

Isotopic Transient Studies of CH₄ and C₃H₆ Reaction Pathways in Solid Oxide Fuel Cells

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Introduction

Isotopic transient technique is a powerful technique for determining the mechanisms of heterogeneously catalyzed reactions. The salient feature of this technique is to perturb the concentration of reactants or their isotopic counterparts, and then monitoring their product response. In the direct hydrocarbon (HC) solid oxide fuel, the catalytic electrochemical oxidation of HC fuels occurs on the anode catalyst surface, producing electricity and CO₂/H₂O. A fundamental understanding of the electrochemical oxidation pathways and the rate-determining step could assist in design of highly effective catalysts for the direct HC SOFC. The objective of this study is to investigate mechanisms of electrochemical oxidation CH₄ and C₃H₆ on a novel lanthanum strontium cobalt ferrite (LSCF) perovskite anode catalyst in SOFC by step and pulse transient techniques.

Materials and Methods

The electrolyte-supported SOFC consists of a 200 μm YSZ (Yttria-Stabilized Zirconia) electrolyte layer, an 50 μm thick anode of LSCF/YSZ, and a 25 μm thick LSM/YSZ cathode, and a 25 μm pure LSM cathode current collector. Both the cathode and anode are then attached Pt grid for current collection. The SOFC disc was adhered to a zirconia tube to form a SOFC reactor with an inlet for supplying the reactant flow and an outlet for an effluent steam.

Transient studies were carried out by (i) step-switching the inlet flow from Ar to hydrocarbon and (ii) pulsing a known amount of hydrocarbon or isotope labeled reactants into a steady state Ar flow under both closed and open circuit modes. The former allows oxygen anion to diffuse across the membrane, providing sufficient amount of oxygen anion on the anode catalyst while the latter limits the amount of oxygen anion for the electrochemical oxidation. The transient responses of the reaction products and current/voltage were determined by mass spectrometer and a Labview data acquisition system, respectively.

Results and Discussion

Figure 1 shows the typical transient responses of reaction products and current/voltage during a step switch of the flow from CH₄ to Ar. Termination of the CH₄ flow by step switch caused an immediate decrease in MS profiles of all of gaseous reactants/products as well as current/voltage. Following an initial decline, the CO₂ profile showed an increase and then decrease again, indicating that CO₂ formation could be inhibited by the presence of CH₄. CO exhibited a rapid decline followed by a gradual decrease. Between 9 and 30 min, the gradual decrease in CO and CO₂ profiles is in line with the decline in current/voltage, suggesting that the low level of the current/voltage produced during this

time period is a result of electrochemical oxidation of carbon. This is in contrast to the initial rapid decline in current/voltage and CH₄/H₂ MS profiles. This rapid depletion of H₂ can be explained by the high reactivity of H₂ toward electrochemical oxidation. The proposed reaction pathways for CH₄ are listed below:

1. CH₄ → *C + 4*H *C: adsorbed carbon; *H: adsorbed hydrogen
2. 2 *H + O²⁻ → H₂O + 2e⁻
3. *C + 2 O²⁻ → CO₂ + 4e⁻

CO₂ and H₂O produced from the above reactions can further react with CH₄ through the reforming processes. These reforming reaction processes play a significant role in controlling the overall performance of the direct CH₄ and C₃H₆ fuel cell because they are highly endothermic and are able to further produce H₂ and CO. We have further determined the role of reforming reaction in the direct CH₄ and C₃H₆ SOFC reactions by pulsing ¹³CO₂, D₂O, and H₂¹⁸O into the steady state CH₄ and C₃H₆ flow. The paper will present the results of transient study and elucidate the CH₄ and C₃H₆ reaction pathways on the LSCF anode.

Significance

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

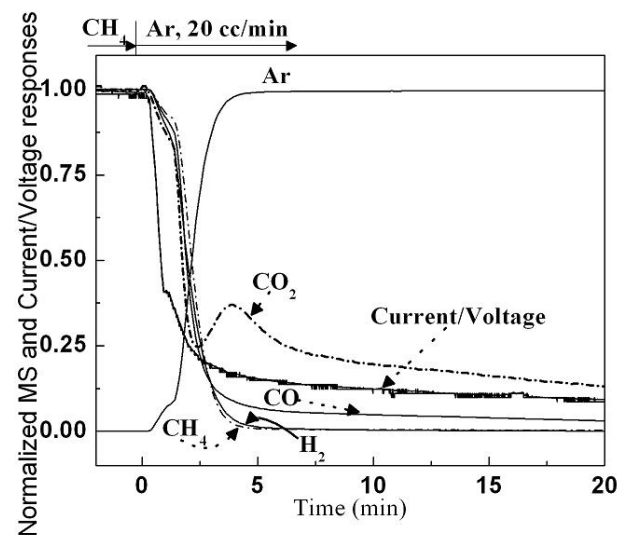


Figure 1. Transient responses of CH₄, gaseous products, and current/voltage during the step switch of the flow from CH₄ to argon.