Solid Oxide Fuel Cells – Evaluating Performance for Light Hydrocarbons

Gregory S. Jackson[1], Robert A. Walker[2], Prof. Bryan Eichhorn[2], A. Mary Sukeshini[2], Michael B. Pomfret[2], Oktay Demircan[2], Bahman Habibzadeh[1], and Steven Decaluwe[1]

[1]Dept. of Mechanical Engineering, [2]Dept. of Chemistry and Biochemistry
University of Maryland, College Park, MD 20742, USA
gsjackso@eng.umd.edu

1. Introduction

Due to their high temperature operation, solid oxide fuel cells (SOFC's) are being considered for operation with hydrocarbons – either with fuel pre-reforming to convert the hydrocarbon to syngas [1,2] or with direct injection of hydrocarbon fuels [3,4]. The potential for stable SOFC operation with hydrocarbon fuels allows for very high efficiency energy conversion to electrical power for applications ranging from handheld power to large-scale central power plants. Current SOFC anode materials and microstructure however has not been well optimized for direct utilization of hydrocarbons, and thus the University of Maryland (UMD) in collaboration with the Colorado School of Mines, California Institute of Technology, and now The Petroleum Institute are exploring both how anode microstructure and material influence electrochemical oxidation in SOFC's and how anode design can be optimized for operation with hydrocarbon reformate (syngas) and/or with direct hydrocarbon feeds.

Studies of hydrocarbon-fueled SOFC's have often been motivated by portable power applications where liquid hydrocarbon fuels are needed for their high power densities. However, SOFC's also offer a unique opportunity for large-scale systems in conjunction with oil recovery operations. SOFC's operating on light hydrocarbon fractions such as naphtha derived from oil recovery provide a means for providing high-efficiency onsite electrical power with well off-gases. Furthermore, the oxide-ion membrane in the SOFC provides an effective means of producing CO_2 and H_2O product that is separated from N_2 dilution derived from more conventional combustion applications. Thus SOFC systems with hydrocarbon fuel feeds provide concentrated product stream of CO_2 and H_2O that might be used readily for enhanced oil recovery. To understand the potential for improving SOFC's for operation through advanced model development, UMD researchers are using microfabricated anodes with electrochemical characterization, *in situ* and *ex situ* surface spectroscopy, and microkinetic/porous media model development. These tools are being used to explore nickel-based and alternative ceria-based anodes for both pre-reformed and direct hydrocarbon fuel feeds for a wide range of SOFC applications.

2. Key Features

The development of adequately detailed quantitative mechanisms for electrochemical oxidation processes remains a key challenge to developing reliable modeling tools for optimizing SOFC electrode microstructure for operation with hydrocarbons. To this end, the UMD team has been addressing this problem by performing experiments on well-characterized micro-fabricated and thin-film anode architectures to isolate the electrochemistry of both reformate and small hydrocarbon oxidation in SOFC anodes. These patterned and thin-film anodes have also allowed for *in situ* Raman spectroscopy to characterize the electrochemical and fuel reforming processes occurring on the anode surfaces [5] as well as electrochemical characterization as a function of anode geometry and fuel composition [2,6]. Initial studies of H_2-CO mixtures to simulate hydrocarbon reformate electrochemistry on Ni anodes on YSZ electrolytes have the importance of water-gas shift reactions in reducing CO oxidation voltage losses. Further studies using Raman spectroscopy have indicated the dependence of fuel cell operating voltage on the rates of carbon deposit formation and destruction. These findings have been informing the development of modeling tools using microkinetic mechanisms and detailed transport models both at UMD and collaborating institutions to predict the performance of Ni/YSZ architectures for electrochemical oxidation with H_2, CO, and hydrocarbon feeds [7,8].

The extensive work with Ni/YSZ anodes has indicated that solid carbon formation within the anode microstructure is extremely difficult to avoid for direct feeds of hydrocarbons larger than CH_4 without the addition of extensive steam and/or air – either of which reduce the power densities and efficiencies of the SOFC system. Because of this, UMD has been investigating alternative ceria anodes and using thin-film architectures as well as conventional porous architectures to investigate the effectiveness of ceria as an

anode material. Results of H_2 and CO oxidation on thin-film ceria have shown strong coupling between anode morphology and electrochemical oxidation performance. Further testing of ceria anodes with light hydrocarbons (such as n-C_4H_{10}), characteristic of naphtha, has indicated that while minimal carbon deposition does occur with these anodes, the ceria anodes avoid runaway carbon growth characteristic of Ni-based anodes, and in fact, stable operation can be maintained with this system. Efforts are underway to develop microkinetic modeling tools for this system validated by the experimental findings, and it is hoped that these tools can be used to explore SOFC design for optimal performance with light hydrocarbons characteristic of oil-well off-gases.

3. Conclusions

Fundamental experiments in well-defined SOFC anodes are providing critical information for understanding how electrochemical oxidation of hydrocarbon reformate and light hydrocarbons behave in both conventional Ni-based anodes as well as alternative ceria-based anodes. The alternative ceria anodes show promise for mitigating detrimental carbon deposition and thereby allowing for direct hydrocarbon feeds in applications involving the use of off-gases from oil wells. These fundamental experiments are providing the bases for the development of SOFC modeling tools that will explore designs both at the microstructure and systems level for successful implementation of SOFC's for a wide array of applications.

4. References and Bibliography

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Author Biographies

Dr. Greg Jackson is an Associate Professor in Mechanical Engineering at the University of Maryland (UMD), USA, who leads research in fuel cells and catalysis for a wide array of energy conversion processes. He is the Principal Investigator for many fuel cell related research projects at UMD after having spent some time in industry working on advanced catalytic combustion system development.

Dr. Bryan Eichhorn is a Full Professor in the Departments of Chemistry and Biochemistry at UMD and leads efforts on materials development including novel work on nano-architectured catalyst for fuel cell and other applications.

Dr. Rob Walker is an Associate Professor in the Departments of Chemistry and Biochemistry at UMD and is a leading expert on high-temperature spectroscopy for characterizing surfaces for energy conversion devices.

Dr. Mary Sukeshini is a Research Assistant Scientist at UMD, exploring the performance of ceria-based anode architectures for SOFC applications.

Michael Pomfret, **Oktay Demircan**, **Bahman Habibzadeh**, and **Steven DeCaluwe** are all Ph.D. students who are working on hydrocarbon SOFC applications for their Ph.D. dissertations research at UMD.