PARTIAL OXIDATION REFORMING OF DRY DIESEL OIL, DIMETHYL-ETHER AND METHANE USING SOFC

Masayuki Dokiya, Masaaki Ubukata, Takuya Kikuchi,
Yokohama National University,
79-7 Tokiwadai, Hodogaya, Yokohama 240-8501, Japan
Lan Tuong Nguyen and Toru Kato
National Institute of Advanced Industrial Science and Technology,
1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan
Iwao Anzai
Nippon Oil Corporation
8, Chidori-cho, Naka-Ku, Yokohama, 231-0815, Japan

INTRODUCTION

Thus far, we proposed (1,2,3) "SOFC Reformer", in which we introduce coal, diesel oil, gasoline, or natural gas, and so forth without large amount of accompanied steam into hot-stand-by SOFC. The concept is schematically shown in **Fig.1**.There occurs

(1) Cracking/H_2 production, then
(2) Electrochemical oxidation of deposited carbon, and hydrogen
(3) Steam reforming by produced H_2O/CO_2 will follows.

Such a system will contribute quick and simple reforming system for automobile fuel cell system and so forth. This system can be said a partial oxidation by SOFC that separates oxygen from air.

Thus far, we had shown that (2,3)

(1) Fe or V anode is tolerable for such a carbon depositing condition, whereas Ni loses its activity quickly.
(2) The deposited carbon can be electrochemically oxidized by Fe-Ni and V-Ni anodes.
(3) The reforming of deposited carbon can be enhanced by steam or CO_2 produced in site.
(4) The 140h and 50h operation were carried out for dry methane and diesel oil.
(5) Especially in the case of CH_4, no remaining carbon was observed after reaction. This suggests the accumulation of deposited carbon can be avoided

In this paper, we summarize the results obtained thus far, and discussed the direction of further improvements.

EXPERIMENTAL

Cell Construction: As electrolyte tubes, commercially available 8mol% YSZ tubes were used. For anodes, Fe_2O_3-NiO-SSZ (Sc stabilized zirconia), or V_2O_5-SSZ or V_2O_5-NiO-SSZ was painted inside or outside YSZ tubes and sintered for 2h at 1300℃ in air or in H_2 (V cases). For cathodes, Pt(14%)-YSZ was painted and sintered for 15min at 1200℃.

Reactions: Dry methane, dimethyl-ether or diesel oil was introduced into SOFC cells through a gas line or through a micro-injector, respectively. The outlet gas was analyzed with two gas chromatographs. The produced steam was estimated from mass balance between current and detected gas. The resistance of cell was analyzed by complex impedance.

RESULTS AND DISCUSSION

Table 1 shows examples of reactions**.** The results can be summarized as follows.

(1) At the present experimental conditions, Fe showed higher activity than V, especially toward carbon.
(2) CO production rate was lower than H_2O production rate. This suggests that the electrochemical oxidation of H_2 is faster than that of carbon, and the produced H_2O reacted toward carbon.
(3) Over-all reactivity was strongly regulated by reaction temperatures. See Cell B from 900℃ to 700℃.
(4) The over-all rate was determined by the thickness of electrolyte. This suggests that the O^{2-} flux is one of essential factors of this system. See the case of cell A, difference of fuels.

Direction of improvement will be,

(1) Both anode and cathode should be improved.
(2) Thin electrolyte of faster electrolyte, such as Lanthanum Galate or SSZ should be examined.
(3) If producible current density, in other words, reaction rate, can be improved further, electricity also can be co-produced.

REFERENCES

1) M.Dokiya et al., Proc.3rd SOFC, Honolulu, p918-925, (1993), The Electrochem. Soc.
2) M.Dokiya et al., Intl.Fuel Cell Conf., Nagoya, p395-398, NEDO (2000)
3) M.Dokiya et al., Intl.Symp.on Fuel Cells for Vehicles, Nagoya, p26-36, The Committee of battery tech., The Electrochem. Soc. Japan (2000)

Table 1. Example of Reactions (Diesel oil 25 μl/min, CH4 50ml/min, DME 5ml/min) (Cell A; t 0.5mm, Φ 20mm, Cell B; t 1mm, Φ10mm, L 40mm) (I; shunt current, mA/cm^2)

Anode Cell type	Outlet Gas/%	Temp/℃, Fuel I; mA/cm^2
Fe-Ni Cell A	CH_4; 5, H_2; 85, CO;10	850℃, Diesel 40mA/cm^2
Fe-Ni Cell A	CH_4; 5, H_2;38, CO; 3 H_2O; 44, Ar;10	700℃, Diesel 40mA/cm^2
Fe-Ni Cell A	CH_4; 8, H_2;30, CO; 10 H_2O; 50, CO_2; 2	700℃, DME 40mA/cm^2
Fe-Ni Cell A	CH_4; 60, H_2; 4, CO; 3 H_2O; 30, CO_2; 2	700℃, CH_4 40mA/cm^2
Fe-Ni Cell B	CH_4;58, H_2;18, CO; 5 H_2O; 19,	900℃, CH_4 120mA/cm^2
Fe-Ni Cell B	CH_4; 86, H_2; 2, CO; 2 H_2O; 10	800℃, CH_4 20mA/cm^2
Fe-Ni Cell B	CH_4;98, H_2;tr, CO; 2	700℃, CH_4 7mA/cm^2
V-Ni Cell B	CH_4;27, H_2;38, CO; 2 H_2O; 13	1000℃, CH_4 50mA/cm^2
V Cell B	CH_4;48, H_2;35, CO; 1 H_2O; 16	1000℃, CH_4 24mA/cm^2
V Cell B	CH_4;15, H_2;52, CO; 1 H_2O; 32	1000℃, Diesel 85mA/cm^2

Fig.1 Concept of SOFC Reformer