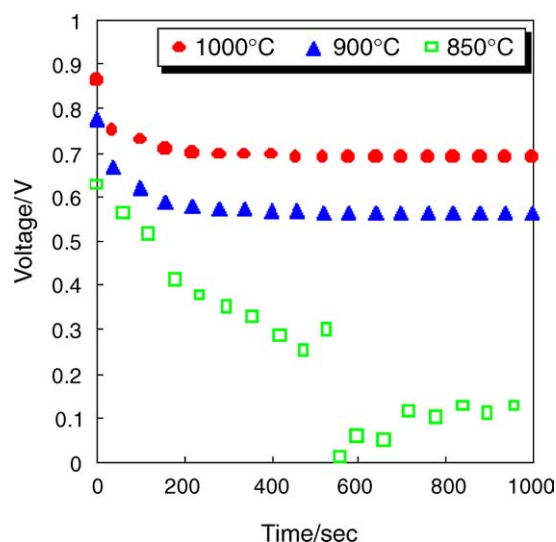


Fig. 11. Temperature dependence of cell voltage at 0.2 A/cm^2 for H_2 -based fuel containing 5 ppm of H_2S [21–24].

mance should be known. The influence of H_2S fuel impurity on power generation characteristics of SOFCs has been analyzed by measuring cell voltage at a given current density with time, as a function of operational temperature, the ratio of H_2 -to- CO , and H_2S concentration [21–24]. As shown in Fig. 11, we have found a slight cell voltage drop at 900° and 1000°C for H_2 -rich fuels, after which cell voltage became stable. However, we found a fatal irreversible degradation at a lower temperature (see Fig. 11) and for CO -rich fuels [21–24], both associated with Ni-sulfate formation [21–24]. Development of sulfur-tolerant SOFC fuel electrodes is therefore desired, especially at lower SOFC operational temperatures and for CO -rich fuels.

4. Conclusions and Outlook

It has been demonstrated that, in principle, alcohols and biogas can be used as SOFC fuels without any reformer, at least, on a device level. Simple external reforming

using Ru-based catalysts may be useful upon applying higher hydrocarbons as SOFC fuels. Higher catalytic activities to enhance reforming reactions and to depress carbon deposition, as well as fuel impurity tolerance of fuel electrodes are desired to realize multi-fuel capable flexible SOFCs.

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