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Ceramic anode catalyst for dry methane type molten carbonate fuel cell

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Abstract

Oxide catalyst materials for methane oxidation were examined in order to develop the anode electrode for molten carbonate type fuel cell (MCFC). As a primary selection, oxides such as lanthanum (La_2O_3) and samarium (Sm_2O_3) were selected from screening experiments of TPD, TG and tubular reactor. Composite materials of these oxides with titanium fine powder were assembled into a cell unit for MCFC as the anode electrode. Steady-state activities were observed with these anode electrode materials when hydrogen was used as a fuel. When methane was directly charged to anode as a fuel (dry methane operation), a power generation with steady state was observed on both lanthanum and samarium composites after gradual decrease of open circuit electromotive force (OCV) and closed circuit current (CCI). The steady-state activity held as long as 144 h of continuous operation.
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1. Introduction

In a fuel cell system, chemical energy for the reaction between air (oxygen) supplied to a cathode and fuel (hydrogen) supplied to an anode is converted directly into electric energy. Hydrogen is usually supplied from external steam reforming unit. Several types of fuel cell (alkaline type, phosphoric acid type, solid oxide type, polymer electrolyte type and molten carbonate type) are suggested and are under investigations. Among them, a molten carbonate type fuel cell (MCFC) has attracted attentions for the practical use because it is operated at rather high temperature (923 K) and can generate electricity with high energy efficiency. It is also stable and is hardly deactivated with CO, SO_x or NO_x and does not need expensive materials such as platinum. The high temperature operation also enables to charge methane directly to fuel cell system such as dry methane operation [1] or direct internal reforming configuration [2]. These operations enable to remove the external steam reforming unit from the system but special care must be taken against carbonaceous deposition on the anode catalyst. Although MCFC has a lot of merits by operation at high temperature, it also has problems such as the corrosion of cell materials by strong alkaline molten carbonate salt at high tempera-

ture. Therefore, the development of material to endure the long-range operation becomes one of the most urgent topics [3,4]. Although nickel is generally used as an electrode catalyst, many problems on nickel electrode have also been pointed out such as the decomposition and particle growth of nickel [5]. The problem for the increase of contact resistance between electrode and electrolyte by creep has also been pointed out [6]. Recently, use of rare earth elements with nickel are proposed as cathode materials [7,8].

We have proposed the fuel cell system, with which methane is directly converted into valuable chemicals, named as "fuel cell reactor". In this system, methane can be oxidized directly on the anode electrode without any internal or external reforming reaction in both cases of SOFC [9–11] and MCFC [12–14]. The efficiency of fuel cell system is expected to increase if the external reforming units can be omitted (dry methane type fuel cell operation).

As methane is directly charged onto anode in this case, the selection and the preparation of anode catalyst is very important for the cell efficiency.

In this study, rare earth oxide catalyst materials for oxidation of methane were examined in order to develop the anode electrode with high activity and stability. From the viewpoint of activation of oxygen species and avoiding carbonaceous deposition, screening test was conducted by combining temperature programmed desorption (TPD) method, thermo-gravimetric (TG) analysis and conventional catalytic oxidation reaction. In order to give an electronic conductivity

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Nomenclature

CCI	closed circuit current (mA/cm^2)
F	Faraday constant (96500 J/(mol V))
ΔG	Gibbs free energy (J/mol)
n	number of electrons (-)
OCV	open circuit electromotive force (V)
R_{CH_4}	rate of methane oxidation (μmol/(s m))
t	operation time (h)
T	operation temperature (K)
W	weight (kg)
X_{CH_4}	methane conversion (-)

to these ceramic anode materials, titanium fine powder was selected as an additive. These composite La_2O_3 and Sm_2O_3 electrodes combined with titanium powder were tested not only with hydrogen but also with methane as a fuel directly charged to the anode.

2. Experimental

2.1. TPD measurement

The nature of adsorbed oxygen species was tested by TPD method with the powder samples.

In TPD studies, a constant weight (0.58 g) of catalyst fine powder was packed in a quartz tube (8 mm o.d., 6 mm i.d). After pretreatment by purified air at 983 K for 16 h, the temperature of the catalyst was lowered to 323 K and kept constant for 0.5 h in air stream. 3.32×10^{-7} m^3/s of helium gas was then passed through the tube by a gas handling valve, and after 10 min the temperature of the catalyst was increased at the rate of 0.104 K/s. The composition of exit gas was monitored by a thermal conductivity cell at 373 K.

2.2. Thermogravimetric measurement

The changes in catalyst weight by deposition of carbonaceous compounds were measured in methane flow (1.5×10^{-5} mol/s) at 975 K with a thermogravimetric analyzer (TGA-50: Shimadzu).

2.3. Reaction conditions for screening with tubular reactor

Reactions with the tubular reactor were conducted in order to select catalyst for an anode electrode. Reactions were conducted at conditions as follows: 3.0 g of catalyst with a size of 200 μm to 300 μm were packed in a quartz tube reactor with 8.0 mm inner diameter, temperature : $T = 873$, 973, 1073 K; gas flow rate: $F_{CH_4,0} = 3.0 \times 10^{-5}$ mol/s, $F_{O_2,0} = 1.5 \times 10^{-5}$ mol/s, $F_{CO_2,0} = 1.5 \times 10^{-5}$ mol/s, $F_{Ar,0} = 6.0 \times 10^{-5}$ mol/s (without carbon dioxide), $F_{Ar,0} = 4.5 \times 10^{-5}$ mol/s (with carbon dioxide).

2.4. Apparatus for MCFC

2.4.1. Cell unit

A single unit cell type MCFC was used in this study. One set of electrolyte plates, which consists of carbonates (Li_2CO_3/K_2CO_3 = 62 mol/38 mol; Wako Chemicals Co. Ltd.) and $LiAlO_2$ (Chemetall Foote Co. Ltd.), was set between the two cell housings. The electrode unit of 3.0 mm ϕ with effective electrode area of 5.1 cm^2 was placed on both the sides of the electrolyte unit.

Details of the cell unit and the operations were given in the previous report [14].

2.4.2. Electrode plate preparation

2.4.2.1. Cathode electrode plate. Porous nickel plate was prepared for the cathode electrode. The 10.5 g of nickel powder (with diameter of 4–7 μm; Nilaco Co. Ltd.) and 3.0 g of PVB were milled with zirconia ball through one night in 14 cm^3 of methanol. The cathode electrode sheet was produced with the doctor blade apparatus. The sheet was cut to circular plates with diameter of 30 mm and thickness of 0.3 mm. The weight of the plate was 0.5 g. In the cell housing, the plate was calcined to vaporize PVB. The porosity of cathode electrode plate was estimated as 70% from the fraction of nickel powder and PVB.

2.4.2.2. Anode electrode plate. Two types of anode electrode plate were prepared.

(1) Nickel and titanium: the nickel catalyst plate for an anode was produced by the same method as the cathode nickel plate. Titanium plate was also prepared by the same procedure with titanium powder (Wako Chemicals Co. Ltd.).
(2) La_2O_3 and Sm_2O_3: rare earth oxide electrodes were prepared by doctor blade method as follows. The composition of the slurry was 5.0 g of La_2O_3 powder (Wako Chemicals Co. Ltd.), 3.0 g of PVB, 2.0 g of titanium powder and 13 cm^3 of methanol. Then, La_2O_3 plate was prepared by the same method as the nickel plate. The weight of the plate was 0.5 g. The Sm_2O_3 plate was produced by the same method as the La_2O_3 plate, by using Sm_2O_3 powder (Wako Chemicals Co. Ltd.), PVB and titanium. The plates of these oxides were also prepared with nickel powder.

2.4.3. Operation conditions of MCFC

MCFC was operated at conditions as follows: temperature: $T = 953$ K, gas flow rate: $F_{Ar,0} = 6.8 \times 10^{-6}$ mol/s, $F_{H_2,0} = 3.4 \times 10^{-6}$ mol/s, $F_{CH_4,0} = 3.4 \times 10^{-6}$ mol/s, $F_{O_2,0} = 3.4 \times 10^{-6}$ mol/s, $F_{CO_2,0} = 6.8 \times 10^{-6}$ mol/s.

After setting the anode and cathode electrode plates in each cell housing, carbonate and $LiAlO_2$ plates were sandwiched between the cell housings. Then, the cell unit was pressed under 3.5 kg load. The temperature was increased

slowly to the reaction temperature with oxygen flow to remove PVB and to calcine the electrode. Then, at first stage, argon was introduced to the anode side and the mixture of oxygen and carbon dioxide to the cathode side. After confirming steady values of open circuit electromotive force (OCV) and closed circuit current (CCI) in this concentration cell operation, hydrogen or methane was introduced to the anode side for the fuel cell operation.

Two series of operation were tested.

(1) Hydrogen was fed to anode to check the behaviors in the case of external reforming system.
(2) Fuel feed was then changed to pure methane in order to test the application to dry methane operation.

3. Results and discussion

3.1. Screening of catalyst

Ceramic materials such as rare earth oxides can be expected to show high stability to strong alkaline molten carbonate salt, high stability to high temperature, high activity to oxidation of methane and high mechanical strength. These characteristics are needed to design electrode materials for MCFC instead of conventional nickel electrode. In viewpoint of activation of oxygen species, TPD measurements of pre-adsorbed oxygen on these materials were examined at the temperature range including operation temperature of MCFC system. Fig. 1 shows the TPD spectra of representative Ln_2O_3 (Ln: rare earth element) powder samples together with the catalytic activity for oxidative coupling of methane at 983 K. About 10% of alumina was mixed with these rare earth samples in order to keep the crystal structure in the experiments shown in Fig. 1. The Z-axis indicates the TPD response against the temperature shown in the X-axis. The catalytic activity in tubular reactor is represented by the rate of methane oxidation in the Y-axis. The details of this activity test were shown elsewhere [15].

Among the representative seven samples, active catalysts (Ln: La, Sm, Nd and Dy) showed oxygen desorption peaks at temperatures between 800 and 983 K which were the operating temperature of MCFC. These peaks decreased with the decrease in activity (Ln: Pr, Ce and Tb). Desorption peaks of oxygen were observed at rather lower temperatures with these samples. The above results suggested that the lanthanum containing catalyst was active and oxygen species were capable of electrochemical transport at the operating temperature of MCFC.

In case of "dry methane operation" of MCFC, methane is directly charged to anode without steam. In these conditions, nickel anode material might be deactivated with carbonaceous deposition. To avoid carbonaceous deposition, use of ceramic anode material is one the possibilities. Experimental study on the carbonaceous depositions was conducted with a flow type TG apparatus. Carbonaceous depositions on electrode materials in a flow of pure methane were measured
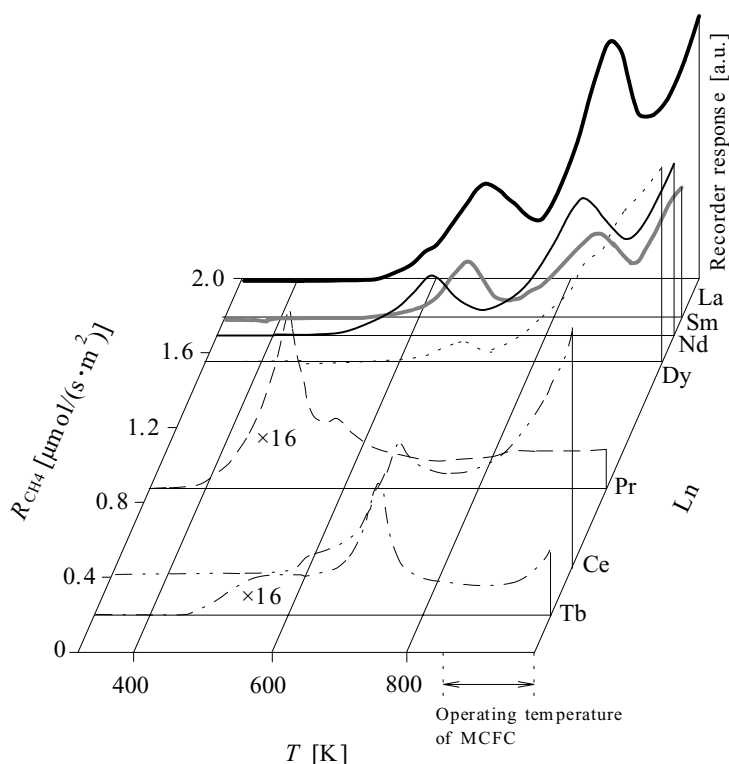

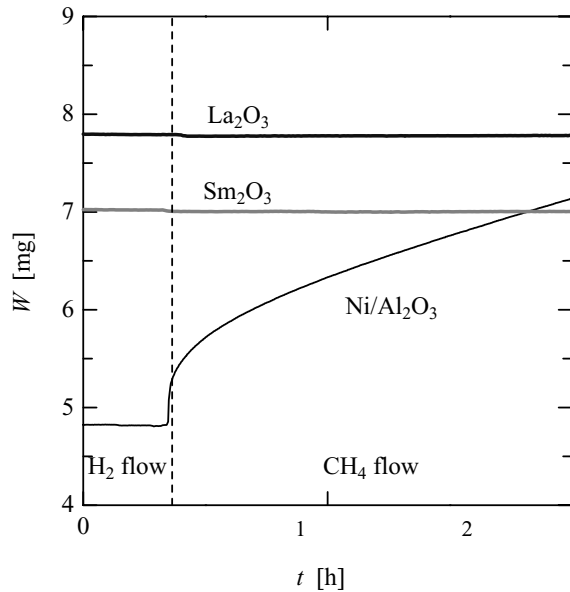Fig. 1. TPD spectra of oxygen on Ln_2O_3 (Ln: rare earth elements).

Fig. 2. Thermo-gravimetric (TG) analysis at 973 K.

by TG analysis. Fig. 2 shows the results of Ni, La_2O_3 and Sm_2O_3. When methane was charged, nickel showed a serious weight increase caused by carbonaceous deposition. On the other hand, very small increase in weight was observed on La_2O_3 and Sm_2O_3 showing the stability of these material to carbonaceous deposition accompanied with a decomposition of methane. These results showed that the La_2O_3 and Sm_2O_3 could be applied for anode of MCFC as carbonaceous deposition-free electrode in case of dry methane (methane-direct) operation.

Oxidation of methane on La_2O_3 was compared to nickel catalyst with a conventional tubular reactor under low oxygen partial pressure. Nickel was supported on alumina coated cordierite in this experiment. As shown in Fig. 3, stable activity was observed on La_2O_3. On the other hand, the activity decreased slowly on nickel catalyst. The decrease of activ-
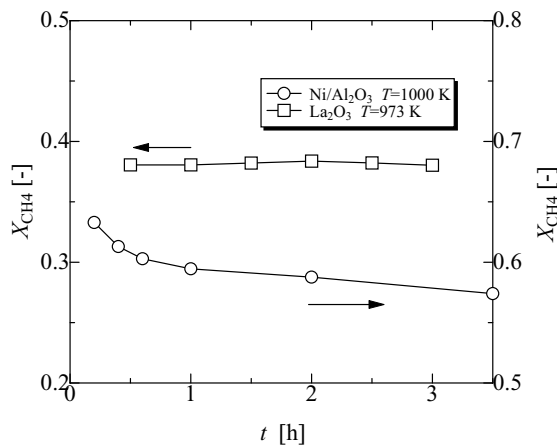

Fig. 3. Methane conversion against operation time with tubular reactor: $F_{CH_4,0} = 3.0 \times 10^{-5}$ mol/s, $F_{O_2,0} = 1.5 \times 10^{-5}$ mol/s, $F_{Ar,0} = 6.0 \times 10^{-5}$ mol/s.
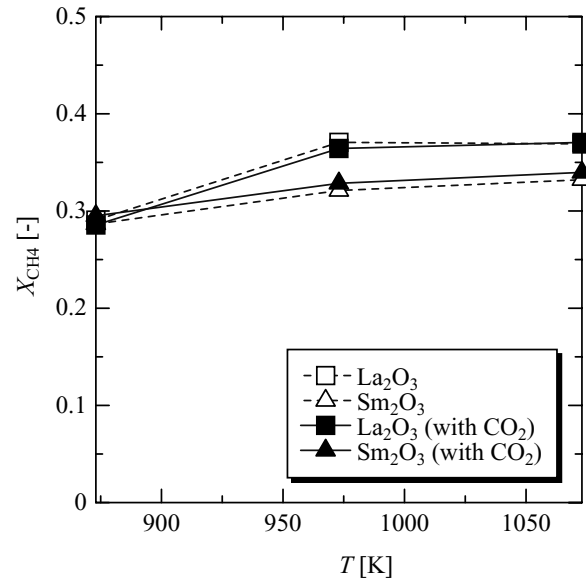

Fig. 4. Effect of carbon dioxide on oxidation of methane with tubular reactor: $F_{CH_4,0} = 3.0 \times 10^{-5}$ mol/s, $F_{O_2,0} = 1.5 \times 10^{-5}$ mol/s, $F_{CO_2,0} = 1.5 \times 10^{-5}$ mol/s, $F_{Ar,0} = 4.5 \times 10^{-5}$ mol/s.

ity on nickel catalyst continued even after 3.5 h of reaction time. These behaviors can be predicted by the carbonaceous deposition by TG study shown in Fig. 2.

In the anode side of MCFC, carbon dioxide should be expected as the same amount as oxygen ion permeated through electrolyte. Therefore, the effect of carbon dioxide on the oxidation of methane was also tested with tubular reactor on La_2O_3 and Sm_2O_3. As shown in Fig. 4, no apparent retardation effect of carbon dioxide was observed at the operating temperature of MCFC. The increase in activity on Sm_2O_3 agrees with reported promotion effect of carbon dioxide on oxidative coupling of methane [16,17].

3.2. Operation of MCFC with nickel and titanium anode electrode

A MCFC operation was tested in the cell system with nickel anode and titanium anode. Fig. 5 shows the results in case of hydrogen as a fuel. Both open circuit electromotive force (OCV) and closed circuit current (CCI) increased gradually with time but the values were unstable on nickel anode. As shown in Fig. 6, both OCV and CCI decreased after the introduction of methane. Similar tendencies were observed in the case of titanium as an anode electrode with hydrogen (Fig. 5). However, the values were more stable in the case of methane as a fuel as shown in Fig. 6. A resistance to carbonaceous deposition might keep the activity of titanium powder more stable.

3.3. Use of La_2O_3 and Sm_2O_3 as anode electrode for MCFC

Application of La_2O_3 and Sm_2O_3 as anode electrode materials for MCFC was tested in the same cell system in the
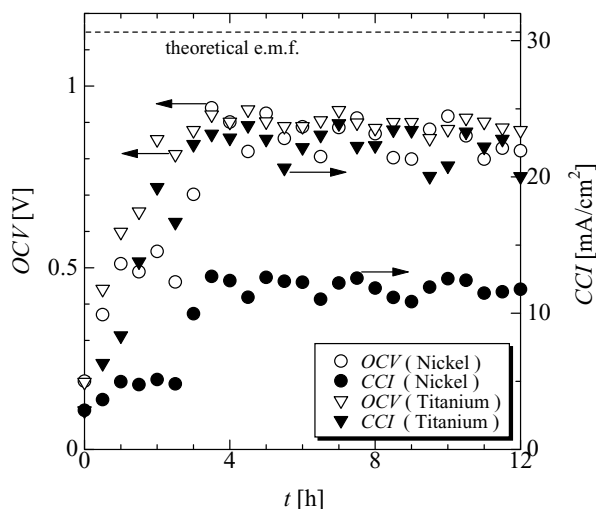
Fig. 5. Operation of MCFC with nickel or titanium as anode under hydrogen flow as a fuel: $T = 953$ K, gas flow rate: $F_{Ar,0} = 6.8 \times 10^{-6}$ mol/s and $F_{H_2,0} = 3.4 \times 10^{-6}$ mol/s for anode; $F_{O_2,0} = 3.4 \times 10^{-6}$ mol/s and $F_{CO_2,0} = 6.8 \times 10^{-6}$ mol/s for cathode.

previous section. Fig. 7 shows the preliminary case of La_2O_3 without any additive. When hydrogen was charged as a fuel, 0.8 V of OCV was observed. This shows the ability of La_2O_3 to oxydize hydrogen. On the other hand, CCI was lower than concentration cell performances and unstable. This should be caused by the lack of electronic conductivity of the ceramic materials.

In order to give electronic conductivity, nickel power was added to La_2O_3. As shown in Fig. 8, higher values of OCV and CCI (1.04 V; 37 mA/cm^2) than those on nickel are observed in the case of hydrogen. In case of nickel electrode, a decrease of OCV by 0.1 V (Fig. 5) from this value was observed mainly because of the local polarization in the metal particles.
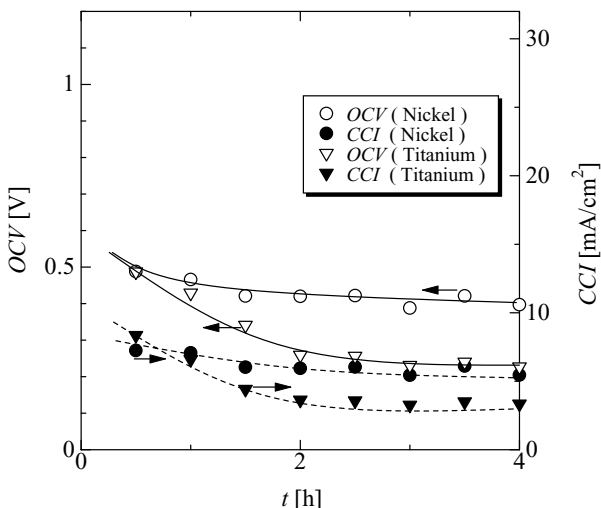

Fig. 6. Operation of MCFC with nickel or titanium as anode under methane flow as a fuel: $T = 953$ K, gas flow rate: $F_{Ar,0} = 6.8 \times 10^{-6}$ mol/s and $F_{CH_4,0} = 3.4 \times 10^{-6}$ mol/s for anode; $F_{O_2,0} = 3.4 \times 10^{-6}$ mol/s and $F_{CO_2,0} = 6.8 \times 10^{-6}$ mol/s for cathode.
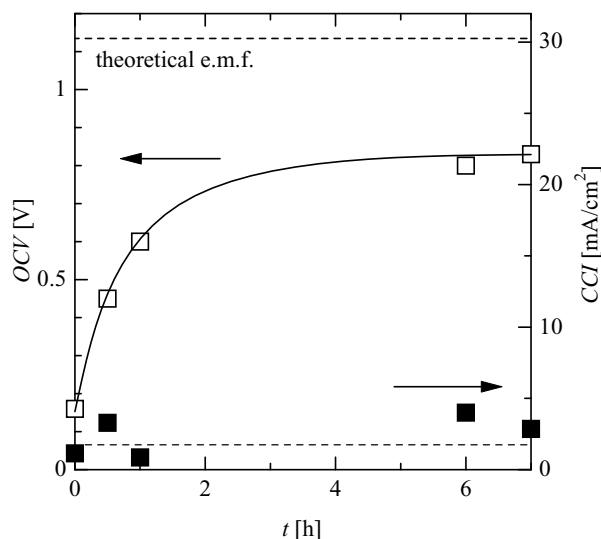

Fig. 7. Operation of MCFC with La_2O_3 without metal component as anode under hydrogen flow as a fuel: operation conditions are the same as Fig. 5.

These values with hydrogen decreased after the introduction of methane as shown in Fig. 9. These results show the capability of these ceramic composite materials as anode electrode of MCFC. The decrease in activity could be avoided if the metallic additives would be stable against carbonaceous deposition. Use of titanium instead of nickel is one of the selections for that purpose. TG measurements of Ti powder under the flow of hydrogen and methane were conducted. No apparent changes in weight were observed both under hydrogen and methane. These results showed that use of titanium powder instead of nickel would satisfy these requirements for use in the dry methane operation.

The results of La_2O_3 and Sm_2O_3 with titanium powder are shown in Figs. 10 and 11. As shown in Fig. 10, high and steady-state OCV and CCI (1.08 V; 26 mA/cm^2, 1.05 V;
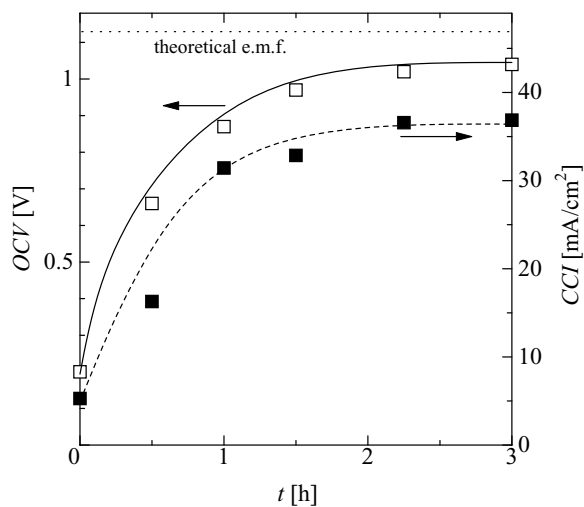

Fig. 8. Operation of MCFC with "La_2O_3 + nickel" as anode under hydrogen flow as a fuel: operation conditions are the same as Fig. 5.
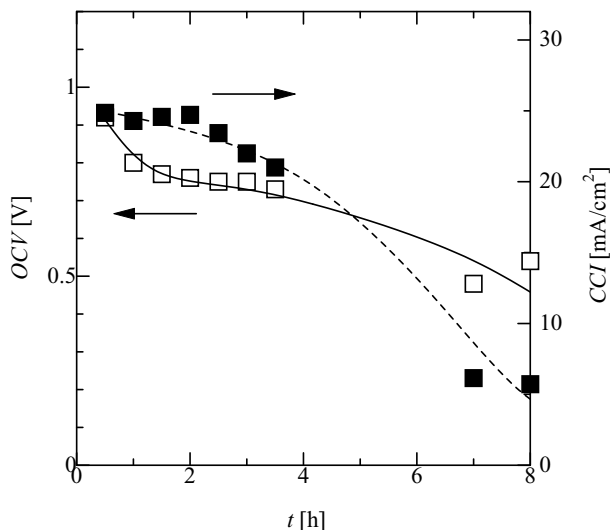
Fig. 9. Operation of MCFC with "La_2O_3+nickel" as anode under methane flow as a fuel: operation conditions are the same as Fig. 6.

23 mA/cm^2) were observed on both La_2O_3 and Sm_2O_3 composites in the case of hydrogen. The OCV is almost agreed with theoretical electromotive force (1.14 V) estimated by the following equation:

$$V = -\frac{\Delta G}{nF}$$

It is known that the distortion of metallic electrode plate will cause the increase of internal resistance of MCFC. The stability of steady-state values in these ceramic electrodes might be realized by the mechanical strength of these ceramic materials compared to the metallic electrode plate (nickel and titanium shown in Fig. 5) prepared by pressing metal powder. The performance of these composite electrodes in dry methane type MCFC was observed in Fig. 11. Transient decrease in OCV and CCI were observed in 2 h
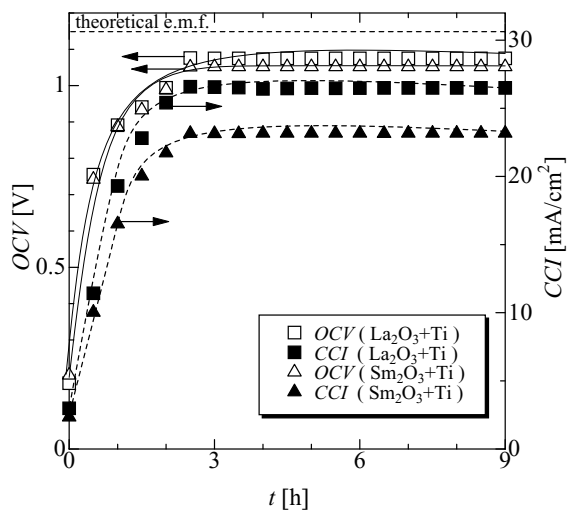

Fig. 10. Operation of MCFC with "Ln_2O_3 + titanium" as anode under hydrogen flow as a fuel: operation conditions are the same as Fig. 5.
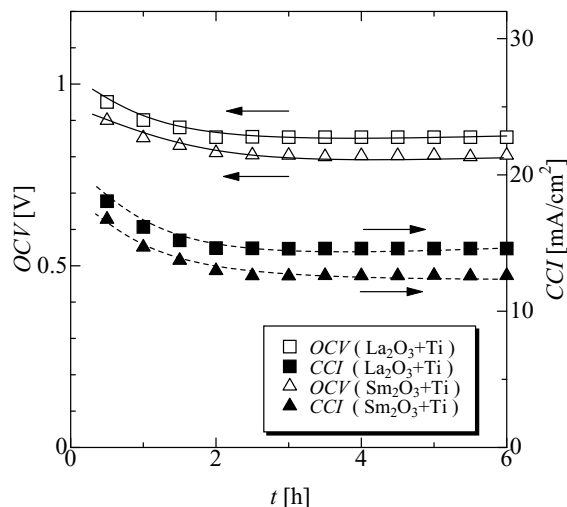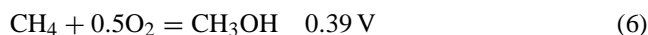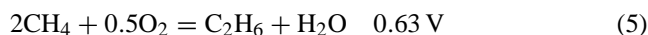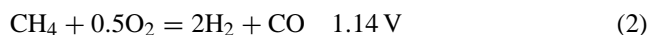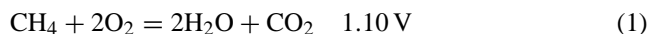

Fig. 11. Operation of MCFC with "Ln_2O_3 + titanium" as anode under methane flow as a fuel: operation conditions are the same as Fig. 6.

after the fuel was changed from hydrogen to methane. Then, the steady-state values were obtained. The OCV and CCI on La_2O_3 and Sm_2O_3 are 0.85 V; 15 mA/cm^2 and 0.8 V; 13 mA/cm^2, respectively. These values were also much higher than the observed concentration cell performances (0.17 V; 3 mA/cm^2 with argon flow) showing electrochemical conversion of methane on these anodes.

Theoretical electromotive forces for representative methane oxidation reactions are calculated from free energy changes as follows;

$$CH_4 + 2O_2 = 2H_2O + CO_2 \quad 1.10\,V \tag{1}$$

$$CH_4 + 0.5O_2 = 2H_2 + CO \quad 1.14\,V \tag{2}$$

$$2CH_4 + O_2 = C_2H_4 + 2H_2O \quad 0.79\,V \tag{3}$$

$$CH_4 + O_2 = HCHO + H_2O \quad 0.77\,V \tag{4}$$

$$2CH_4 + 0.5O_2 = C_2H_6 + H_2O \quad 0.63\,V \tag{5}$$

$$CH_4 + 0.5O_2 = CH_3OH \quad 0.39\,V \tag{6}$$

The observed OCV values are smaller than the theoretical values of the complete oxidation (Eq. (1)) and the synthesis gas formation (Eq. (2)). These values are larger than the ethane formation (Eq. (5)) and methanol formation (Eq. (6)). The values are similar to either oxidative coupling to ethene (Eq. (3)) or formaldehyde formation (Eq. (4)). The GC analysis of exhaust gas showed small amounts of ethane with ethane in addition to majority of combustion gases (CO_2 + H_2O) but formaldehyde was not observed. These suggest that the primary electrochemical oxidation on anode with methane may be oxidative coupling of methane but most of formed ethane should be oxidized completely on the catalyst by surface oxygen species. These assumptions are supported by the facts that the rare earth oxides showed catalytic activity for oxidative coupling of methane [9,10,15,16,17]. These show the possibility of operation for the dry methane

type MCFC by using this ceramics-titanium composite anode electrode. As for the reaction mechanism of dry methane operation, further studies are needed including the analysis of exhaust gas in details.

The fuel cell operation for 14 h followed by the concentration cell operation (operation with inert gas) for 10 h were repeated at 953 K for 6 times with total operation time of 144 h. No apparent decreases in OCV and CCI were observed with this continuous operation test, suggesting the short term stability of this electrode system. A long term stability of this system has not been tested yet.

In this study, a mechanical alloying method was applied to obtain "hybrid material" of rare earth oxide and stable titanium fine powder. This method could provide high surface area of electrode, which might promote the activity and also could support fine powder of oxide materials onto stable titanium metal, which might promote the stability. Thus, further optimization of preparation conditions for anode is important in order to improve the cell efficiency and stability.

4. Conclusions

Ceramic oxidation catalyst materials were examined in order to develop the anode electrode for MCFC. A primary selection was conducted with TPD, TG and plug flow reactor. Oxide such as lanthanum (La_2O_3) and samarium (Sm_2O_3) were selected.

These materials were required to have electronic conductivity for using as an anode electrode. These composite materials with titanium fine powder were assembled into a cell unit for MCFC as an anode electrode. Steady-state activities were observed with these anode electrode materials when hydrogen was used as a fuel. When methane was used directly as a fuel, a steady state was realized after gradual decrease in OCV and CCI. These suggested that the dry methane type MCFC could be realized with these ceramics-titanium composite anode electrode materials. Comparing the observed OCV with theoretical electromotive force, a reaction path via electrochemical oxidative coupling of methane on the electrode catalyst was suggested.

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