

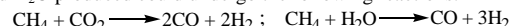
## ■ Mechanism of the Methane Electrochemical Oxidation and Reforming on Cu and Ni Anode Catalysts in SOFC

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### Introduction

The solid oxide fuel cell (SOFC) has shown significant advantages over other types of fuel cells because of its ability to directly electrochemically oxidize hydrocarbons to produce electricity. The direct use of hydrocarbons as the feed to the SOFC will allow elimination of the reformer, simplifying the SOFC system and decreasing the system cost [1].

The first reaction step in the direct CH<sub>4</sub> SOFCs is  $\text{CH}_4 + 4\text{O}^{2-} \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 8\text{e}^-$ . CO<sub>2</sub> and H<sub>2</sub>O produced could undergo the following reactions:



The occurrence of these reforming reactions on the anode could further influence the overall performance of the direct CH<sub>4</sub> SOFC. A better understanding of the direct CH<sub>4</sub> SOFC reaction mechanisms could assist in the design of highly efficient SOFCs. This paper reports results of a mechanistic study of the direct CH<sub>4</sub> reaction and its related reactions on Cu and Ni anode catalysts using transient techniques.

### Materials and Methods

The SOFC used for this study consisted of YSZ (Yttrium stabilized Zirconia) as an electrolyte (150 μm), and 50:50 wt% LSM/YSZ (Lanthanum Strontium Manganite) as a cathode (25 μm). Cu/SDC/YSZ anode (110 μm) was prepared by the impregnation of Cu, Ce, and Sm nitrates concurrently into the porous YSZ and subsequent firing at 750 °C; 50:50 wt% Ni/YSZ anode was prepared by sintering of physical mixed NiO and YSZ powder at 1400 °C and reducing at 750 °C. The bilayer of dense and porous YSZ layer for the preparation of Cu/SDC/YSZ anode was fabricated by reducing a co-pressed bilayer disk of YSZ and 50:50 wt% NiO/YSZ and then leaching Ni out by nitric acid [2].

Steady state flows of H<sub>2</sub>, CH<sub>4</sub>, and 3 vol% D<sub>2</sub>O/CH<sub>4</sub> were admitted into the SOFC separately for determining their performances at 750 °C. The transient study was carried out by (i) step switch of the flow from CH<sub>4</sub> to D<sub>2</sub>O/CH<sub>4</sub> and (ii) pulse of CH<sub>4</sub> and D<sub>2</sub>O/CH<sub>4</sub> into the Ar flow.

### Results and Discussion

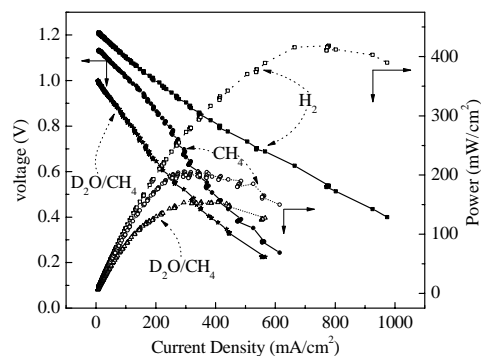
Figure 1 shows the results of the Cu/SDC anode performance. The maximum current and power densities generated by this SOFC were 0.97 A/cm<sup>2</sup> at 0.40 V and 418 mW/cm<sup>2</sup> for H<sub>2</sub>, 0.61 A/cm<sup>2</sup> at 0.24 V and 205 mW/cm<sup>2</sup> for dry CH<sub>4</sub>, and 0.56 A/cm<sup>2</sup> at 0.23 V and 157 mW/cm<sup>2</sup> for CH<sub>4</sub> with 3 vol% D<sub>2</sub>O. The addition of D<sub>2</sub>O into the CH<sub>4</sub> flow further decreased the both maximum current and power densities of the SOFC.

Figure 2 shows the normalized MS and current/voltage responses resulted from step switching of the flow from CH<sub>4</sub> to Ar into the SOFC. The step switch resulted in a sudden termination of the CH<sub>4</sub> fuel, causing decreases in MS profiles of CH<sub>4</sub>, H<sub>2</sub>, CO<sub>2</sub>, and CO as well as the

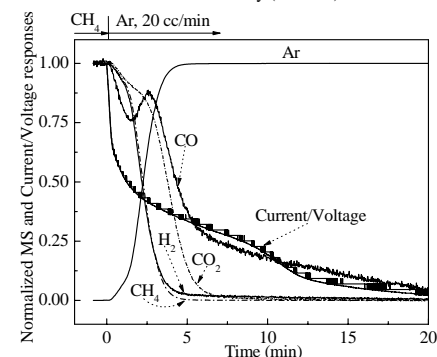
current/voltage responses. The initial rapid drop in the current/voltage responses corresponds to the decrease in H<sub>2</sub>; the latter trailing of the current/voltage responses appears to relate to the gradual decline in CO<sub>2</sub> and CO concentrations. The results suggest that electrochemical oxidation of methane involves with the oxidation of hydrogen and then the oxidation of carbon; the rate of electrochemical oxidation of hydrogen is higher than that of carbon in CH<sub>4</sub>. In this paper, we will further discuss the reaction pathways elucidated from results of the electrochemical oxidations of hydrogen and methane as well as the CH<sub>4</sub> reforming reactions with CO<sub>2</sub> and H<sub>2</sub>O on both Cu and Ni anode catalysts.

### Significance

The reaction mechanism elucidated from this study could assist in the design of highly efficient direct HC SOFCs.



**Figure 1:** SOFC performances with H<sub>2</sub>, CH<sub>4</sub>, and D<sub>2</sub>O/CH<sub>4</sub> as fuels at 750 °C.



**Figure 2:** Normalized MS and current/voltage responses to the step switch from CH<sub>4</sub> to Ar into SOFC at 750 °C.

### References

1. Chuang, S.S.C. in "Catalysis of solid oxide fuel cells", Catalysis, Vol. 18, pp. 186, Spivey, J.J., Roberts, G.W., The Royal Society of Chemistry, 2005.
2. McIntosh, S., Gorte, R.J., *Chem. Rev.* 4845, 104 (2004).