

Transient studies of perovskite anode catalyst for a direct CH₄ Solid Oxide Fuel Cell

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Introduction:

The direct use of CH₄ as the feed to the solid oxide fuel cell (SOFC) will allow elimination of a reformer, simplifying the SOFC system and decreasing the system cost [1]. The overall reaction on the anode catalyst in the direct CH₄ SOFC is the electrochemical oxidation of CH₄: $\text{CH}_4 + 4\text{O}^{2-} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 8\text{e}^-$. Due to the nature of hydrocarbon reactions at high temperature and the reducing environment of the anode chamber, an effective anode catalyst must possess oxidation activity, thermal stability, and coking resistance. Perovskites have shown the ability to oxidize CH₄ while inhibiting catalyst coking [3]. The objective of this study is to investigate the catalytic reaction pathway of CH₄ on a Ni anode-supported SOFC promoted with lanthanum strontium cobalt ferrite (LSCF) perovskite using transient techniques. The Ni anode-supported SOFC is selected for this study because of its robustness under SOFC operating conditions and potential for improving its coking resistance. A fundamental understanding of the reaction pathway on LSCF-promoted Ni/YSZ anodes will allow fine-tune the composition of the anode catalyst for effective use of CH₄ and natural gas for electric power generation.

Materials and Methods:

The electrolyte disk consists of YSZ powder (Tosoh, TZ-8Y) co-axially pressed and sintered at 1450 °C to form a 100 μm thick electrolyte disk. The 25 μm LSCF/YSZ anode and 10 μm LSM/YSZ cathode were applied in a 1:1 weight ratio. Current collectors consist of Pt screens and Pt wires which were adhering onto on the anode and cathode surfaces with platinum paste (Engelhard, A3788A). The electrolyte-supported cell was attached to a ceramic tube for testing.

The anode-supported SOFC consists of a 20 μm Yttria-Stabilized Zirconia (YSZ) electrolyte layer, a 10 μm Ni/YSZ interlayer anode, a 1 mm Ni/YSZ anode, a 25 μm thick LSM/YSZ cathode, and a 25 μm LSM cathode current collector [4]. LSCF was screen printed on to the sintered SOFC anode and heated to 1100 °C.

Testing of the electrolyte and anode-supported SOFC was carried out by heating to 800 °C in flowing H₂. Ar was flown to purge the system before introduction of CH₄. Transient studies were carried out by step switching the inlet flow using a 4-port valve while monitoring the gas effluent responses by a mass spectrometer and the current/voltage response by a Solartron 7400E. Impedance measurements were conducted during steady state operation of the SOFC. XRD and SEM with EDS were used to characterize the anode after testing of SOFC.

Results and Discussion:

LSCF has been tested as the anode on an electrolyte-support SOFC. Fig. 1 illustrates the transient profiles (i.e. responses) of the concentration of the gaseous species in the SOFC effluent, current and voltage resulting from a step switch of the inlet flow from Ar to CH₄ at a constant external load of 2 ohms. Fig. 1 (i) shows Ar and CH₄ curves crossed at the normalized value of 0.5, indicating that a near perfect switch of the inlet flow Ar to CH₄ was achieved. Fig. 1 (ii) shows that the H₂ response led that of CO₂ and CO, giving higher

concentration of H₂ than that of CO₂ and CO from the SOFC effluent. CO₂ emerged before CO suggesting that both CO₂ and CO are produced from a parallel reaction pathway: $\text{C} + 2\text{O}^{2-} \rightarrow \text{CO}_2$; $\text{C} + \text{O}^{2-} \rightarrow \text{CO}$, where the intrinsic rate constant is higher for the formation of CO₂ than that of CO. Fig. 1 (iii) shows the initial sharp current and voltage response followed by a gradual rise to a steady state value.

These results indicate LSCF is catalytically active towards electrochemical oxidation of CH₄ in the SOFC anode environment. This paper will present similarities and differences of the CH₄ reaction pathway on the electrolyte-supported SOFC with a LSCF anode and a Ni/YSZ anode-support SOFC with LSCF layer with detailed characterization of the structure and composition of the anode catalysts.

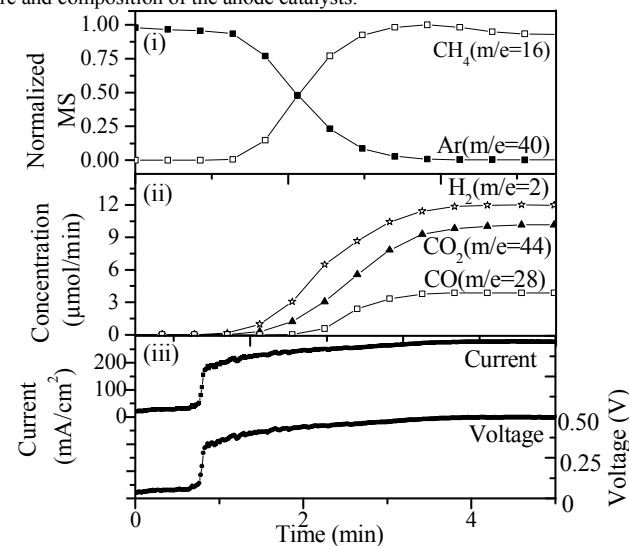


Fig. 1: Product and performance analysis during CH₄ introduction to the SOFC. (□) methane; (■) argon; (□) carbon dioxide; (▲) carbon monoxide; (☆) hydrogen.

Significance:

The direct CH₄ SOFC eliminates the need for the external reforming process, significantly simplifying the overall fuel cell system. The mechanistic information obtained from this transient study could guide the development of an effective anode catalyst for the direct CH₄ SOFC.

References:

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