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Novel anode materials for multi-fuel applicable solid oxide fuel cells

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Abstract

New anode materials based on Fe-doped $CaTiO_3$ and ruthenium were examined to enhance the fuel flexibility of SOFCs. An optimum weight ratio between NiO and $Ca(Fe)TiO_3$, RuO_2 and YSZ (yttria-stabilized zirconia) was determined for Ni–$Ca(Fe)TiO_3$ and Ru–YSZ anodes, respectively, and sintering temperature was investigated to achieve high power generation characteristics. The Ni–$Ca(Fe)TiO_3$ anode of NiO:$Ca(Fe)TiO_3$ = 4:1 sintered at 1300 °C showed better current–voltage characteristics than those sintered at 1200 and 1400 °C, which was comparable to Ni–YSZ anode. When a constant current of 200 mA/cm^2 was applied by feeding a gas mixture of methane, H_2O, and N_2 at steam-to-carbon (S/C) ratio of 1.6 at 1000 °C, terminal voltage over SOFCs with the Ni–$Ca(Fe)TiO_3$ and Ru–YSZ anode was stable in 20 h, whereas that over Ni–YSZ decreased significantly. The catalytic activity of the anode materials for carbon formation was evaluated by methane decomposition rate measurements. Carbon deposition rates over the Ni–$Ca(Fe)TiO_3$ and Ru–YSZ were found to be lower than that over Ni–YSZ, possibly leading to the stable power generation at the low S/C ratio.

Keywords: Solid oxide fuel cells; Anode; Methane; Fe-doped $CaTiO_3$; Ru; Yttria-stabilized zirconia

1. Introduction

Solid oxide fuel cells (SOFCs) are operated at high temperatures and so have advantageous features such as fuel flexibility and high efficiency in conversion of chemical energy into electrical energy [1]. The fuel flexibility is derived from the high temperature operation that allows reforming of carbon-containing fuels and from oxygen ionic conductivity of the solid oxide electrolytes. In order to achieve high conversion efficiency, it is needed to attain high ionic conductivity of the electrolytes and to reduce overpotentials associated with the electrode reactions. Rare-earth elements play important roles in SOFCs such as solid oxide electrolyte itself [2–5], components for cathode and interconnect materials [6,7], and additives to the electrolytes to improve the ionic conductivity as well as the stability of the electrolytes [8,9]. Transition metals are also important and used in SOFCs as the additives to anode and cathode to improve the electrochemical performances, chemical and thermal stability, and fuel flexibility of the anode. Among the various materials used in SOFCs including rare-earth materials and transition metals, this paper examines the effect of Fe, Ti, and Ru on the anode performance, and on coke formation characteristics over the anode materials.

When multi-fuels such as hydrocarbons and alcohols are directly applied to SOFCs, deactivation of the anode due to carbon deposition and pore closure in the anode will be serious problems. An excess amount of steam is usually added to the fuels to avoid carbon formation. However, even when higher hydrocarbons are mixed with a sufficient amount of H_2O and introduced to SOFCs, carbon formation on a conventional Ni–YSZ anode can proceed, and deterioration in power generation characteristics is inevitable (e.g. [1]). In addition, an excess amount of steam decreases electromotive force, and thus, gives rise to decrease in power generation efficiency. Therefore, it would be desirable to reduce the amount of steam introduced to the anode as low as possible.

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New SOFC anodes have been proposed for direct introduction of hydrocarbons and for suppression of carbon formation during power generation such as Cu-containing anodes [10], alkali earth oxide additives to Ni–YSZ anode [11], CeO_2-based oxides [12], TiO_2-based oxides [13]. In the present paper, novel anode materials based on Ni–Ca(Fe)TiO_3, and Ru–YSZ were examined to enhance the fuel flexibility of SOFCs. Since Ca(Fe)TiO_3 has electron conductivity, oxygen ion conductivity comparable to YSZ, and proton solubility, it is expected to lower the amount of Ni in the cermet anode, and thus, to decrease carbon formation rate on the anode. The oxygen ion conductivity and proton solubility may be effective in suppressing carbon formation [14]. Ruthenium is well known as an excellent catalyst for steam reforming of hydrocarbons [15], and thus, carbon formation would be suppressed by substituting Ru for Ni in the anode. In this study, preparation of the anodes with the novel materials was optimized to achieve maximum power generation characteristics. Catalytic activity of the materials for carbon formation was also investigated.

2. Experimental

2.1. Preparation of cermets and power generation experiments

NiO, RuO_2 (Wako Pure Chemical Industries), Fe-doped $CaTiO_3$ (Praxair, hereafter abbreviated as FCT, $CaFe_{0.1}Ti_{0.9}O_{3-\delta}$), and 8 mol% Y_2O_3-stabilized ZrO_2 (Tosoh Co., TZ-8YS, hereafter abbreviated as YSZ) were used to prepare cermets in a disk electrode. A mixture of NiO and FCT, RuO_2 and YSZ, or NiO and YSZ was milled for 24 h, the mixture was calcined in air for 5 h. The weight ratio of NiO:FCT was 6:1, 4:1, and 1:1, RuO_2:YSZ was 7:1, 4:1, and 2:1, NiO:YSZ was 4:1. The calcination temperature was 1200 °C for NiO/FCT mixture, 900 °C for RuO_2/YSZ mixture, and 1400 °C for NiO/YSZ mixture. The calcined samples were then pulverized into powder or granular shape. This cermet powder was mixed with polyethylene glycol (Wako Pure Chemical Industries) to form slurry, with which one side of an YSZ disk of 20 mm in diameter and 0.5 mm in thickness was painted. Then the disk with the Ni–FCT cermet powder painted was calcined at 1200, 1300, and 1400 °C for 5 h in air, Ru–YSZ was at 1100 and 1400 °C for 5 h in H_2, and Ni–YSZ was at 1400 °C for 5 h in air. In the following part of this paper, an anode prepared using cermet powder of, for example, NiO:FCT = 4:1, is represented as Ni–FCT (4:1).

A perovskite-type $La_{0.6}Sr_{0.4}MnO_3$ mixed oxide was prepared as follows: La, Sr, and Mn acetates (Wako Pure Chemical Industries) with the stoichiometric ratio were dissolved in water and then water was removed from the solution at 100 °C and dried at 120 °C overnight. Resulting powders were milled for 24 h and calcined at 900 °C for 10 h, and subsequently, mixed with polyethylene glycol to form slurry. This slurry was applied on the other side of the YSZ disk. It was calcined at 1150 °C for 5 h in air. Prior to the power generation experiments, the anodes were reduced in a 50% H_2/N_2 stream from room temperature to 1000 °C at a constant heating rate of 200 °C/h.

In power generation experiments, H_2 humidified by bubbling at 0 °C or a gaseous mixture of CH_4, H_2O, and N_2 was supplied as anode gas to the cermets at 150 ml(STP)/min. Gaseous oxygen was fed to the $La_{0.6}Sr_{0.4}MnO_3$ cathode, and current–voltage characteristics as well as impedance spectra at open circuit condition were measured at 1000 °C on a Solartron 1287 potentiostat/galvanostat with a Solartron 1260 frequency response analyzer.

2.2. Evaluation of carbon deposition rate

Methane was decomposed at atmospheric pressure using a thermogravimetric analyzer (Shimadzu, TGA-50), with catalyst sample loaded in the basket of the balance. The catalyst samples were prepared by applying a paste of the cermet powder obtained as mentioned above onto an YSZ disk of 200 μm in thickness and 8 mm in diameter. Prior to the reaction, catalysts were reduced in the stream of 5% H_2/Ar from the room temperature to 1000 °C at a constant heating rate of 10 °C min^{-1}, and the temperature was held at 1000 °C for 10 min. Then, the H_2/Ar flow was changed to the flow of 67% methane and 33% N_2. The carbon deposition rate for the first 1 min was given by:

$$\text{Carbon deposition rate}\,(C\,(\text{g})/\text{cermet}\,(\text{g min})) = \frac{\text{weight increase by deposited carbon}}{\text{cermet weight} \times \text{reaction period}} \qquad (1)$$

3. Results and discussion

3.1. Power generation characteristics of SOFCs with Ni–FCT, Ru–YSZ, and Ni–YSZ anodes

The Ni–FCT anode (4:1) was sintered on an YSZ disk at 1200, 1300, and 1400 °C, and the power generation characteristics at 1000 °C using H_2 as fuel were investigated, as shown in Fig. 1. The current–voltage characteristics of SOFCs with the Ni–FCT anode (4:1) sintered at 1300 °C were significantly higher than those at 1200 and 1400 °C. The Ni–FCT anode (4:1) sintered at 1300 °C exhibited a power generation performance comparable to that with Ni–YSZ anode, though the difference in the terminal voltage between the anodes gradually increased in higher current densities. From visual observation, no apparent change was recognized for the Ni–FCT anodes sintered at 1200 and 1300 °C in air for 5 h, whereas the anode sintered at 1400 °C turned to be metallic at the surface. In the comparison of the impedance spectra taken at OCV condition with 10 mV amplitude, an expansion was observed in the semicircle at the characteristic frequency of 0.1–10 Hz, when the sintering temperature was raised from 1300 to 1400 °C, which indicates that the porous structure

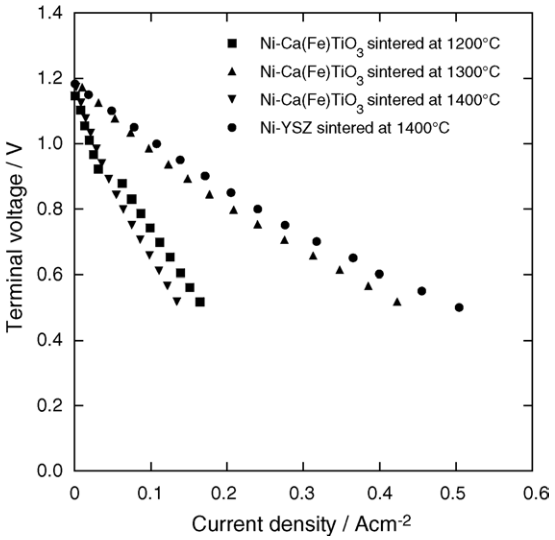

Fig. 1. Effect of sintering temperature on current–voltage characteristics of SOFCs with Ni–Ca(Fe)TiO_3 and Ni–YSZ as anode at 1000 °C using H_2 humidified by bubbling at 0 °C. Ni–FCT and Ni–YSZ were prepared using cermet powder of NiO:FCT = 4:1 and NiO:YSZ = 4:1, respectively. Cell: H_2, Ni–FCT/YSZ/$La_{0.6}Sr_{0.4}MnO_3$, O_2, or H_2, Ni–YSZ/YSZ/$La_{0.6}Sr_{0.4}MnO_3$, O_2.

of the Ni–FCT anode was collapsed by sintering at the high temperature. It was confirmed by SEM observation that the porous structure of the Ni–FCT anode was clogged by the grain particle growth during the sintering at 1400 °C. It can be, therefore, considered from these results that the anode structure was considerably changed during the sintering at 1400 °C, giving rise to the degradation in the power generation characteristics.

Fig. 2 shows the effect of the weight ratio of NiO and FCT on current–voltage characteristics of H_2-fueled SOFCs at 1000 °C. The weight ratio of NiO to FCT was varied in the range of 1:1, 4:1, and 6:1, and the Ni–FCT anodes were sintered to an YSZ disk at 1300 °C. The Ni–FCT anode (4:1) showed the best power generation characteristics among the Ni–FCT anodes tested. Considering the catalytic activity for carbon formation, it would be desirable to reduce the amount of nickel contained in the cermet anode, in order to attain stable power generation characteristics by suppressing carbon formation. The Ni–FCT (1:1) displayed the power generation characteristics comparable to the more Ni-containing Ni–FCT anode (6:1), and thus, the Ni–FCT anode (1:1) can be expected to show better stability under power generation at low steam/carbon ratio.

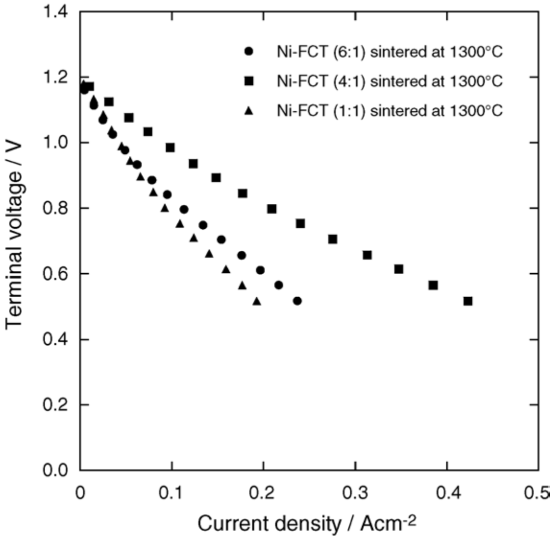

Fig. 2. Power generation characteristics of SOFCs with Ni–FCT anodes of NiO:FCT = 6:1, 4:1, and 1:1 at 1000 °C using H_2 humidified by bubbling at 0 °C. Cell: H_2, Ni–FCT/YSZ/$La_{0.6}Sr_{0.4}MnO_3$, O_2.

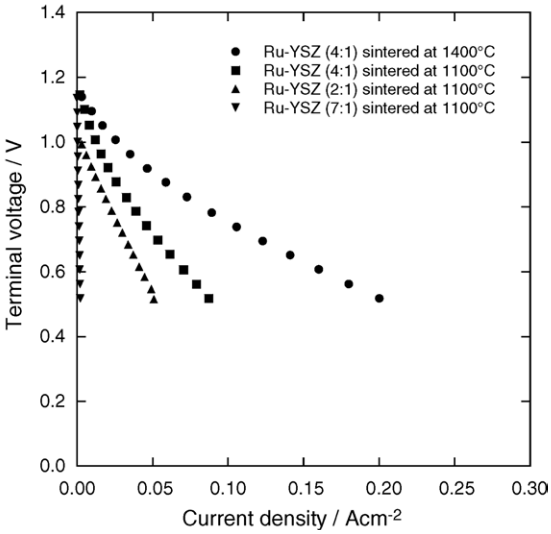

Fig. 3. Power generation characteristics of SOFCs with Ru–YSZ anodes of RuO_2:YSZ = 7:1, 4:1, and 2:1 at 1000 °C using H_2 humidified by bubbling at 0 °C. The Ru–YSZ anodes were sintered at 1100 and 1400 °C in H_2 for 5 h. Cell: H_2, Ru–YSZ/YSZ/$La_{0.6}Sr_{0.4}MnO_3$, O_2.

In Fig. 3, power generation characteristics with H_2 humidified by bubbling at 0 °C are shown for SOFCs with Ru–YSZ anodes prepared via various weight ratios between RuO_2 and YSZ, and sintered at different temperatures. The Ru–YSZ cermet powders were sintered to an YSZ disk at 1100, or 1400 °C in a reducing atmosphere by feeding H_2 to avoid evaporation of ruthenium. When the Ru–YSZ was sintered at 1100 °C, Ru–YSZ anode (4:1) exhibited better current–voltage characteristics than those with the other weight ratios. In the case of RuO_2:YSZ = 7:1, the activation and concentration resistances measured by ac impedance spectroscopy increased significantly, giving rise to the steep decrease in the terminal voltage from the open circuit voltage for the slight increase in the current density. This may be partly because the excess amount of RuO_2 caused smaller length of triple phase boundary that led to the increase in the activation polarization resistance, and partly because the volumetric change of the anode during reduction of RuO_2 to metallic Ru by H_2 reduction treatment destroyed the anode structure that possibly resulted in the increase in the concentration polarization resistance. When the amount of ruthe-

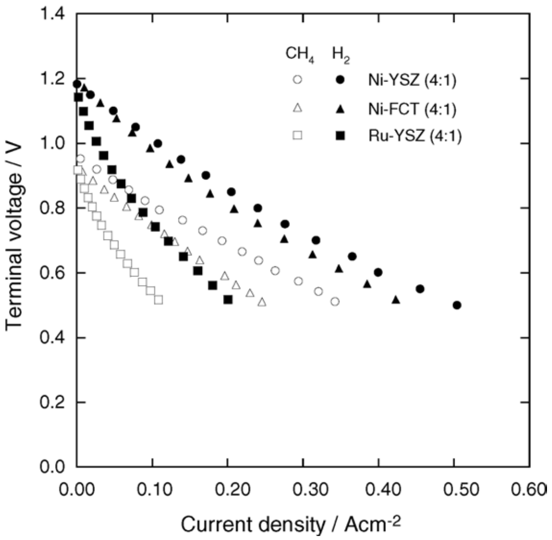

Fig. 4. Power generation characteristics of SOFCs with Ni–FCT (4:1), Ru–YSZ (4:1), and Ni–YSZ (4:1) anodes at 1000 °C using H_2 humidified by bubbling at 0 °C and methane at steam/carbon ratio of 1.6.

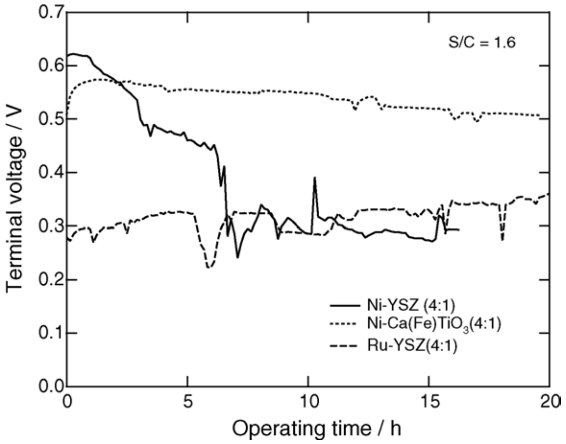

Fig. 5. Time dependence of terminal voltage of CH_4–fueled SOFCs with Ni–FCT (4:1), Ru–YSZ (4:1), and Ni–YSZ (4:1) anodes for S/C = 1.6 at 1000 °C under constant current density of 200 mA/cm^2.

nium in the Ru–YSZ anode was lowered by changing the weight ratio of RuO_2:YSZ from 4:1 to 2:1, the power generation characteristics was slightly degraded, and this degradation was accompanied by the expansion of high frequency arc with the characteristic frequency of ca. 1 kHz on the impedance spectra. This result indicates that smaller amount of Ru gave rise to smaller length of triple phase boundary, and consequently resulted in the increase in the activation polarization resistance.

When the sintering temperature was raised to 1400 °C, the power generation characteristics were largely improved as shown in Fig. 3. It can be, therefore, considered that the Ru–YSZ was not sintered well onto the YSZ disk at 1100 °C and indicated that sintering at the temperature as high as 1400 °C is needed to attain sufficient adhesion between the anode and electrolyte in the case of Ru–YSZ.

Fig. 4 summarizes the power generation characteristics at 1000 °C using H_2 and CH_4 as fuel over the Ni–FCT, Ru–YSZ, and Ni–YSZ anodes optimized, respectively, according to the preparation conditions determined as mentioned above: the Ni–FCT anode (4:1) was sintered at 1300 °C in air for 5 h, and the Ru–YSZ (4:1) was sintered at 1400 °C in H_2 for 5 h. The Ru–YSZ anode exhibited poorer power generation characteristics than those of Ni–FCT and Ni–YSZ, irrespective of the fuels used. When methane was used as a fuel with a steam-to-carbon ratio of 1.6, the Ni–FCT anode also displayed power generation characteristics comparable to Ni–YSZ as in the case of H_2 fuel, although the Ni–YSZ anode exhibited still better performance and the difference in the power generation characteristics between the Ni–YSZ and Ni–FCT anodes became larger in the CH_4-fueled SOFCs than in the H_2-fueled SOFCs. Since FCT has smaller apparent density than YSZ and the weight ratio of nickel to FCT and YSZ was the same, the amount of nickel exposed on the anode surface can be less for the case of Ni–FCT than Ni–YSZ, giving rise to a decrease in the active sites for CH_4 steam reforming and consequently to the larger deviation in CH_4-fueled power generation.

Fig. 5 shows the variation in the terminal voltage at 1000 °C in 20 h measured for SOFCs with the optimized Ni–FCT and Ru–YSZ, and conventional Ni–YSZ anodes under a constant current load of 200 mA/cm^2 by feeding a gaseous mixture of CH_4, H_2O, and N_2 with steam-to-carbon ratio of 1.6 at 150 ml(STP)/min. The terminal voltage measured for the Ni–YSZ anode (4:1) was drastically dropped and almost stable at 0.3 V, which was almost half of the value at the beginning of this experiment. On the other hand, the terminal voltage for the Ni–FCT anode (4:1) was almost stable, though it gradually decreased from 0.57 to 0.5 V during the operation for 20 h. This result implies that the Ni–FCT anode was thermally and chemically stable under the experimental conditions investigated. As for the power generation with the Ru–YSZ anode (4:1), the terminal voltage was as low as 0.3 V at the initial stage of the constant current–load experiment, and then it increased gradually up to 0.35 V in the continuous operation for 20 h. This might be because better conduction passes for electric current were produced in the anode by passing continuously constant current.

3.2. *Methane decomposition over Ni–FCT, Ru–YSZ, and Ni–YSZ*

Carbon deposition rates over Ni–FCT, Ru–YSZ, and Ni–YSZ are summarized in Table 1. These carbon depo-

Table 1
Comparison of carbon deposition rate over Ni–FCT, Ru–YSZ, and Ni–YSZ

Cermet	Weight ratio	Carbon deposition rate (C (g)/cermet (g min))
Ni–YSZ	4.0:1.0 (NiO:YSZ)	0.199
Ni–FCT	4.0:1.0 (NiO:FCT)	0.089
Ru–YSZ	2.0:1.0 (RuO_2:YSZ)	0.048
Ru–YSZ	4.0:1.0 (RuO_2:YSZ)	0.062

sition rates were determined by measuring weight change with a thermogravimetric analyzer by feeding dry methane to the catalyst samples at 1000 °C. The Ni–FCT, Ru–YSZ, and Ni–YSZ catalyst samples were prepared in the way mentioned above. The weight ratio and sintering temperature was as follows: Ni–FCT (4:1) was sintered at 1300 °C in air for 5 h, Ru–YSZ (2:1) and (4:1) were at 1400 °C in H_2 for 5 h, Ni–YSZ (4:1) was at 1400 °C in air for 5 h. It is obvious that carbon deposition rates over the Ni–FCT and Ru–YSZ samples are much smaller than that over the Ni–YSZ sample. These lower carbon deposition rates can explain the stable power generation characteristics of the SOFCs with the Ni–FCT and Ru–YSZ anodes even at low steam/carbon rate as shown in Fig. 5. The effect of FCT on suppressing carbon deposition can be explained as follows according to Horita et al. [14]. In CH_4 decomposition over Ni–FCT and Ni–YSZ, dissociation of C–H bond and formation of C–C bond are catalyzed by the nickel metal, and thus, carbonaceous species is formed on the Ni surface. This carbonaceous species can be removed by forming CO in the reaction with oxygenous species formed by dissociation of H_2O on the Ni surface and those diffusing from FCT or YSZ to the Ni surface. Therefore, carbon deposition is significantly affected by the concentration of the oxygenous species on the Ni surface. The atomic hydrogen (H) produced via the dissociation of H_2O on the Ni surface is transported to the Ni/FCT interface and can be ionized and dissolved in FCT as protons (H^+) due to the electronic conductivity and proton solubility of FCT. These protons can react with oxygen ion in FCT and be released as H_2O, leading to an increase in the partial pressure of H_2O in close proximity of the Ni surface. As a consequence, adsorption of H_2O onto the Ni surface can be promoted to raise eventually the concentration of oxygenous species on the Ni surface. On the other hand, in the case of Ni–YSZ, because of low proton solubility of YSZ, the H_2O formation via the mechanism above-mentioned is confined to the gas/Ni/YSZ interface, leading to lower concentration of the oxygenous species and the increase in carbonaceous species on the Ni surface.

In the case of Ru–YSZ, the measured carbon deposition rate was smaller than that over Ni–FCT and Ni–YSZ, and increased when the amount of ruthenium in Ru–YSZ was raised. Because Ru activates both dissociation and formation of C–H bond, it may be that the carbonaceous species on the Ru surface could be removed by forming methane, giving rise to the lower carbon deposition rate. When a sufficient amount of H_2O exists as in the case of the actual power generation condition for SOFCs, the carbon species decomposed on the Ru surface can effectively removed by the reactions with steam such as [16]:

$$C + H_2O \rightarrow CO + H_2 \quad (2)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (3)$$

Therefore, power generation using CH_4 can be stably carried out over Ru–YSZ even at low steam/carbon ratio, as shown in Fig. 5.

4. Conclusions

Novel anode materials employing Ni–Ca(Fe)TiO_3 and Ru–YSZ were investigated to improve the fuel flexibility of SOFCs. Preparation procedure of the Ni–FCT and Ru–YSZ anodes was optimized and evaluation of power generation characteristics with the anodes was carried out. The weight ratio of NiO and Ca(Fe)TiO_3, and RuO_2 and YSZ, as well as sintering temperature was varied for optimization. The Ni–FCT (4:1) anode sintered at 1300 °C gave the highest performance comparable to that of a conventional Ni–YSZ anode. Though the Ru–YSZ anode prepared using cermet powder of RuO_2:YSZ = 4:1 and sintered at 1400 °C in H_2 displayed the best current–voltage characteristics among the Ru–YSZ anodes, it was not so high performance as Ni–YSZ and Ni–FCT. When a constant current of 200 mA/cm^2 was applied by feeding a gas mixture of methane, H_2O, and N_2 at steam-to-carbon (S/C) ratio of 1.6 at 1000 °C, terminal voltage over SOFC with Ni–FCT (4:1) and Ru–YSZ (4:1) anodes was stable with time, whereas that over Ni–YSZ decreased significantly with time. Carbon deposition rate over Ni–FCT, Ru–YSZ, and Ni–YSZ was evaluated with thermogravimetric analyzer by feeding dry methane at 1000 °C. Ni–FCT and Ru–YSZ exhibited lower carbon deposition rate than Ni–YSZ. This low carbon deposition rate may result in the stable power generation characteristics at the low S/C conditions over the SOFC with the Ni–FCT and Ru–YSZ anodes.

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References

[1] K. Eguchi, H. Kojo, T. Takeguchi, R. Kikuchi, K. Sasaki, Solid State Ionics 152–153 (2001) 411–416.
[2] H. Yahiro, K. Eguchi, H. Arai, Solid State Ionics 36 (1989) 71–75.
[3] K. Eguchi, T. Setoguchi, T. Inoue, H. Arai, Solid State Ionics 52 (1992) 165–172.
[4] B. Steele, Solid State Ionics 129 (2000) 95–110.
[5] T. Ishihara, H. Matsuda, Y. Takita, J. Am. Chem. Soc. 116 (1994) 3801–3803.
[6] H. Yokokawa, N. Sakai, T. Horita, K. Yamaji, Fuel Cells 1 (2001) 117–131.
[7] C. Milliken, S. Dlangovan, A. Khandkar, in: S.C. Singhal, H. Iwahara (Eds.), Proceedings of the Third International Symposium on SOFC, The Electrochemical Society Proceeding Series, vol. 93–4, Honolulu, Hawaii, 1993, p. 335.
[8] B.C.H. Steele, in: T. Takahashi (Ed.), High Conductivity Solid State Ionic Conductors, World Scientific, Singapore, 1989, p. 402.
[9] O. Yamamoto, Y. Takeda, R. Kanno, T. Kamiharai, J. Mater. Sci. Lett. 8 (1989) 198–200.

[10] H. Kim, S. Park, J.M. Vohs, R.J. Gorte, J. Electrochem. Soc. 148 (2001) A693–A695.
[11] T. Takeguchi, Y. Kani, T. Yano, R. Kikuchi, K. Eguchi, K. Tsujimoto, Y. Uchida, A. Ueno, K. Omoshiki, M. Aizawa, J. Power Sources 112 (2002) 588–595.
[12] O.A. Marina, C. Bagger, S. Primdahl, M. Mogensen, Solid State Ionics 123 (1999) 199–208.
[13] P. Holtappels, J. Bradley, J.T.S. Irvine, A. Kaier, M. Mogensen, J. Electrochem. Soc. 148 (2001) A923–A929.
[14] T. Horita, K. Yamaji, T. Kato, N. Sakai, H. Yokokawa, J. Power Sources 131 (2004) 299–303.
[15] J.P. Van Hook, Catal. Rev. Sci. Eng. 21 (1980) 1–51.
[16] T. Takeguchi, R. Kikuchi, T. Yano, K. Eguchi, K. Murata, Catal. Today 84 (2003) 217–222.