ABSTRACT

One of the most attractive features of solid oxide fuel cells is their flexibility for fuels. In this study, power generation characteristics for alcohol- and hydrocarbon-based fuels are measured and compared with those for simulated reformed gases in equilibrium compositions. We have succeeded to demonstrate direct-alcohol SOFCs for methanol, ethanol, propanol, and butanol. As higher hydrocarbon, n-dodecane (C_{12}H_{26}) is highlighted as simulated kerosene, and power generation characteristics for this fuel are evaluated with both internal and external reforming.

INTRODUCTION

Solid oxide fuel cells are the most flexible fuel cells with respect to their multi-fuel capability, so that not only hydrogen and carbon monoxide but also various other kinds of fuels including hydrocarbons and alcohols can be used via internal reforming and/or via simple external reforming (1-7). SOFCs may become attractive for automobile applications if direct-alcohol SOFCs can be realized. Furthermore, alcohols can be produced from bio-energy resources, and their use as SOFC fuels may enable realizing a carbon-neutral zero-emission energy system (2). Also, in order to reduce the consumption of fossil raw oil, the use of synthesized fuels such as GTL (gas-to-liquid) kerosene, which is produced from relatively abundant natural gas, is of technological interest. Since the energy density of kerosene is relatively high, it is inexpensive, and the content of sulfur impurities is negligible, its use as SOFC fuel may contribute to a reduction of SOFC operational costs.

The purpose of this study is therefore to examine power generation characteristics of SOFCs for alcohol- and higher-hydrocarbon-based fuels. First, we carry out thermochemical calculations to reveal equilibrium gas compositions. Power generation characteristics of SOFCs operated with alcohol- and hydrocarbon-based
fuels via internal reforming or via external reforming are then measured. For alcohol-based fuels, the fuels with carbon number up to 4 (butanol) are directly supplied to the anode and their power generation characteristics are compared with those operated with simulated reformed gas in thermodynamic equilibrium. Fuel gas compositions are analyzed with gas chromatograph and the results are compared with electrochemical properties.

EQUILIBRIUM GAS COMPOSITIONS

Thermochemical calculations of gas compositions at elevated temperatures were performed using a software, HSC chemistry (Outokumpu, Finland) (3-5). Thermochemical data of ca. 100 compounds consisting of carbon, hydrogen and/or oxygen were taken into account. Equilibrium compositions were derived via the Gibbs-energy minimization procedure. The calculations were carried out in the temperature range between 100° and 1000°C in steps of 10°C.

![Figure 1. The amounts of products from the 90%CH₃OH+10%H₂O fuel assuming thermodynamic equilibrium.](image)

The carbon-hydrogen-oxygen (C-H-O) ternary diagrams reported elsewhere (3-5) indicate that the position of pure methanol in the C-H-O diagram lies very near the boundary line of the carbon deposition region at 1000°C. Therefore an addition of a small amount of H₂O, for example, is essential to prevent carbon deposition in case thermodynamic equilibrium is reached. In this study, we thus used the 9-to-1 mixture of methanol and water as the methanol-based fuel. Figure 1 shows the amount of products from the 90% CH₃OH + 10% H₂O fuel assuming thermodynamic equilibrium. For other alcohol-based fuels, the initial fuel contents were adjusted to fix the C-H-O ratio, that is, 45% C₂H₅OH + 55% H₂O, 30% C₃H₇OH + 70% H₂O,

1296

Electrochemical Society Proceedings Volume 2003-07
and 22.5% C₄H₉OH + 77.5% H₂O. Note that the C-H-O ratio of CH₃OH, C₂H₅OH + H₂O, C₃H₇OH + 2H₂O, and C₄H₉OH + 3H₂O is 1:4:1.

Figure 2. Fuel gas compositions at thermodynamic equilibrium for n-dodecane with the S/C of 2.5, 3.5, and 4.5 at 1000°C.

Table 1. Gas compositions of the n-dodecane-based fuels at thermodynamic equilibrium and theoretical electromotive force (E_theo. vs. air) at 1000°C.

| S/C | mol%  | H₂  | H₂O | CO  | CO₂  | O₂   | E_theo. vs.air / V |
|-----|-------|-----|-----|-----|------|------|------------------|
| 2.5 | 28.29 | 15.57 | 9.147 | 2.994 | 8.569×10⁻¹⁴ | 0.909 |
| 3.5 | 26.3  | 23.7 | 7.043 | 3.772 | 2.295×10⁻¹³ | 0.882 |
| 4.5 | 24.46 | 30.47 | 5.601 | 4.149 | 4.389×10⁻¹³ | 0.864 |

Consequently, the equilibrium gas compositions for all these alcohol-based fuels are identical to those shown in Fig. 1. The major constituents of the equilibrium gas were H₂(g), H₂O(g), CO(g), CO₂(g), CH₄(g), and C(s). The concentrations of other compounds were very low. As the water vapor concentration is ca. 3% and the ratio of H₂ and CO is ca. 2:1, high power generation characteristics are expected (7), provided that decomposition and reforming reactions of alcohols are fast enough.

Electrochemical Society Proceedings Volume 2003-07 1297
As higher hydrocarbon, we chose n-dodecane (C\textsubscript{12}H\textsubscript{26}) as a model since the typical carbon number of kerosene is 12. Equilibrium gas compositions for the steam-to-carbon ratio (S/C) of 2.5, 3.5, and 4.5 are shown in Fig. 2. For electrochemical measurements in this study, nitrogen gas was used as a carrier gas, and this was taken into account in the calculation. Equilibrium concentrations of major constituents and theoretical electromotive force at 1000°C are listed in Table 1. Figure 2 clearly shows that no carbon deposition is expected for S/C=3.5 and 4.5 as well as for S/C=2.5 above 150°C. Assuming complete equilibrium, open circuit voltage is expected to be ca. 0.9 V for these higher-hydrocarbon-based fuels.

![Figure 3. Schematic drawing of the electrochemical measurement and gas analysis setup.](image)

**EXPERIMENTAL PROCEDURE**

Power generation characteristics were examined by using planar-type SOFCs with ZrO\textsubscript{2}-based electrolyte (8mol% Y\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2}, 200 μm thickness, produced by Tosoh). The starting powders for anodes were prepared by mixing NiO and YSZ with the weight-ratio of 8:2, followed by mechanical mixing for 24 hours and by calcination at 1400°C for 5 hours. The starting powders for cathodes were prepared by drying the aqueous solution of lanthanum acetate, strontium acetate, and manganese acetate. The powders obtained were ball-milled and then calcined at 900°C for 10 hours to obtain La\textsubscript{0.6}Sr\textsubscript{0.4}MnO\textsubscript{3} powder. The electrodes (5 × 5mm\textsuperscript{2}) were prepared via screen-printing technique (8). The heat-treatment temperatures of anodes and cathodes were 1400°C and 1150°C, respectively.

For electrochemical measurements, dry air was supplied to the cathode, and fuel gas based on methanol, ethanol, propanol, butanol, n-dodecane, or simulated reformed gas was supplied to the anode. For alcohol-based fuels, steam-to-carbon ratio was adjusted to apply the common C-H-O ratio as mentioned before. Schematic drawing
of the evaluation system for alcohol-based fuels is shown in Fig. 3. The cell operating temperature was 1000°C. Electrochemical measurements were carried out using a galvanostat (Hokuto Denko, HC-111). Gas analysis was performed using gas chromatograph (Shimadzu, GC-8A) combined with gas chromatograph mass spectrometer (Shimadzu, GCMS-QP5050A).

![Schematic diagram of the experimental set-up.](image)

Results and Discussion: Alcohols

Current - Voltage Characteristics

Fig. 5 shows current-voltage characteristics for various alcohol-based fuels at 1000°C. Even though the C-H-O ratio was the same and thus the same open circuit voltage (OCV) was expected assuming complete equilibrium, OCV for the simulated reformed gas was the highest and it decreased with increasing carbon number of alcohols. This carbon-number dependency held for the butanol-based fuel.
While OCV for the methanol-based fuel was slightly lower than that for the simulated reformed gas, cell voltage became identical with increasing current density. This tendency has been reported previously, explained by an enhanced decomposition and/or reforming reactions at the anode under current flow (6). In addition, we have found a dependence of current-voltage characteristics on carbon number of alcohols. This may be because decomposition/reforming reactions become slower and complicated with increasing carbon number of alcohols from methanol through ethanol and propanol, to butanol.

Gas Compositions

In order to understand the difference in current-voltage characteristics, gas compositions under various conditions were analyzed. Figure 6 shows the gas compositions (1) without electrode (i.e., we used a YSZ electrolyte plate without electrodes as a cell), (2) under open circuit conditions, and (3) in operation at 0.4 Acm⁻², along with the gas compositions calculated at thermodynamic equilibrium. For the methanol-based fuel, the gas compositions even without electrode were almost identical to the equilibrium composition. This is the reason why the current-voltage characteristics for the methanol-based fuel were almost identical to those for the simulated reformed gas. For ethanol- and propanol-based fuels, the concentrations of H₂ and CO were much lower and the concentrations of by-products including CH₄ increased. These results indicate that decomposition/reforming reactions became sluggish with increasing carbon number of alcohols, especially from methanol (C₁) to ethanol (C₂). The decrease in concentrations of H₂ and CO
may be the reason for the lower open circuit voltages and lower electrochemical performance with increasing carbon number. In addition, by comparing the compositions under open circuit condition and in operation with current density of 0.4 Acm$^{-2}$, it can be found that the concentrations of H$_2$ and CO further decreased and those of other products increased.

![Figure 6. Gas compositions of alcohol-based fuels; ① Without electrode; ② Under open circuit condition; ③ In operation at 0.4 Acm$^{-2}$.](image)

**Analysis of By-Products**

Gas analysis of by-products was performed, which detected more than 10 kinds of gaseous species. Methane concentration was higher than that expected in thermodynamic equilibrium, so that methane can be regarded as an intermediate product. Among others, the presence of a small amount of benzene was identified and its concentration was found to increase with increasing carbon number. In addition, as a by-product, the presence of ethylene was identified for the alcohol-based fuels with carbon number more than 2. On the other hand, ethylene was not detected for the methanol-based fuel. For all these fuels, the increase in concentrations of other products, denoted as "others" in Fig. 6, by current flow (0.4 Acm$^{-2}$) is partly attributed to the oxidation of fuel species to form H$_2$O and CO$_2$.

**RESULTS AND DISCUSSION: HIGHER HYDROCARBONS**

In order to analyze electrochemical performance for higher hydrocarbons, current-voltage characteristics for the n-dodecane-based fuels were examined (9). The results for various steam-to-carbon ratios are shown in Fig. 7. Ru/Al$_2$O$_3$ catalyst was used.
for external reforming, and space velocity for liquid fuels was defined as

\[ \text{LHSV} \left[ \text{h}^{-1} \right] = \frac{V_{\text{LiquidFuel}} \left[ \text{ml} \cdot \text{h}^{-1} \right]}{V_{\text{Catalyst}}} \]

where, \( V_{\text{LiquidFuel}} \) is the volume of n-dodecane in the liquid state and \( V_{\text{Catalyst}} \) is the volume of the Ru/Al\(_2\)O\(_3\) reforming catalyst. For the experimental results shown in Fig. 7, LHSV was 1.0h\(^{-1}\) and the temperature of Ru/Al\(_2\)O\(_3\) was set at 800°C. For these S/C values, the OCV was almost identical to that expected in thermodynamic equilibrium shown in Table 1. In addition, no carbon formation was distinguished under these operational conditions. These results indicate that reforming reactions were fast enough to obtain satisfactory electrochemical performance. At a higher LHSV (4.0h\(^{-1}\)) by using a less amount of Ru/Al\(_2\)O\(_3\) catalyst, similar current-voltage characteristics were obtained.

![Figure 7](image-url)

**Figure 7. Current-voltage characteristics of a cell for n-dodecane(C\(_{12}\)H\(_{26}\))-based fuels at 1000°C.**

Time-dependent cell voltage in power generation was also evaluated. Figure 8 shows cell voltage at 0.2 Acm\(^{-2}\) for the n-dodecane-based fuel at S/C=3.5 upon internal or external reforming. In the external reforming situation, the Ru/Al\(_2\)O\(_3\) catalyst was used with LHSV=1.0h\(^{-1}\). Without Ru/Al\(_2\)O\(_3\) catalyst (i.e., internal reforming), carbon deposition was observed and a rapid decrease in cell voltage was found within a short time period. This result indicates that internal reforming SOFC operation for higher hydrocarbons is difficult. On the other hand, under proper operational conditions, a stable electrochemical performance can be obtained by just using external reforming catalyst in the gas channel leading to the fuel electrode. Experimental results in detail along with results for GTL kerosene have been reported elsewhere (9).
Figure 8. Change in cell voltage with time at 0.2 Acm$^{-2}$ for the n-dodecane(C$_{12}$H$_{26}$)-based fuel at 1000°C.

SUMMARY AND CONCLUSIONS

We have succeeded in demonstrating direct-alcohol SOFCs with carbon number of alcohols up to 4. In particular, decomposition and reforming reactions for the methanol-based fuel were fast enough to reach thermodynamic equilibrium, and thus an electrochemical performance similar to that for the simulated reformed gas consisting mainly of H$_2$ and CO was obtained. With increasing carbon number of alcohols, a decrease in H$_2$ and CO concentrations, an increase in concentrations of by-products including methane, ethylene, and benzene, and thus a decrease in cell voltage for given current densities was observed. For alcohols with a higher carbon number, an optimization of operational conditions and an improvement of fuel electrode materials are thus desired. As a model higher hydrocarbon, n-dodecane (C$_{12}$H$_{26}$) was used as an SOFC fuel. Internal reforming SOFC operation for the n-dodecane-based fuel was difficult, associated with carbon deposition and a rapid decrease in cell voltage. However, simple external reforming using Ru/Al$_2$O$_3$ catalyst in the gas supply channel was helpful to obtain a stable power generation.

ACKNOWLEDGEMENT

Research grant ("Shourei Kenkyu") from Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, is gratefully acknowledged. The initial stage of this study was supported through the Industrial Technology Research Grant Program in 00° from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.
REFERENCES

1. B. C. H. Steele and A. Heinzel, Nature, 414, 345-52 (2001).
2. K. Sasaki, Research Report of the Industrial Research Grant Program in 2000, New Energy and Industrial Technology Development Organization (NEDO), 2002.
3. K. Sasaki and Y. Teraoka, 9th FCDIC Symp. Fuel Cell Proceedings, Fuel Cell Development Information Center, p. 381-88 (2002).
4. K. Sasaki and Y. Teraoka, J. Electrochem. Soc., submitted.
5. K. Sasaki and Y. Teraoka, “Equilibria in Fuel Cell Gases”, This Proceeding.
6. K. Sasaki, H. Kojo, Y. Hori, R. Kikuchi, and K. Eguchi, Electrochemistry, 70 [1], 18-22 (2002).
7. K. Sasaki, Y. Hori, R. Kikuchi, K. Egichi, A. Ueno, H. Takeuchi, M. Aizawa, K. Tsujimoto, H. Tajiri, H. Nishikawa, and Y. Uchida, J. Electrochem. Soc., 149 [3], A227-A233 (2002).
8. K. Sasaki, J.P. Wurth, R. Gschwend, M. Gödicke meier, and L.J. Gauckler, J. Electrochem. Soc., 143 [2] 530-43 (1996).
9. K. Shiosaki, K. Sasaki, Y. Teraoka, and A. Ueno, Proc. 11th Symp. Solid Oxide Fuel Cells Japan, (2002), in press.