

# Characterization of a $\text{Cu}_{0.8}\text{Ni}_{0.2}\text{-CeO}_2\text{-YSZ}$ Anode-Composite for the Direct Oxidation of Dry Methane

C. Lu<sup>a</sup>, W. L. Worrell<sup>a</sup>, H. Kim<sup>b</sup>, R. J. Gorte<sup>b</sup> and J. M. Vohs<sup>b</sup>

<sup>a</sup>Department of Materials Science and Engineering

<sup>b</sup>and Chemical Engineering,

University of Pennsylvania, PA 19104 – 6272, USA

## Introduction

A  $\text{Cu}_{0.8}\text{Ni}_{0.2}$  anode-composite has been used with dry  $\text{CH}_4$  fuel at  $800^\circ\text{C}$  (1), but reactions within the anode-composite have not been characterized. Electrochemical impedance spectroscopy (EIS) has been used extensively to characterize electrode reactions in SOFCs (2, 3). In this paper we report the use of EIS to examine the behavior of a  $\text{Cu}_{0.8}\text{Ni}_{0.2}$  anode-composite in dry  $\text{CH}_4$  at  $800^\circ\text{C}$ .

## Experimental

The cell preparation is described elsewhere (1). The exact composition of the  $\text{Cu}_{0.8}\text{Ni}_{0.2}$  anode-composite is  $(\text{Cu}_{0.8}\text{Ni}_{0.2})_{15.4\%}\text{-}(\text{CeO}_2)_{7.7\%}\text{-YSZ}_{76.9\%}$  (wt%). The electrochemical cell has a  $\sim 40$  micron YSZ electrolyte, and a YSZ-LSM (50:50 wt%) cathode-composite. Platinum and gold current collectors are attached to the cathode and anode using Pt and inks.

The cell is heated to  $700^\circ\text{C}$  in  $\text{H}_2$  and held for 2 hours. After replacing  $\text{H}_2$  with dry  $\text{CH}_4$ , the temperature is raised to  $800^\circ\text{C}$ . The current density vs. voltage curves (I-V) and impedance spectra are determined at different times. Seven days after the introduction of  $\text{CH}_4$  into the composite anode, the current collector wires are disconnected, and a gas mixture of 5%  $\text{CO}$  and 95%  $\text{CO}_2$  flows through the anode for three hours. Dry  $\text{CH}_4$  is then reintroduced for more impedance measurements to investigate carbon formation inside the anode-composite environment.

## Results and Discussion

Fig. 1 displays the I-V curves of the  $\text{Cu}_{0.8}\text{Ni}_{0.2}$  anode-composite SOFC. The maximum cell power density increases from  $8.6\text{mW}/\text{cm}^2$  to  $137\text{mW}/\text{cm}^2$  with time, due to the decreasing total cell resistance indicated in the corresponding impedance spectra (Fig. 2).

The model depicted in Fig. 3 is proposed to explain the cell ohmic-resistance drop shown in Fig. 2. The  $\text{Cu}_{0.8}\text{Ni}_{0.2}$  anode-composite could have a significant ohmic resistance if the impregnated alloy particles are not well connected. And the deposited carbon could increase the electrical conductivity in the anode-composite by creating electronic-conduction paths between the initially isolated alloy particles. As a consequence, the ohmic resistance will decrease.

A fixed mixed-gas (5 vol%  $\text{CO}$  and 95 vol%  $\text{CO}_2$ ) environment has been established in the anode-composite chamber to test this model. Thermodynamic-calculations indicate that this atmosphere will oxidize the carbon without the oxidation of copper or nickel in the alloy. After exposing the anode-composite to the mixed gas for 3 hrs, dry  $\text{CH}_4$  is then reintroduced. Then impedance spectra are measured again after 32 hrs in the flowing  $\text{CH}_4$ , as shown in Fig. 4c. The cell ohmic resistance of  $\sim 4\text{ ohm}\cdot\text{cm}^2$  return its previous value of  $\sim 4.1\text{ ohm}\cdot\text{cm}^2$  (curve (a)). These results indicate that carbon formation takes place in our anode-composite in a flowing dry  $\text{CH}_4$  environment, and it can improve the electrical conductivity of the anode-composite and decreases the ohmic resistance of the cell.

## Conclusions

The behavior of a novel  $\text{Cu}_{0.8}\text{Ni}_{0.2}$  anode-composite in a SOFC using dry  $\text{CH}_4$  at  $800^\circ\text{C}$  has been investigated. The cell current and power density improved during a 7-day operation due to an observed decrease in total cell resistance. Impedance spectra show a shape change, with the high-frequency arc diminishing. The low-frequency arcs gradually dominate the impedance spectra, indicating that the ohmic resistance of the cell decreases. A model involving carbon deposition inside the anode-composite is proposed to explain these variations of

ohmic resistance.

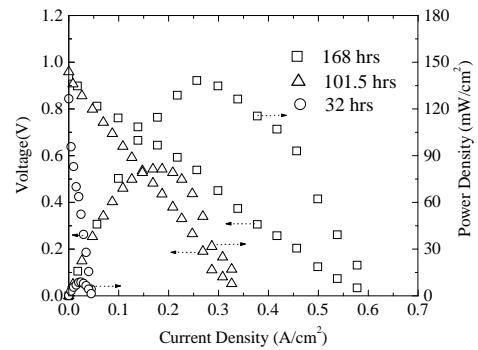


Fig. 1. Variation of I-V and power density of the anode-composite SOFC in dry  $\text{CH}_4$  at  $800^\circ\text{C}$ .

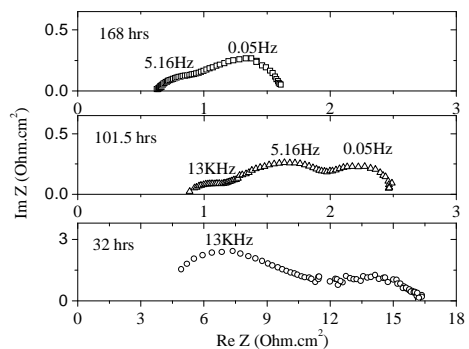


Fig. 2. Corresponding impedance spectra change of the anode-composite SOFC in dry  $\text{CH}_4$  at  $800^\circ\text{C}$ .

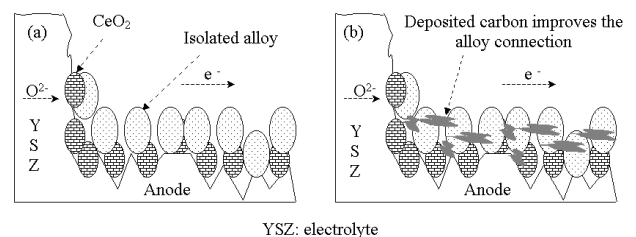


Fig. 3. Schematic pictures of the porous anode-composite (a) before and (b) after introduction of  $\text{CH}_4$  at  $800^\circ\text{C}$ .

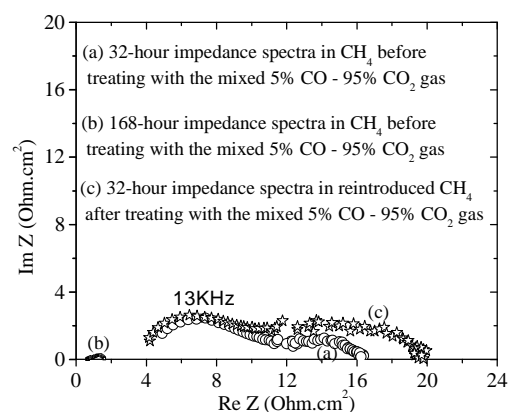


Fig. 4. Impedance spectra change of the anode-composite SOFC in dry  $\text{CH}_4$  at  $800^\circ\text{C}$  before and after treating the anode-composite with 5%  $\text{CO}$ -95%  $\text{CO}_2$  mixed gas.

## Acknowledgement

The financial support of the U. S. Office of Naval Research is gratefully acknowledged.

## References

1. H. Kim, C. Lu, W. L. Worrell, J. M. Vohs and R. J. Gorte, accepted by *J. Electrochem. Soc.*
2. T. Tsai and S. A. Barnett, *J. Electrochem. Soc.* **145**, 1696-1701(1998).
3. M. Brown, S. Primdahl and M. Mogensen, *J. Electrochem. Soc.*, **147**, 475-485(2000).