

Solid Oxide Fuel Cells for Energy Recovery from Light Hydrocarbons

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Abstract

Solid-oxide fuel cells (SOFC's) offer significant potential for efficiently capturing energy from light hydrocarbons streams derived from petroleum extraction and/or processing. To date, however, development of SOFC's for large-scale applications with hydrocarbons have not come to fruition due to concerns about the long-term stability of conventional Ni-YSZ SOFC anode materials. This study is a multi-scale effort to explore the effectiveness of SOFC anodes operating either on reformat derived from light hydrocarbons or on light hydrocarbons directly. Anode-supported solid oxide fuel cells (SOFCs) utilizing Ni-CeO₂-YSZ composite anode architectures were fabricated and tested on hydrogen and syngas fuel feeds to evaluate the effect of adding ceria on the effectiveness on Ni-based anodes on operating with these carbonaceous fuels. These studies are being combined with detailed SOFC modeling to develop an understanding of the kinetic behavior of Ni and CeO₂ for stable operation with carbonaceous fuel feeds in composite anode materials. These studies are providing the basis for developing models for assessing the behavior of SOFC electrochemical cells for larger-scale applications with the hope that further progress can be made on SOFC anode design for stable operation in future large-scale applications for petroleum processing and other applications.

1. Introduction

Solid oxide fuel cells (SOFC's) have been under development for small-scale operation with hydrocarbons by numerous research and development groups [1-3], but concerns about anode durability [4, 5] and carbonaceous deposits with hydrocarbon feeds [6] have caused developers to shy away from large-scale applications above a few 100 kW. This hesitancy to develop large scales has called for further fundamental studies as the one discussed here on SOFC anode designs that provide a basis for developing SOFC approaches that will work well for operation with hydrocarbons – either with fuel pre-reforming to convert the hydrocarbon to syngas [7, 8] or with direct injection of hydrocarbon fuels [3, 9]. Anode designs that provide stable SOFC operation with hydrocarbon fuels will provide the basis for future development and eventual introduction of systems for larger MW-scale applications. One such application includes the use of off-gases from oil recovery as well as light gases from petroleum processing for electrical conversion and subsequent CO₂ sequestration. SOFC's separate oxidation products (CO₂ and H₂O) from the air stream and thus provide ideal systems to produce electrical energy from hydrocarbons and provide concentrated streams for reinjection into oil reservoirs or other sequestration sites.

To explore the effectiveness of different anode microstructures on SOFC operation, this work has been investigating different anode fabrication strategies and microstructures for operating with a model light hydrocarbon (n-butane) typical of naphtha or with a reformat stream derived from light hydrocarbon reforming. These tests are complemented by modeling studies of SOFC performance to explore a broad range of conditions characteristic of what might be expected over the range of conditions in a larger-scale SOFC system. These experimental and modeling efforts provide a fundamental basis for exploring the larger scale system approaches which may provide a means for energy-efficient and environmentally responsible means of processing light hydrocarbons produces in petroleum recovery and processing.

2. Experimental Studies

Because typical Ni-YSZ anodes implemented for small-scale SOFC applications are known to be troubled with carbon deposit build-up [6] during operation with hydrocarbon feeds, this work has explored alternative anode compositions and has identified Ni/CeO₂/YSZ composites as a promising approach to providing high-power density performance. This composite is motivated by the high power density of Ni electrocatalysts and the tendency for CeO₂ for suppressing carbon deposition [10]. Tests were performed on a range of syngas compositions characteristics of different conversions (of H₂ and CO) down an SOFC anode channel. The 0% conversion was derived from equilibrium conversion of butane/steam mixtures

with a 1.5 steam to carbon ratio. These results were compared with SOFC performance of a direct butane/steam mixture (also with a 1.5 steam to carbon) ratio. Results are highlighted in Figure 1 which shows single cell power densities ($V_{cell} \cdot i$) up to 0.6 W/cm^2 on syngas and up to 0.35 W/cm^2 on butane at $800 \text{ }^\circ\text{C}$. Butane has not been tested for different conversions in the same way that syngas has been tested because it is expected that substantial internal reforming inside an SOFC channel flow path will cause a large fraction of the butane to be transformed into syngas [11]. Thus, for such hydrocarbon feeds down the channel conversion will consist of substantial syngas formation and hopefully minimal carbon deposits with properly designed anode microarchitectures and materials. These results and others like it are providing the basis for evaluating expected power densities and efficiencies (a function of V_{cell}) for SOFC system models to be developed for large-scale system analysis.

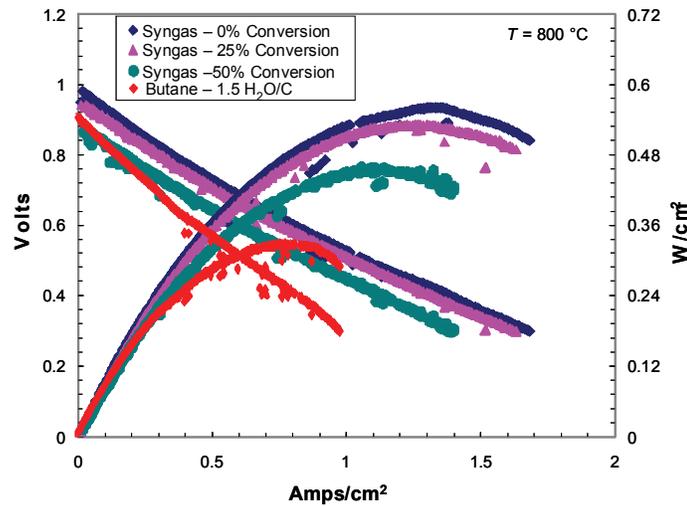


Figure 1. Voltage and power density vs. current density for co-fired Ni/CeO₂/YSZ anode-supported MEA's operating at $T_{cell} = 800 \text{ }^\circ\text{C}$ on n-butane with steam and on a range of syngas compositions at various locations along an SOFC channel (representing different total fuel conversions).

3. Modeling Studies

Modeling efforts of typical SOFC performance have been ongoing to explore the effects of SOFC architectures on performance for the range of fuels of interest. To date the models have been employing detailed Ni and YSZ chemistry for fuels up to CH₄ as developed by this effort [12] and that of others [13]. Example results of local SOFC performance on syngas are shown in Figure 2 for a range of syngas conversions for this sample anode architecture. The results for this SOFC architecture indicate that up to 60% conversion, power densities at typical V_{cell} SOFC operating regimes (0.65-0.75 V/cell) only drop by

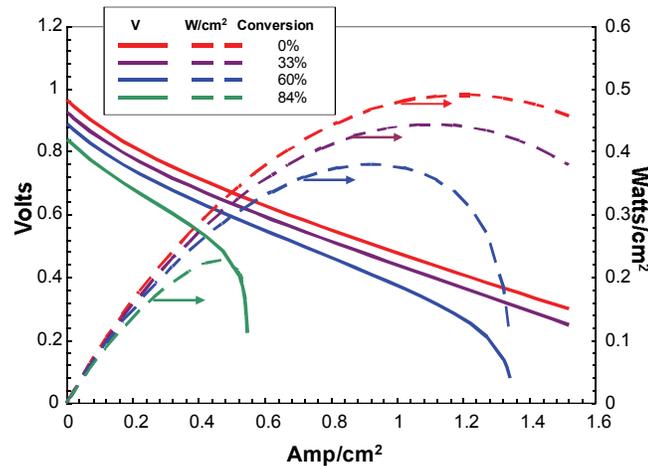


Figure 2. Example simulation results of local SOFC performance for an Ni-based anode-supported cell with a thin YSZ electrolyte and an LSM/YSZ cathode. Operating conditions are $800 \text{ }^\circ\text{C}$.

30%. However, at 84% conversion, single cell power density drops off dramatically particularly because of the low concentration of reactants and the associated increases in both transport and activation losses. Results from the 1-D model provide a basis for assessing how much conversion can be tolerated for a constant voltage cell operation before significant penalties would be incurred at the downstream end of the cell. The model has been used to predict internal reforming of CH₄ and its effects on SOFC performance, but efforts are still on-going to develop higher hydrocarbon kinetic mechanisms to predict internal reforming of hydrocarbons such as n-butane. The models are being used in down-the-channel models with to explore what is the total fuel conversion that can be expected to be safely achieved with syngas. This is important for assessing how the anode exhaust stream might be processed for subsequent exhaust injection back into underground reservoirs for CO₂ sequestration and enhanced oil recovery.

4. Conclusions

This study is the beginning of a study to assess the potential of SOFC's for large-scale power applications for recovering energy from light hydrocarbons in petroleum recovery and processing. This effort has begun with fundamental studies that have identified promising anode architectures based on Ni/CeO₂/YSZ composites as ideal for running either with hydrocarbon reformates or directly with light hydrocarbons characteristic of naphtha feeds. Models of SOFC performance on a per cell basis provides the background for future larger-scale analysis for systems that may come to fruition in energy-efficient, environmentally responsible applications.

5. References

1. Shao, Z.P., et al., "A thermally self-sustained micro solid-oxide fuel-cell stack with high power density". *Nature*, Vol. 435(7043): 2005. pp. 795-798.
2. Cheekatamarla, P.K., C.M. Finnerty, and J. Cai, "Internal reforming of hydrocarbon fuels in tubular solid oxide fuel cells". *Intl. J. Hydrogen Energy*, Vol. 33(7): 2008. pp. 1853-1858.
3. McIntosh, S. and R.J. Gorte, "Direct hydrocarbon solid oxide fuel cells". *Chemical Reviews*, Vol. 104(10): 2004. pp. 4845-4865.
4. Yokokawa, H., et al., "Fundamental mechanisms limiting solid oxide fuel cell durability". *J. Power Sources*, Vol. 182(2): 2008. pp. 400-412.
5. Kee, R.J., et al., "Solid oxide fuel cells: Operating principles, current challenges, and the role of syngas". *Combustion Science And Technology*, Vol. 180(6): 2008. pp. 1207-1244.
6. Kim, T., et al., "A study of carbon formation and prevention in hydrocarbon-fueled SOFC". *J. Power Sources*, Vol. 155(2): 2006. pp. 231-238.
7. Weber, A., et al., "Oxidation of H₂, CO and methane in SOFCs with Ni/YSZ-cermet anodes". *Solid State Ionics*, Vol. 152: 2002. pp. 543-550.
8. Suresh, A.M., et al., "Electrochemical oxidation of H₂, CO, and CO/H₂ mixtures on patterned Ni anodes on YSZ electrolytes". *J. Electrochemical Society*, Vol. 153(4): 2006. pp. A705-A715.
9. Murray, E.P., et al., "Direct solid oxide fuel cell operation using isooctane". *Electrochemical And Solid State Letters*, Vol. 9(6): 2006. pp. A292-A294.
10. Costa-Nunes, O., R.J. Gorte, and J.M. Vohs, "Comparison of the performance of Cu-CeO₂-YSZ and Ni-YSZ composite SOFC anodes with H₂, CO, and syngas". *J. Power Sources*, Vol. 141(2): 2005. pp. 241-249.
11. Gupta, G.K., et al., "Comparison of conversion and deposit formation of ethanol and butane under SOFC conditions". *J. Power Sources*, Vol. 158(1): 2006. pp. 497-503.
12. DeCaluwe, S.C., et al., "Importance of anode microstructure in modeling solid oxide fuel cells". *Journal Of The Electrochemical Society*, Vol. 155(6): 2008. pp. B538-B546.
13. Janardhanan, V.M., V. Heuveline, and O. Deutschmann, "Performance analysis of a SOFC under direct internal reforming conditions". *J. Power Sources*, Vol. 172(1): 2007. pp. 296-307.

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