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Combined reforming of methane with carbon dioxide and oxygen in molten carbonate fuel cell reactor†

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An application of a molten carbonate fuel cell (MCFC) system to the reforming reactor is proposed. Molten carbonate is regarded as a permselective membrane for oxygen and carbon dioxide. A combination of partial oxidation of methane with carbon dioxide reforming of methane is possible by applying the MCFC-type reactor as a membrane reactor. The energy of the reaction can be directly converted into electric power. This suggested the possibility of chemicals (syn-gas) and energy (electric power) co-generation and a new way of utilizing carbon dioxide. The selection of the anode catalyst is essential for the reforming reaction. Several transition metals, rare earth metals and noble metals (especially ruthenium) were tested. Among them, nickel was selected as a material for the anode catalyst. The effect of lithium addition was also studied. Copyright © 2001 John Wiley & Sons, Ltd.

Keywords: fuel cell; molten carbonate; MCFC reactor; anode catalyst; methane reforming; carbon dioxide reforming; partial oxidation; nickel catalyst

1 INTRODUCTION

Catalytic conversion is quite important for the utilization of carbon dioxide. In spite of enthusiastic development of catalysts, few studies have been done on the development of reactors and reaction systems. This study proposes an application of the molten carbonate fuel cell (MCFC) system to a catalytic reactor for conversion of methane into synthesis gas by utilizing carbon dioxide.

The effective utilization of methane and carbon dioxide as chemical resources has been strongly desired from the viewpoints of reducing greenhouse gases and for the development of new carbon sources.[1] This technology can also utilize low-quality natural gas, which contains a large amount of carbon dioxide and remains in some unused fields in South-East Asia.[1] Carbon dioxide reforming of methane, reaction [1], is a particularly efficient process for producing synthesis gas from these two substrates:

$$\begin{aligned} &CH_4 + CO_2 = 2H_2 + 2CO \\ &\Delta H = 248 \text{ kJ mol}^{-1} \end{aligned} \qquad [1]$$

This can provide synthesis gas with a low H_2/CO ratio, which is efficient for producing oxygenates such as alcohol or aldehyde.[2]

The partial oxidation of methane (abbreviated to POM) also attracts attention as a means for producing synthesis gas having a desirable H_2/CO ratio for methanol synthesis. This reaction, which is slightly exothermic, is economically more useful to produce synthesis gas than the conventional steam reforming reactions (highly endothermic).

Several supported transition metal catalysts were used for these reactions.[3] Nickel-based catalysts were mainly used in industry owing to their low costs. However, it is easy for carbonaceous deposition to occur followed by catalyst deactivation.[4] We have reported the reaction mechanism and performance of several industrial nickel catalysts for carbon dioxide reforming[5,6] and the POM.[7] In a previous paper,[8] we reported that the effect of carbonaceous deposition could be suppressed using a macroporous ceramic foam catalyst in carbon dioxide reforming. We also proposed a

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novel pretreatment, which was called deposition–removal (D–R) treatment, for suppressing carbonaceous deposition for carbon dioxide reforming[9] and POM[7] on the basis of the existence of two types of active site, where one mainly participated in the main reaction and the other in carbonaceous deposition.[6]

Reforming reactions have economic disadvantages due to a high endothermic heat of the reaction. The POM reaction can provide such a heat for the reaction but has a risk for explosion resulting from the mixture of methane and oxygen in a high temperature situation. To solve these problems, a combined reaction of reforming and POM has been proposed.[10]

A fuel-cell-type reactor is one of the most important technologies for solving these problems. In a fuel-cell-type reactor, the electrolyte, which is used as a permselective membrane, is located between the oxygen feed and the reactant feed. This reactor can avoid the mixing of gaseous oxygen and methane; thus direct methane combustion does not occur. The energy of oxidation, which is converted as a potential energy between cathode and anode, can be used as the electric power. From our previous investigations on a solid oxide fuel cell (SOFC)-type reactor, it was found that the key to the application as a reactor was the design and preparation of the electrode catalyst.[11–13]

The basic concept of the MCFC system is shown in Fig. 1. A mixture (1:2) of oxygen and carbon dioxide is activated on the cathode catalyst to form carbonate anion, $CO_3{}^{2-}$, by reaction [2]:

$$\tfrac{1}{2}O_2 + CO_2 + 2e^- = CO_3^{2-} \qquad [2]$$

The carbonate ion is selectively transferred to the anode through a molten carbonate salt. The ion is decomposed into activated oxygen and carbon dioxide on the anode catalyst by reaction [3]. The products are further reacted with methane by reactions [4] and [5]. Two types of reaction, that is, POM [4] and carbon dioxide reforming [5], take place in the MCFC reactor:

$$CO_3{}^{2-} = O_{active} + CO_2 + 2e^- \qquad [3]$$

$$CH_4 + O_{active} = 2H_2 + CO \qquad [4]$$

$$CH_4 + CO_2 = 2H_2 + 2CO \qquad [5]$$

Thus, carbon dioxide is essential to this reactor and can be used quite efficiently. As for the activation of reactants, great attention must be paid to the design and the preparation of the electrode catalyst.

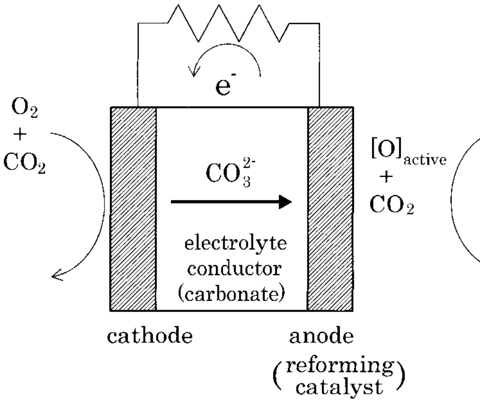

Figure 1 Concept of MCFC system, which is applied to the methane reforming reaction as a reactor.

Undesirable side reactions, which are related with total oxidation, can occur in the reaction system as follows:

$$CH_4 + 4O_{active} = 2H_2O + CO_2 \qquad [6]$$

$$H_2 + O_{active} = H_2O \qquad [7]$$

$$CO + O_{active} = CO_2 \qquad [8]$$

Catalysts that realize desirable reactions should be selected for producing useful chemicals.

During MCFC reactions carbonaceous deposition on nickel catalyst can occur, as in the reforming reaction. This may cause a dramatic decrease in catalyst performance.

$$CH_4 + Ni = CH_x\text{– } Ni + (4 - x)/2H_2 \qquad [9]$$

It is thought that the alkali metals (lithium and potassium) in the molten carbonate salt will be moved to the catalyst. It was reported that these alkali metals were effective as a co-catalyst and produced some interesting effects, such as the suppression of carbonaceous deposition,[14,15] and a stabilizing activity on the MCFC reaction,[15] but a slight decrease of reaction activity.[14,15] In this study, the selection of an anode catalyst for the MCFC reactor will be reported. From the above-mentioned basic investigations, nickel catalysts supported on ceramic foam with alkali metals were prepared for the anode of the MCFC reactor.

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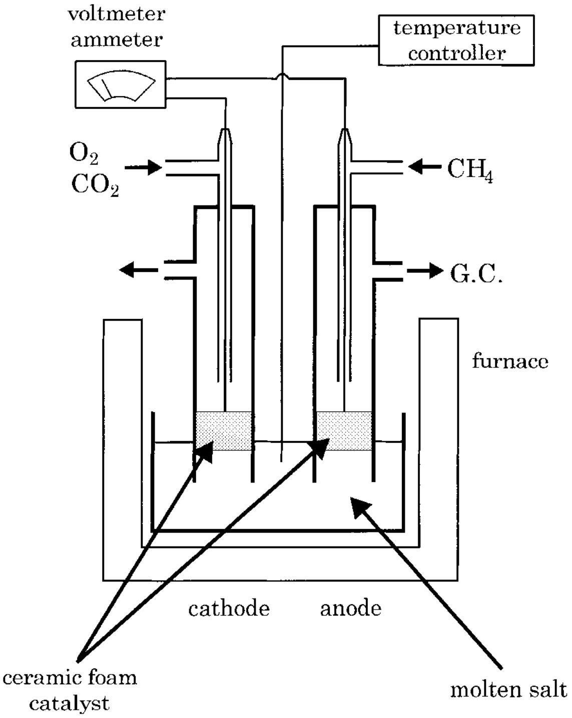

Figure 2 Set up of MCFC reactor, where two electrode units were set in the molten salt bath.

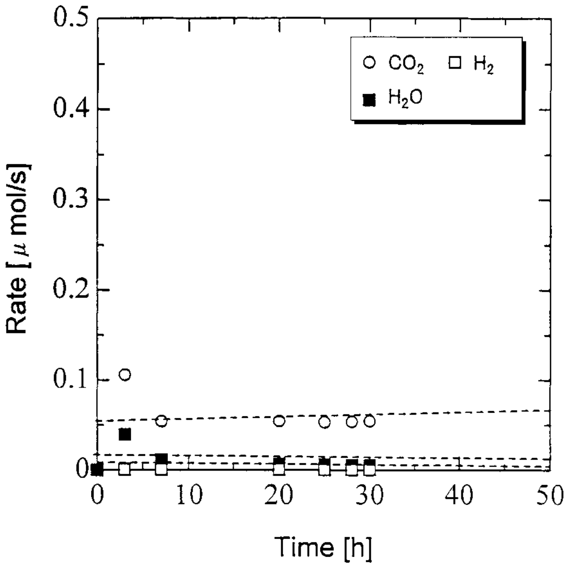

Figure 3 Blank operation of MCFC reactor without anode electrode material at 953 K under the following conditions: $F_{CH_4} = 1.0 \times 10^{-5}$ mol s^{-1}, $F_{CO_2} = F_{O_2} = 1.0 \times 10^{-5}$ mol s^{-1}, P_{total} is atmospheric pressure.

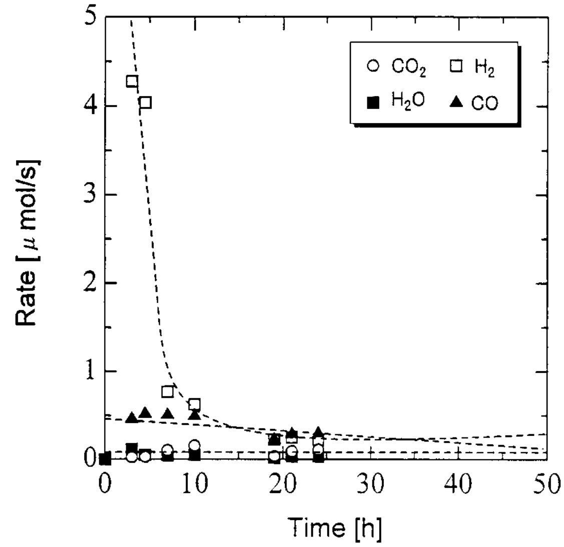

Figure 4 Activity of iron electrode in MCFC reactor at 953 K under the following conditions: $F_{CH_4} = 1.0 \times 10^{-5}$ mol s^{-1}, $F_{CO_2} = F_{O_2} = 1.0 \times 10^{-5}$ mol s^{-1}, P_{total} is atmospheric pressure, $W_{cat} = 3.0$ g.

2 EXPERIMENTAL

2.1 Catalysts preparation

2.1.1 Foam-supported catalyst for MCFC electrode

Catalysts were prepared by impregnating various electrode materials on the ceramic foam support as follows. An aqueous solution of nitrate salt was impregnated on the ceramic foam, which was heated on a hot plate at 453 K. Then, the catalysts were dried and calcined in air at 603 K for 5 h ($F_{air} = 1.5 \times 10^{-4}$mol s^{-1}). The nickel oxide content was adjusted to 20 wt%.

The ceramic foam catalyst with additive was also prepared by impregnating a mixed aqueous solution of nitrate salts.

2.1.2 Alkali metal–nickel/alumina catalyst for tubular-type fixed bed reactor

The effect of additive was studied by impregnating nickel and alkali metal on alumina (γAl_2O_3; Syokubaikasei) with an aqueous solution of nickel nitrate and alkaline materials. These were dried in an oven at 383 K and each was calcined in air at 603 K for 5 h ($F_{air} = 1.5 \times 10^{-4}$ mol s^{-1}). The catalysts were crushed into 20 to 32 mesh size. Nickel contents were 30 wt%. The mole ratio of

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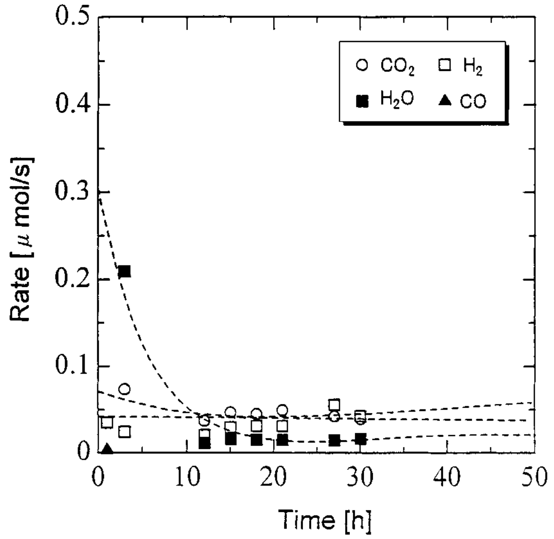

Figure 5 Activity of cobalt electrode in MCFC reactor at 953 K under the following conditions: $F_{CH_4} = 1.0 \times 10^{-5}$ mol s^{-1}, $F_{CO_2} = F_{O_2} = 1.0 \times 10^{-5}$ mol s^{-1}, P_{total} is atmospheric pressure, $W_{cat} = 3.0$ g.

alkali metal (Li, K or Cs)/Ni was 0, 0.2, 0.5 and 1.0. From the results with the fixed-bed reactor, a mole ratio of Li/Ni = 1.0 was selected for the electrode catalyst in the MCFC reactor.

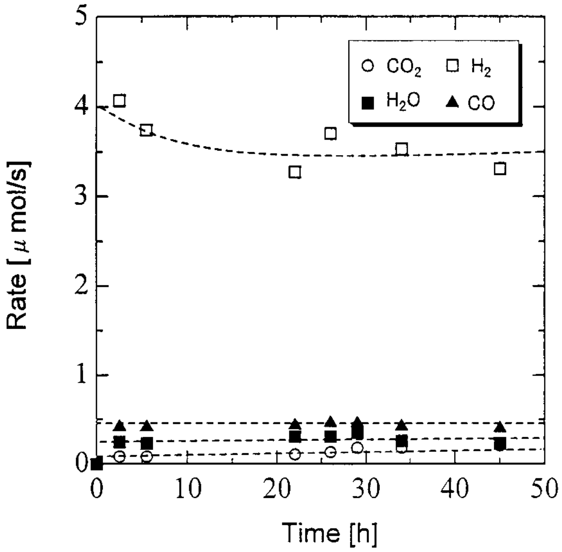

Figure 6 Activity of nickel electrode in MCFC reactor at 953 K under the following conditions: $F_{CH_4} = 1.0 \times 10^{-5}$ mol s^{-1}, $F_{CO_2} = F_{O_2} = 1.0 \times 10^{-5}$ mol s^{-1}, P_{total} is atmospheric pressure, $W_{cat} = 3.0$ g.

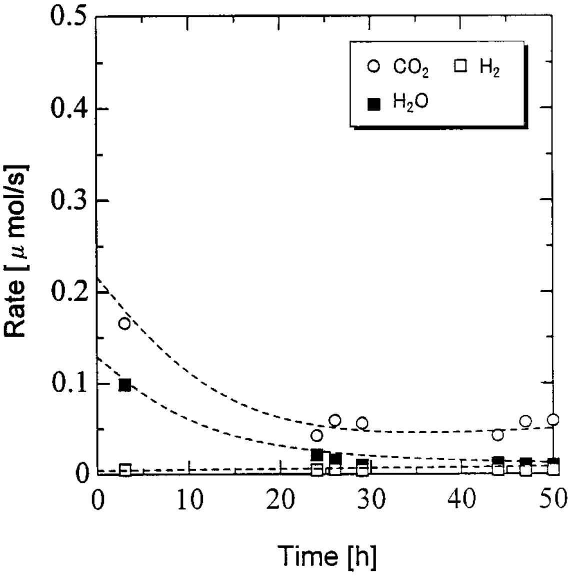

Figure 7 Activity of copper electrode in MCFC reactor at 953 K under the following conditions: $F_{CH_4} = 1.0 \times 10^{-5}$ mol s^{-1}, $F_{CO_2} = F_{O_2} = 1.0 \times 10^{-5}$ mol s^{-1}, P_{total} is atmospheric pressure, $W_{cat} = 3.0$ g.

2.2 Apparatus and reaction conditions

2.2.1 Tubular-type fixed bed reactor for carbon dioxide reforming

Carbon dioxide reforming was conducted in a tubular-type continuous flow fixed-bed reactor. Catalyst and quartz powder of the same size were packed in the reactor in a quartz tube of 8.0 mm inner diameter. The temperature was measured with a thermocouple inserted in the catalyst bed. The catalysts were reduced in a hydrogen flow of 5.0×10^{-6} mol s^{-1} at 1073 K for 1 h just before the reaction was started. Methane and carbon dioxide were introduced after a helium purge at 1000 K. Standard conditions of CO_2 reforming are as follows: $F_{CH_4} = 1.5 \times 10^{-4}$ mol s^{-1}, $F_{CH_2} = 3.0 \times 10^{-4}$ mol s^{-1}, P_{total} is atmospheric pressure, $T = 1000$ K, $W_{cat} = 10$ mg, $W_{SiO_2} = 5.0$ g. The products were measured with an on-line gas chromatograph equipped with a thermal conductivity detector (TCD). Details of the apparatus are in a previous paper.[9]

2.2.2 Thermogravimetric (TG) analysis

The changes in catalyst weight were measured in a methane flow with a TG analyzer (TGA-50, Shimadzu). The standard TG conditions are as

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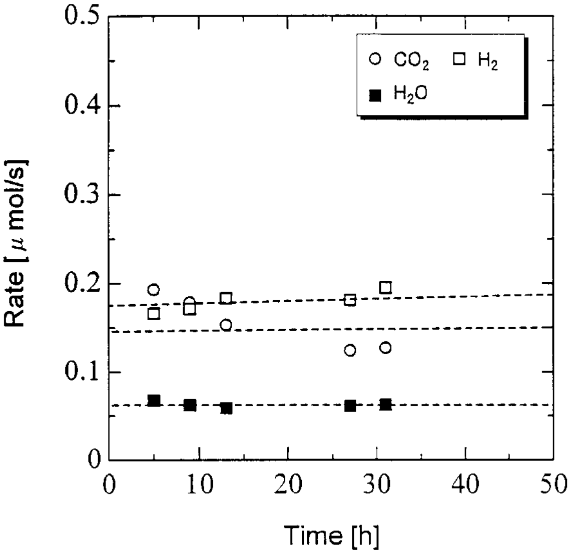

Figure 8 Activity of La_2O_3 electrode in MCFC reactor at 953 K under the following conditions: $F_{CH_4} = 1.0 \times 10^{-5}$ mol s^{-1}, $F_{CO_2} = F_{O_2} = 1.0 \times 10^{-5}$ mol s^{-1}, P_{total} is atmospheric pressure, $W_{cat} = 3.0$ g.

follows: $F_{CH_4} = 1.5 \times 10^{-5}$ mol s^{-1}, P_{total} is atmospheric pressure, $T = 1000$ K, $W_{cat} = 10$ mg. Detailed explanations are given in a previous paper.[9]

2.2.3 MCFC reactor

Figure 2 shows the MCFC reactor. The ceramic foam anode unit was set in a ceramic tube into which methane was introduced separately from oxygen. Nickel-supported cermaic foam was used as a cathode unit and set in the ceramic tube. These tubes were inserted in a crucible, which was then located in the furnace and filled with carbonate salt in order to contact the catalysts. Carbonate salt, which consisted of an Li_2CO_3 (62 mol%) and K_2CO_3 (38 mol%) mixture, was used as a conductor of CO_3^{2-} in the crucible at 1053 K. An equimolar mixture of carbon dioxide and oxygen was supplied to the cathode. Methane was introduced to the anode. Standard conditions for MCFC reaction are as follows: $F_{CH_4} = 1.0 \times 10^{-5}$ mol s^{-1}, $F_{CO_2} = F_{O_2} = 1.0 \times 10^{-5}$ mol s^{-1}, $T = 953$ K, P_{total} is atmospheric pressure, $W_{cat} = 3.0$ g. All products were measured using an on-line TCD gas chromatograph. Current and electromotive force were measured with a multi-meter connected to the anode and cathode with platinum wire.

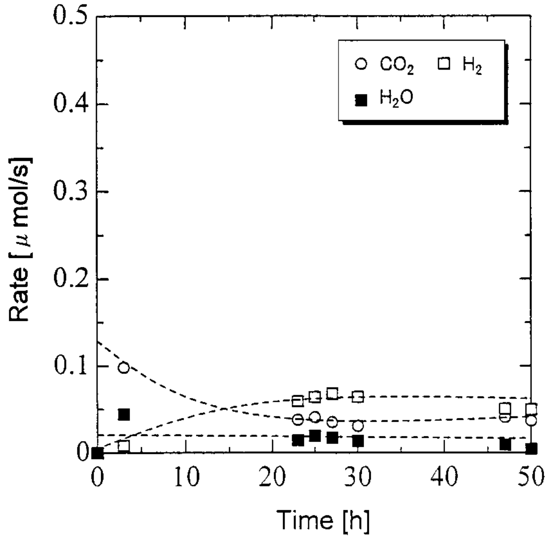

Figure 9 Activity of Sm_2O_3 electrode in MCFC reactor at 953 K under the following conditions: $F_{CH_4} = 1.0 \times 10^{-5}$ mol s^{-1}, $F_{CO_2} = F_{O_2} = 1.0 \times 10^{-5}$ mol s^{-1}, P_{total} is atmospheric pressure, $W_{cat} = 3.0$ g.

3 RESULTS AND DISCUSSIONS

3.1. Selection of anode materials in MCFC reactor

The selection of the anode materials was conducted by using the MCFC reactor at a standard operating conditions. Iron, cobalt and copper, in addition to nickel, were selected to represent transition metals. From the viewpoint of oxygen activation,[11] rare earth elements lanthanum and samarium were tested. Noble metals are expected to be stable against carbon deposition, and ruthenium was tested. Figure 3 shows the results of a blank test without anode materials. A small amount of CO_2 and a negligible amount of H_2O were detected. Figures 4–7 show the results for iron, cobalt, nickel and copper respectively. The iron anode showed a high activity in the first 10 h, but the activity decreased steeply. The amount of CO was quite low at the initial stage compared with hydrogen; this suggested the formation of carbonaceous deposition, which reduced the original activity. It is considered that the main reactions are Eqns [4], [5] and [9]. Cobalt shows total oxidation activity at the initial stage, represented by the formation of H_2O. The activity also decreased steeply in the first 10 h (Eqns [6]–[9]). Nickel shows high activity and the activity is stable for more than 50 h. Hydrogen and

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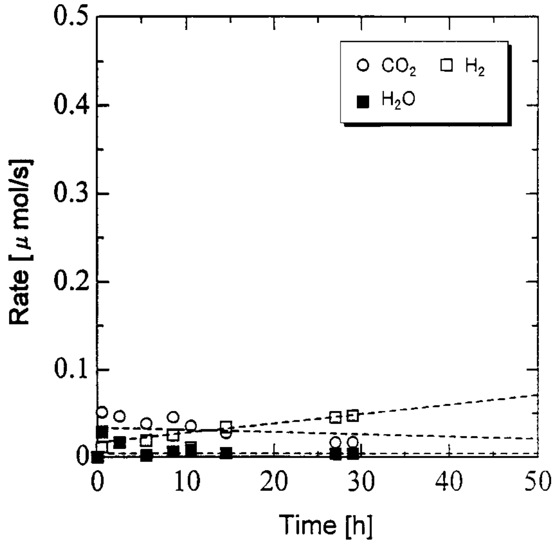

Figure 10 Activity of ruthenium electrode in MCFC reactor at 953 K under the following conditions: $F_{CH_4} = 1.0 \times 10^{-5}$ mol s^{-1}, $F_{CO_2} = F_{O_2} = 1.0 \times 10^{-5}$ mol s^{-1}, P_{total} is atmospheric pressure, $W_{cat} = 3.0$ g.

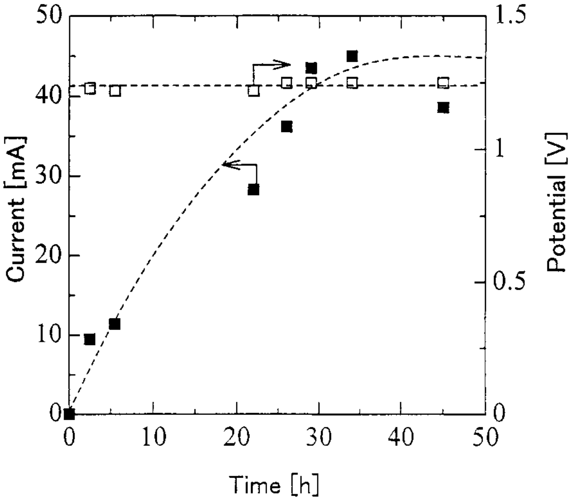

Figure 11 Electromotive force and current of nickel electrode in MCFC reactor at 953 K under the following conditions: $F_{CH_4} = 1.0 \times 10^{-5}$ mol s^{-1}, $F_{CO_2} = F_{O_2} = 1.0 \times 10^{-5}$ mol s^{-1}, P_{total} is atmospheric pressure, $W_{cat} = 3.0$ g.

carbon monoxide were detected as products, although the H_2/CO ratio was quite high (Eqns [4], [5] and [9]). Copper produced H_2O and CO_2, showing total oxidation activity. It also decreased within 20 h (Eqn [6]). Figures 8 and 9 show the results of lanthanum and samarium respectively. Both materials show stable activity, but the product distribution suggests that the reforming reaction and total oxidation proceed in a parallel manner at steady state (Eqns [4]–[8]). Figure 10 shows results for ruthenium, which shows total oxidation activity at the initial stage but reforming activity developed after 20 h of time on stream. The formation of CO was quite low, suggesting the deposition of carbonaceous materials (Eqn [6] then Eqns [4], [5] and [9]). These results show that anode materials can control both the activity and selectivity and the selection of anode materials should be essential for the design of the reaction system. Although each catalyst has reforming ability (Eqns [3]–[5]) or total oxidation (Eqns [6] and [7]), nickel only keeps a high reforming activity after several hours of time on stream. These results suggest that nickel is one of the desired components for anode materials in the reforming reactor. Figure 11 shows the electromotive force and current during the reaction with the nickel electrode shown in Fig. 6. The stable potential of 1.25 V agrees approximately with the theoretical value evaluated from the free energy change. This fact shows that the internal resistance of the reactor is quite small. The gradual increase in current, coupled with the stability in electromotive force (Fig. 11) and reaction activity (Fig. 6), indicates that the system is not in the steady state at the initial stage and a long-term test is needed for the evaluation of the total system. The initial change in current might show that a considerable amount of carbon dioxide and oxygen originating from the carbonate salt were produced in a non-electrochemical manner and reacted with methane at the initial stage. However, the stable value of electromotive force is reliable evidence for the reaction proceeding electrochemically at the same time. As this reactor requires about 30 h until a steady state is achieved, the improved thin-membrane-type MCFC reactor is needed to shorten the leading period.

These results show that this system converts the change of the chemical energy directly into electrical power during the valuable chemical production and chemicals–energy co-generation is possible by using the MCFC reactor.

3.2 Selection of additive raw materials for nickel component

In spite of the results presented in Section 3.1 the nickel electrode showed unstable activity depend-

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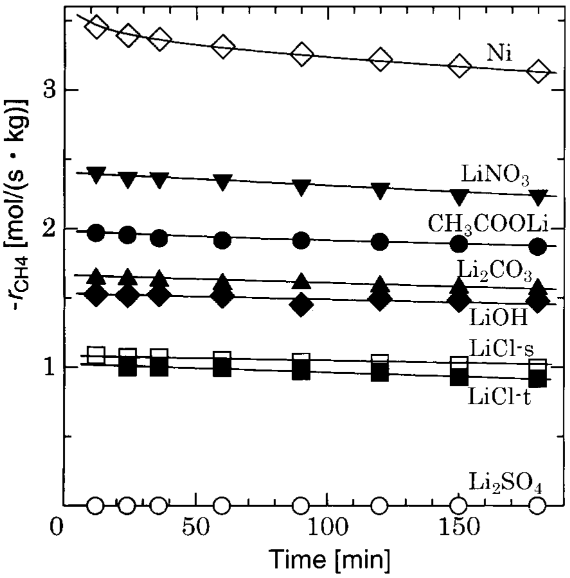

Figure 12 Effect of lithium source on CO_2 reforming of methane with a PFR at 1000 K under the following conditions: $F_{CH_4} = 1.5 \times 10^{-4}$ mol s^{-1}, $F_{CO_2} = 3.0 \times 10^{-4}$ mol s^{-1}, P_{total} is atmospheric pressure, W_{cat} = 10 mg.

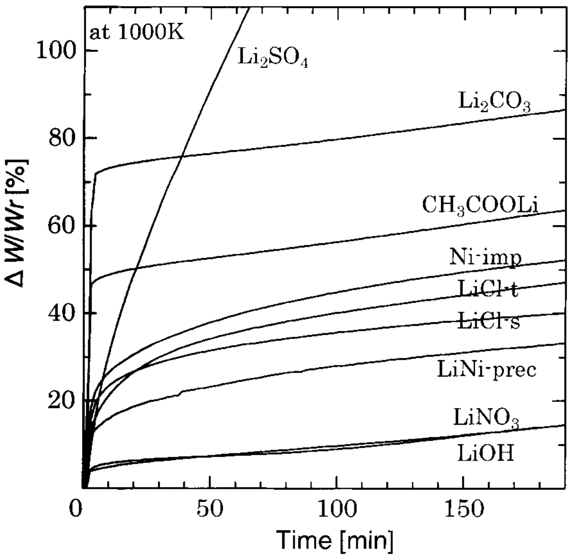

Figure 13 Effect of lithium source on carbon deposition by TG analysis at 1000 K under the following conditions: $F_{CH_4} = 1.5 \times 10^{-5}$ mol s^{-1}, P_{total} is atmospheric pressure, W_{cat} = 10 mg.

ing on the reaction conditions.[15] In order to design a stable electrode, lithium was selected as the component from among the alkali metals.[15] In this section, the selection of raw materials for the lithium additive is reported. For the selection of additives, a plug flow-type fixed-bed reactor (PFR) was used to evaluate CO_2 reforming activity. TG analysis was also used to estimate the deposition of carbonaceous materials. CO_2 reforming activity tested with the PFR is shown in Fig. 12. Li_2SO_4 completely deactivated nickel electrode. All the lithium compounds tested decreased the original activity of the nickel electrode. The means of introduction of LiCl (s: nickel was supported and then lithium was supported; t: nickel and lithium were supported at the same time) did not make a big difference. Among them, $LiNO_3$ shows the highest activity as an additive.

The deposition of carbonaceous material was tested by TG analysis in a flow of methane at 1000 K. The results are shown in Fig. 13. Li_2SO_4, Li_2CO_3, CH_3COOLi increased the deposition compared with the nickel electrode without additives (Ni-imp: prepared by impregnation method). LiCl, $LiNO_3$ and LiOH reduced the carbonaceous deposition. These two sets of results shown in Figs 12 and 13 suggest that addition of $LiNO_3$ can improve the catalyst by imparting high resistance to carbonaceous deposition while keeping a relatively high and stable reforming activity. Thus, $LiNO_3$ is a good precursor as an additive for the nickel anode electrode. The activity of this Ni–Li electrode in the MCFC reactor has already been shown elsewhere.[15]

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