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Carbon Dioxide Reforming of Methane on Ni-ceria-based Oxide Cermet Anode for Solid Oxide Fuel Cells

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Introduction

Development of solid oxide fuel cells (SOFCs)

Intermediate temperature operation

Highly active Ni-samaria-doped ceria (SDC) cermet anode with hydrogen fuel at intermediate temperatures

1) T. Inagaki *et. al.*, *J. Alloys and Compounds*, **408-412**, 512 (2006).

2) M.Kawano *et. al.*, *Solid State Ionics*, **177**, 3315 (2006).

Use of hydrocarbon fuel instead of hydrogen fuel

Methane is a typical hydrocarbon fuel

Steam reforming operation on Ni-SDC cermet anode at intermediate temperature with methane fuel

3) M. Kawano *et. al.*, *J. Power Sources*, **182**, 496 (2008).

Aims of This Study

Reforming operation of SOFC

- Steam generator is not necessary
- CH_4, CO_2 → Main constituents of biogas

Steam reforming

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H^0_{298} = 206\ \text{kJ mol}^{-1} \qquad (1)$$

Carbon dioxide reforming

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H^0_{298} = 247\ \text{kJ mol}^{-1} \qquad (2)$$

Carbon dioxide reforming operation has not been really investigated as a practical SOFC application.

Aims of this study

- Investigation of dependence of temperature and fuel conditions for carbon dioxide reforming of methane to reveal the electrochemical and the reforming activities.
- External and direct internal carbon dioxide reforming operations were compared
- Estimation of the durability of the cell performance

Experimental : Cell Configuration

●Electrolyte : Thickness : 200μm

$La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_{3-\delta}$ (LSGMC)

● Cathode : 120 mmφ

$Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC)

● Anode : 120 mmφ

$NiO\text{-}Ce_{0.8}Sm_{0.2}O_{1.9}$ (samaria-doped ceria ; SDC) composite particles synthesized by spray pyrolysis→Ni-SDC cermet
Ni/SDC volume ratio＝60/40

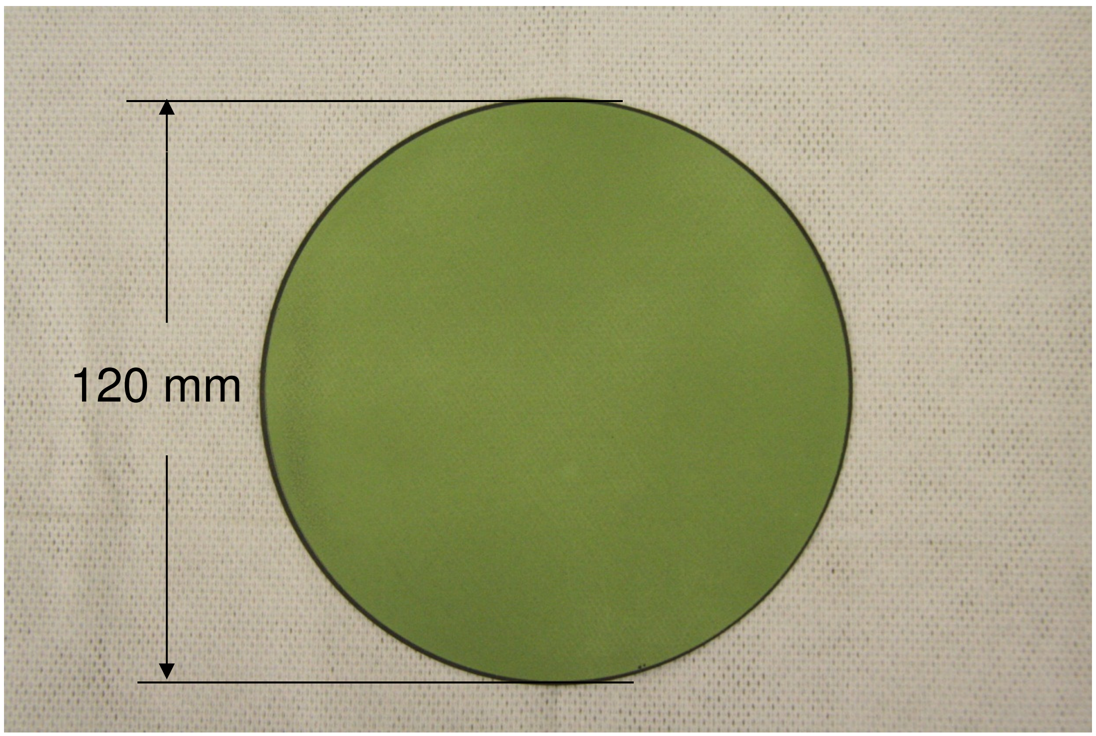
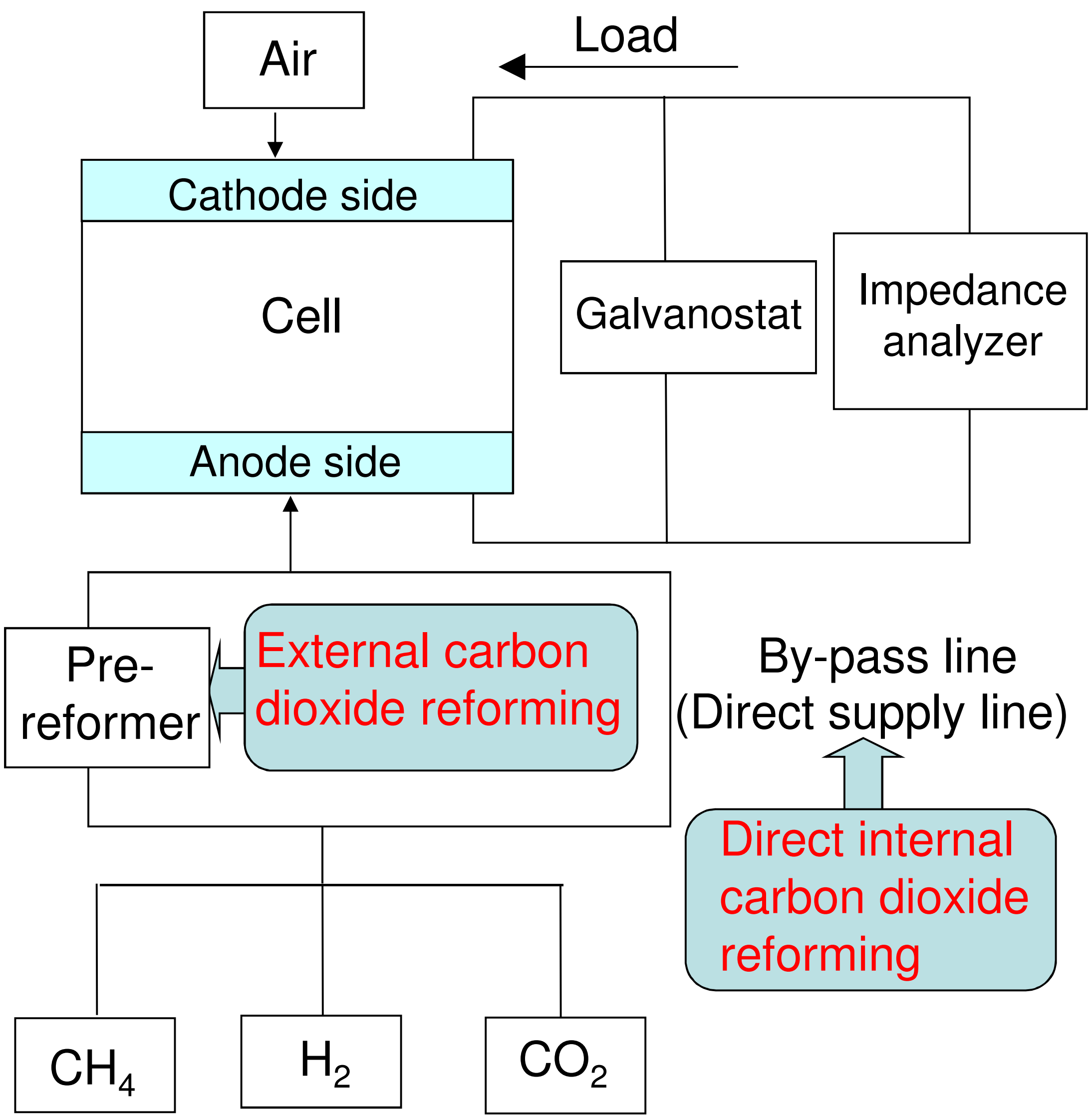


Figure. Photograph of an electrolyte-supported planar-type cell from the anode side before power generation.

Experimental : SOFC Operation System



Operating temperature : 750, 700, 650°C
Cell stack : seal-less structure
Oxidant : Air 15 ml cm^{-2} min^{-1}

Fuel : CH_4 or Dry H_2
CO_2 -reformed CH_4
CH_4 fuel ; 0.75 ml cm^{-2} min^{-1}
CO_2 ; 3.00, 2.25, 1.50 ml cm^{-2} min^{-1}
CH_4/CO_2 =1/4, 1/3, 1/2
Dry H_2 ; 3.00 ml cm^{-2} min^{-1}

External carbon dioxide reforming ≡ ECDR

Direct internal carbon dioxide reforming ≡ DICDR

Electrochemical characterization
***I-V* characteristics, Durability test, Impedance spectra**

I-V characteristics : Comparison between ECDR and DICDR at various operation temperatures

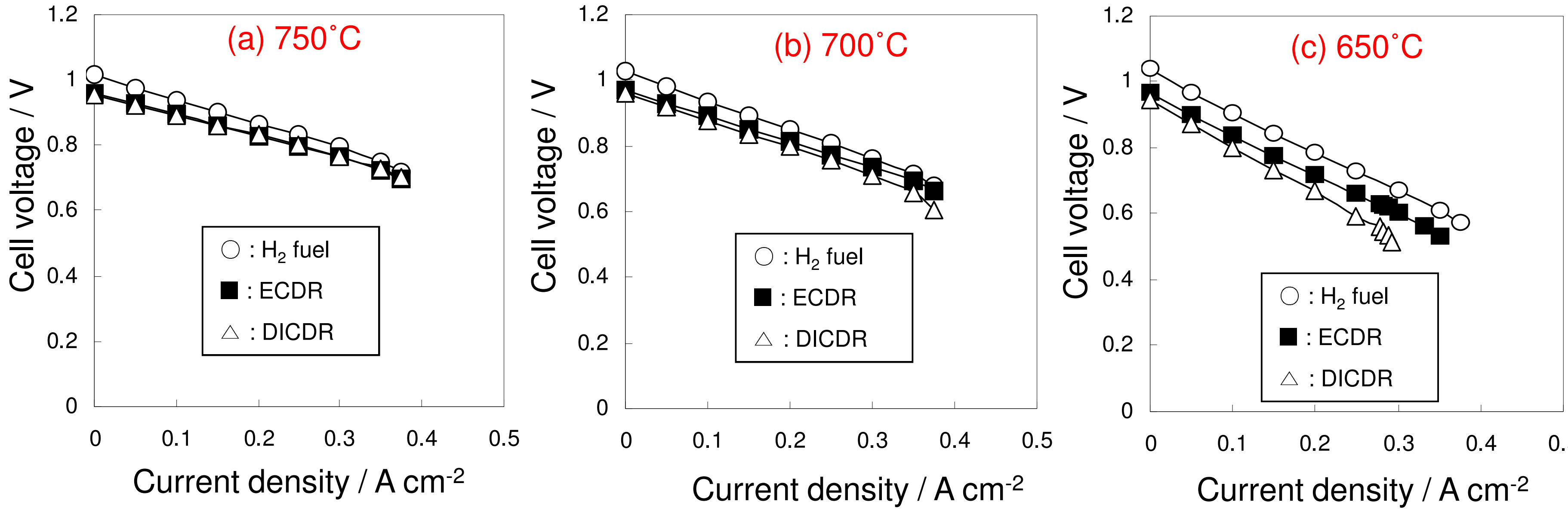


Figure. *I-V* characteristics of a single cell by feeding external and direct internal carbon dioxide-reformed methane fuels (CH_4/CO_2 =1/4) and dry hydrogen fuel at (a) 750, (b) 700, and (c) 650˚C.

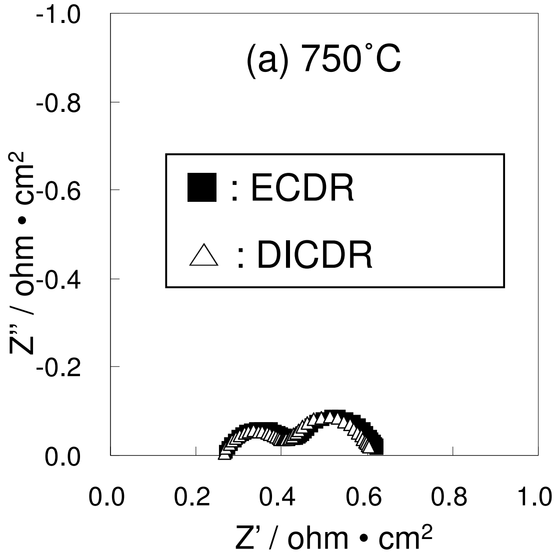
- Cell performance at 750˚C : DICDR ≒ ECDR ≒ H_2 fuel

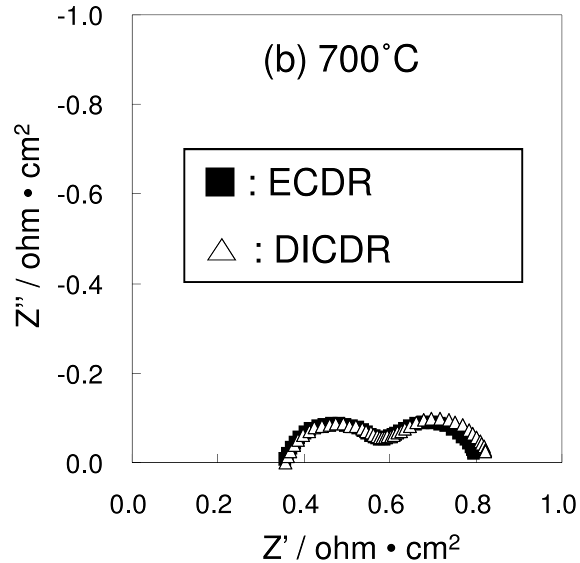
→Methane conversion for DICDR at 750˚C→Sufficient

- Cell performance at 700˚C : DICDR < ECDR < H_2 fuel
- Cell performance at 650˚C : DICDR << ECDR << H_2 fuel

→Methane conversions for DICDR at 700 and 650˚C →Incomplete

Impedance spectra : Comparison between ECDR and DICDR at various operation temperatures





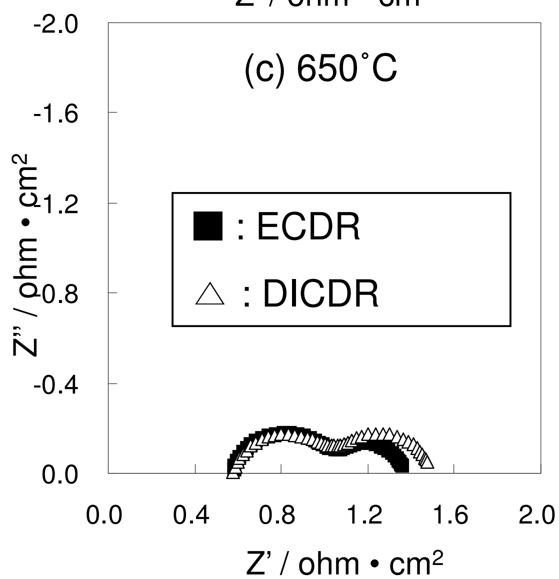


Figure. Impedance spectra for the cell with the open circuit condition by feeding external and direct internal carbon dioxide-reformed methane fuels (CH_4/CO_2 =1/4) at (a) 750, (b) 700, and (c) 650˚C.

- High-frequency semicircle (Resistance due to the activation polarization) :

  ECDR = DICDR

  at 750, 700, 650˚C

- Low-frequency semicircle (Resistance due to the concentration polarization) :

  ECDR ≒ DICDR at 750˚C

  ECDR < DICDR at 700˚C

  ECDR << DICDR at 650˚C

- Lower operation temperatures

  →Insufficient conversion of methane on Ni-SDC anode

I-V Characteristics：Comparison between ECDR and DICDR at 750˚C for various CH_4/CO_2 ratio

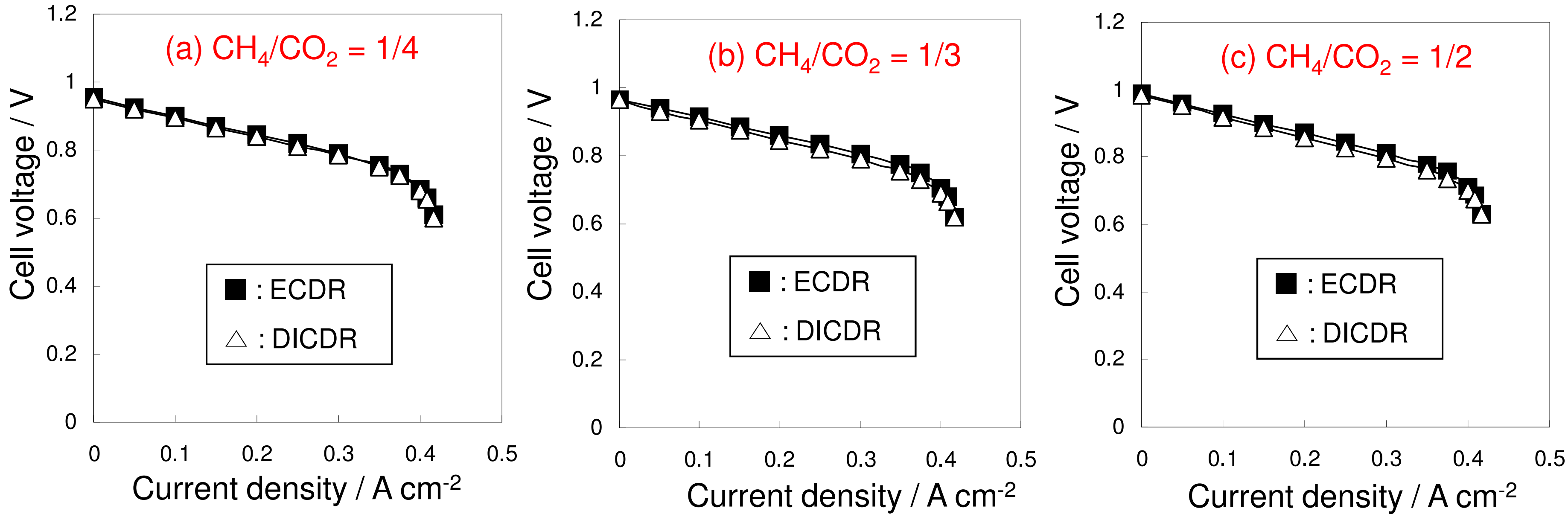


Figure. *I-V* characteristics of a single cell at 750˚C with external and direct internal carbon dioxide reforming of methane; CH_4/CO_2 = (a)1/4, (b)1/3, and (c)1/2.

- ECDR = DICDR (CH_4/CO_2 = 1/4, 1/3, 1/2)
- These results suggest that methane fuel was sufficiently reformed on Ni-SDC anode at 750˚C regardless of the operation runs for the ECDR and DICDR with these methane to carbon dioxide ratios (CH_4/CO_2 = 1/4, 1/3, 1/2).
- Methane conversion for DICDR operation is suggested to be sufficient.

The durability test of DICDR operation at 750˚C

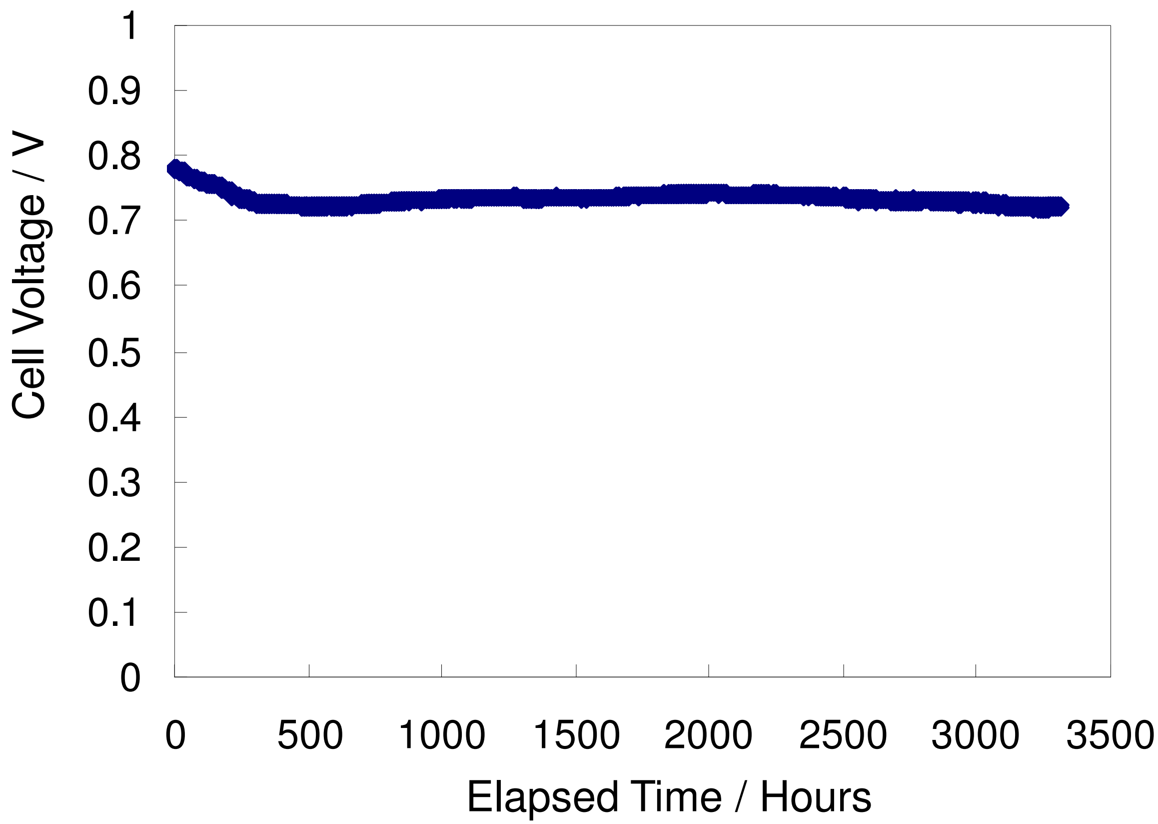


Figure Time course of cell voltage for a single cell (Ni-SDC│LSGMC│SSC) with supply of carbon dioxide-reformed methane (CH_4 /CO_2 = 1/3) with the conditions of 0.3 A cm^{-2} at 750˚C.

- CH_4 / CO_2 =1/3
- Operation temperature : 750 ˚C
- Current Density : 0.3 A cm^{-2} (Uf: 70%)
- The durability test of DICDR operation for about 3300 hours has been conducted.
- Slight voltage drop was confirmed at the initial stage.
- The stable cell performance was confirmed from 500 hours to 3300 hours.
- This result of durability test showed that almost stable cell performance was confirmed for the DICDR operation at 750 ˚C.

Experimental : Gas analysis

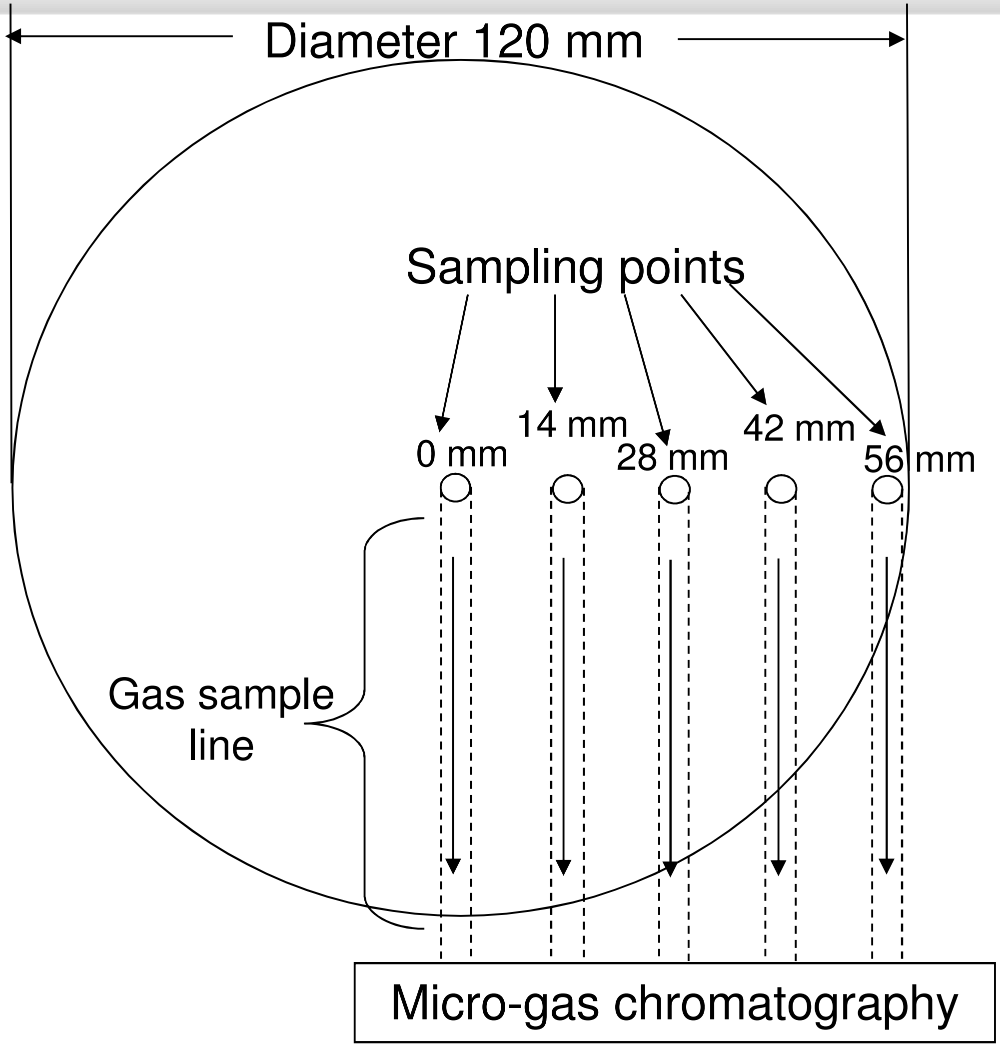


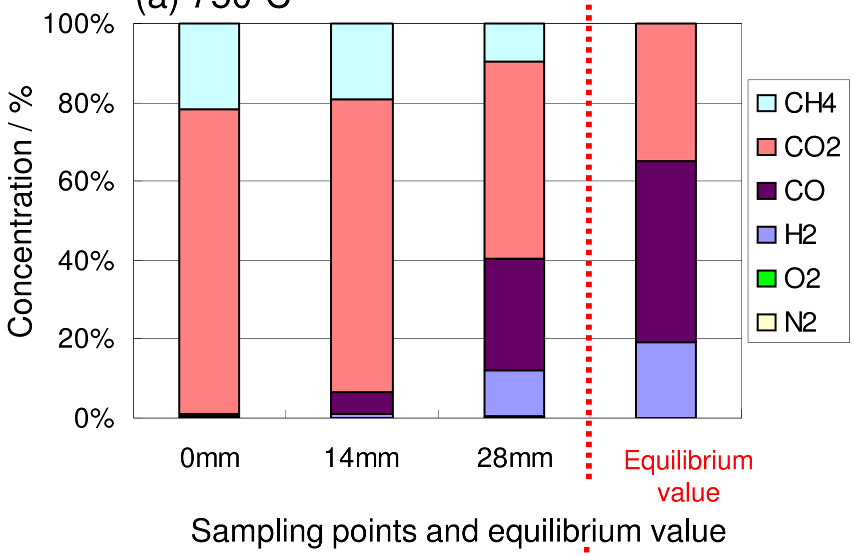
Figure. Schematic view of the anode separator for gas analysis.

Gas analysis method

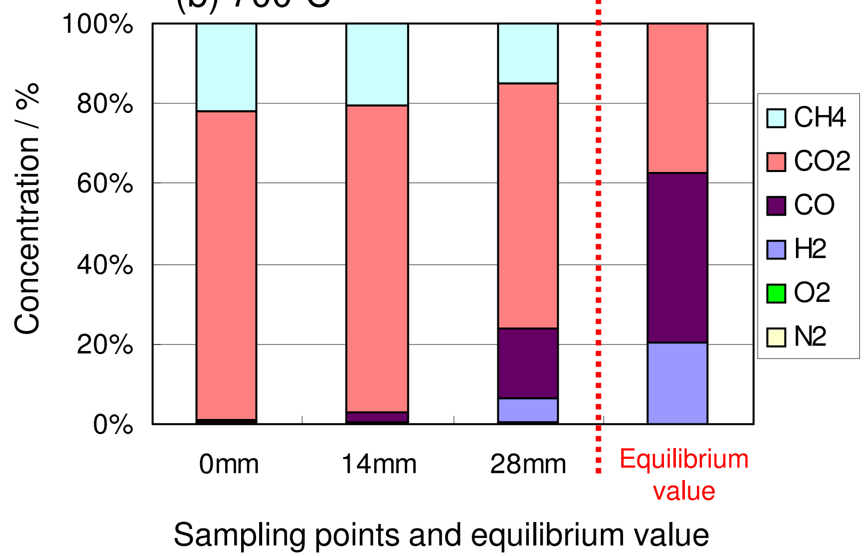
- **Sampling points : Five points 0, 14, 28, 42, 56 mm The distance from the center hole**
- **The fuel was supplied from the center hole**
- **The composition of the gaseous species except for water vapor was measured by micro-gas chromatography**
- **Water vapor could not be analyzed because of the restriction of the micro-gas chromatograph equipment.**

Results of gas analysis at various operation temperatures

(a) 750˚C



(b) 700˚C



(c) 650˚C

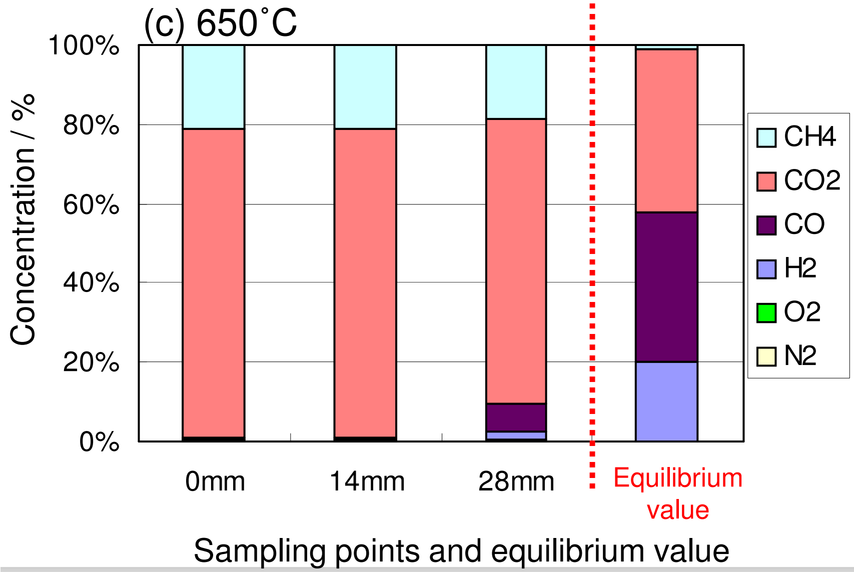


Figure. The results of gas analysis in the radial direction for a single cell by feeding carbon dioxide-reformed methane (CH_4 /CO_2 = 1/4) with the conditions of open circuit voltage at (a) 750, (b) 700, and (c) 650˚C.

・CH_4 was converted to H_2 and CO in the radial direction on practical size Ni-SDC anode at 750, 700 and 650˚C.

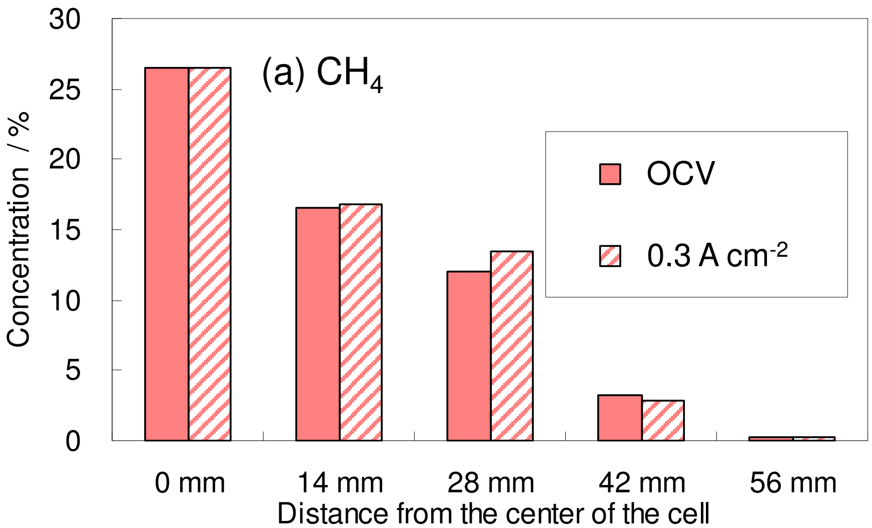
・The deviation from the equilibrium value of CH_4 conversion

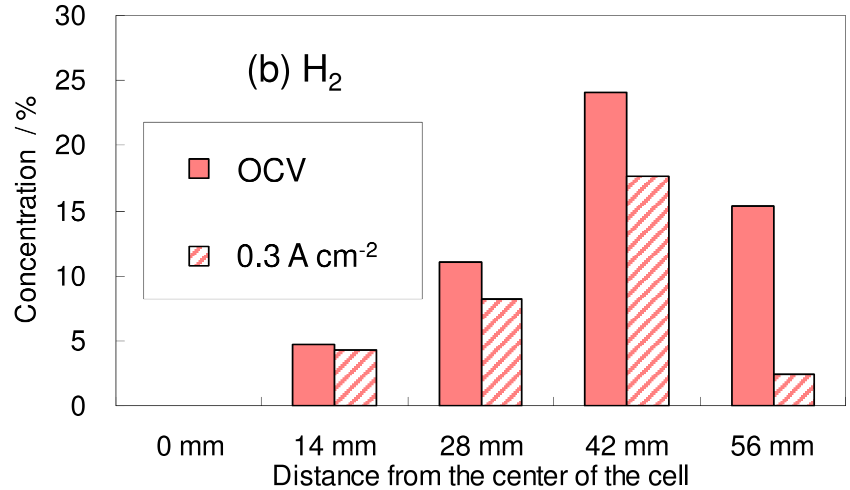
750˚C < 700˚C < 650˚C

・CH_4 was not effectively converted at lower temperatures (700 and 650˚C)

・Decrease of reformed fuel species (H_2 and CO) due to the low conversion of CH_4 at 700 and 650˚C
→Deterioration of cell performance

Results of gas analysis
Comparison between OCV and discharged conditions





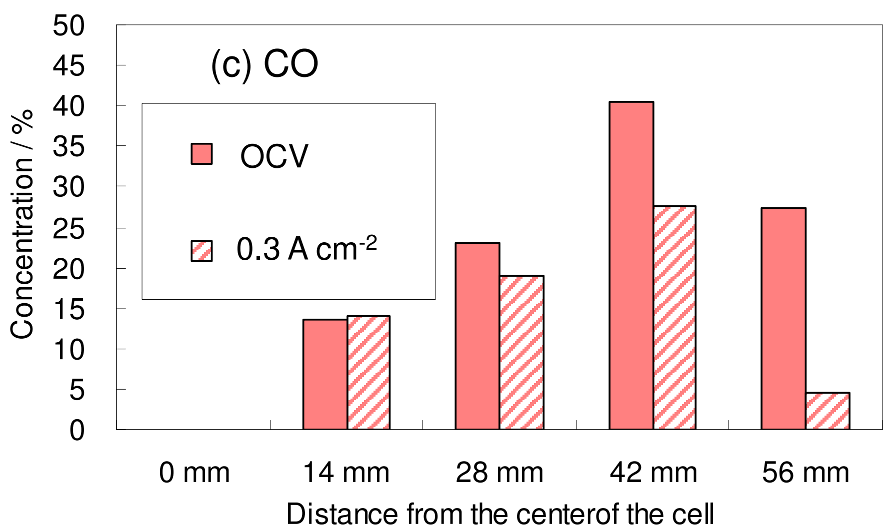


Figure. Gas analyzing results for (a) CH_4, (b) H_2, and (c) CO in the radial direction for a single cell by feeding carbon dioxide-reformed methane (CH_4 /CO_2 = 1/3) with the conditions of open circuit voltage and 0.3 A cm^{-2} at 750℃ after 2000 h operation.

- Increase of current density

→Decrease of hydrogen and carbon monoxide
→Methane did not decrease.

- Hydrogen and carbon monoxide →Fuel species for eletrochemical reaction

- Methane was not used for eletrochemical reaction.

Conclusions

- Investigation of temperature dependence
  →Methane conversion for DICDR at 750˚C→Sufficient,
  at 700 and 650˚C →Incomplete

- Investigation of the dependence of fuel conditions
  ECDR ≒ DICDR (CH_4/CO_2 = 1/4, 1/3, 1/2) at 750˚C→ Methane conversions is sufficient

- The durability test of DICDR operation at 750˚C → Stable cell performance

- Results of gas analysis
  The deviation from equilibrium value of CH_4 conversion : 750˚C < 700˚C < 650˚C
  At 750˚C : Methane →Hydrogen, Carbon monoxide
  Hydrogen, Carbon monoxide, not Methane → Fuel species for eletrochemical oxidation reaction

- It is concluded that DICDR operation is strongly influenced by the operation temperature, and that carbon dioxide reforming attained sufficient level of conversion for long-term power generation with methane to carbon dioxide ratios being 1/4, 1/3, 1/2 at 750˚C on Ni-ceria-based oxide cermet anode of practical size SOFCs.

Comparison between steam reforming and carbon dioxide reforming

Steam reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$	(1)
Carbon dioxide reforming	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	(2)

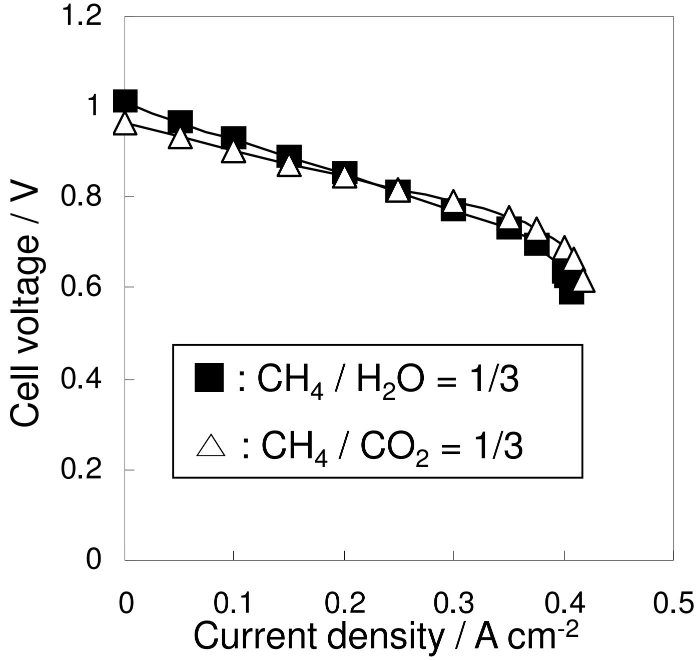


Figure 1. The comparison of *I-V* characteristics for a single cell between direct internal steam-reformed methane (CH_4 /H_2O = 1/3) and carbon dioxide-reformed methane (CH_4 /CO_2 = 1/3) at 750˚C.

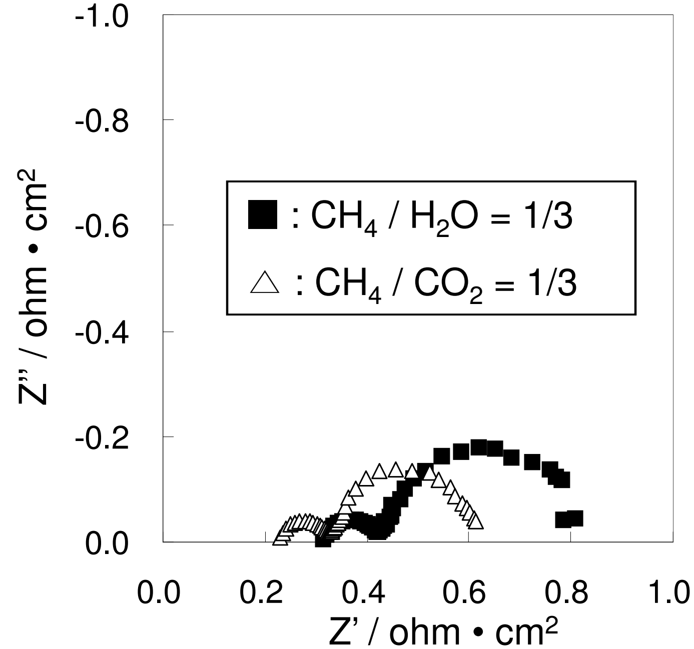
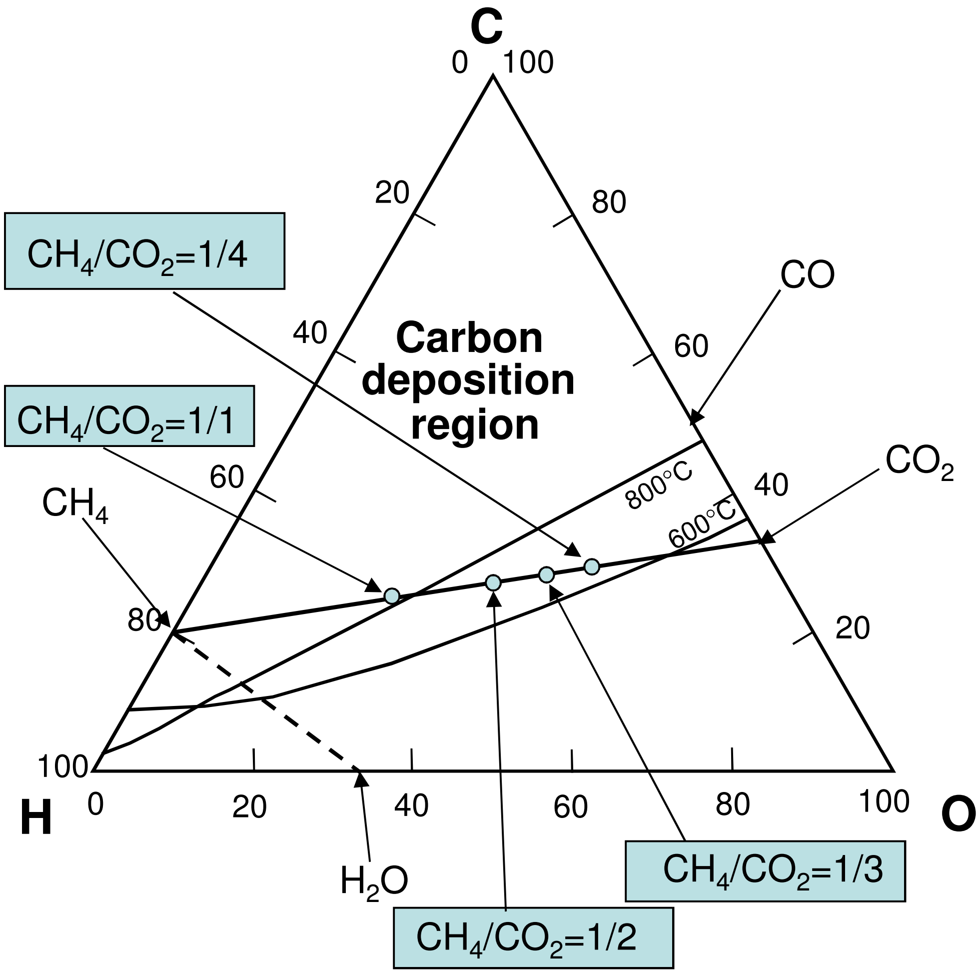


Figure 2. The comparison of impedance spectra for a single cell between direct internal steam-reformed methane (CH_4 /H_2O = 1/3) and carbon dioxide-reformed methane (CH_4 /CO_2 = 1/3) with the discharged conditions of 0.3 A cm^{-2} at 750˚C.

- Cell performance : carbon dioxide reforming ≒ steam reforming
- Carbon dioxide operation is considered to be useful for practical size Ni-SDC anode.

Carbon deposition region with thermodynamic calculation



Carbon dioxide reforming reaction

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H^0_{298} = 247 \text{ kJ mol}^{-1}$$

Steam reforming reaction

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H^0_{298} = 206 \text{ kJ mol}^{-1}$$

The other reaction

- Shift reaction

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^0_{298} = -41 \text{ kJ mol}^{-1}$$

- Carbon deposition reaction

$$CH_4 \rightarrow C + 2H_2 \qquad \Delta H^0_{298} = 75 \text{ kJ mol}^{-1}$$

$$2CO \rightarrow C + CO_2 \qquad \Delta H^0_{298} = -173 \text{ kJ mol}^{-1}$$

Figure Equilibrium diagram of the region for carbon deposition at 600-800ºC with 1 atm for the various kinds of hydrocarbon fuels.