Advances in Solid Oxide Fuel Cells IX

Ceramic Engineering and Science Proceedings
Volume 34, Issue 4, 2013

Edited by
Narottam P. Bansal
Mihails Kusnezoff

Volume Editors
Soshu Kirihara and Sujanto Widjaja

The American Ceramic Society

WILEY

Advances in Solid Oxide Fuel Cells IX

A Collection of Papers Presented at the 37th International Conference on Advanced Ceramics and Composites
January 27–February 1, 2013
Daytona Beach, Florida

Edited by
Narottam P. Bansal
Mihails Kusnezoff

Volume Editors
Soshu Kirihara
Sujanto Widjaja

The American Ceramic Society

WILEY

Cover Design: Wiley

Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

Library of Congress Cataloging-in-Publication Data is available.

ISBN: 978-1-118-80764-4
ISSN: 0196-6219

Printed in the United States of America.

10 9 8 7 6 5 4 3 2 1

Advances in Solid Oxide Fuel Cells IX

Preface

The tenth international symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science, and Technology was held during the 37th International Conference and Exposition on Advanced Ceramics and Composites in Daytona Beach, FL, January 27 to February 1, 2013. This symposium provided an international forum for scientists, engineers, and technologists to discuss and exchange state-of-the-art ideas, information, and technology on various aspects of solid oxide fuel cells. A total of 85 papers were presented in the form of oral and poster presentations, including twenty invited lectures, indicating strong interest in the scientifically and technologically important field of solid oxide fuel cells. Authors from 22 countries (Austria, Brazil, Bulgaria, Canada, China, Denmark, Egypt, Estonia, France, Germany, India, Italy, Japan, Netherlands, Norway, Portugal, South Korea, Sweden, Switzerland, Taiwan, United Kingdom, and U.S.A.) participated. The speakers represented universities, industries, and government research laboratories.

These proceedings contain contributions on various aspects of solid oxide fuel cells that were discussed at the symposium. Thirteen papers describing the current status of solid oxide fuel cells materials, Science and technology are included in this volume. Each manuscript was peer-reviewed using the American Ceramic Society review process.

The editors wish to extend their gratitude and appreciation to all the authors for their contributions and cooperation, to all the participants and session chairs for their time and efforts, and to all the reviewers for their useful comments and suggestions. Financial support from the American Ceramic Society is gratefully acknowledged. Thanks are due to the staff of the meetings and publications departments of the American Ceramic Society for their invaluable assistance. Advice, help and cooperation of the members of the symposium's international organizing committee (J. S. Chung, Tatsumi Ishihara, Nguyen Minh, Mogens Mogensen, J. Obrien, Prabhakar Singh, Jeffry Stevenson, Toshio Suzuki, and Eric Wachsman) at various stages were instrumental in making this symposium a great success.

We hope that this volume will serve as a valuable reference for the engineers, scientists, researchers and others interested in the materials, science and technology of solid oxide fuel cells.

NAROTTAM P. BANSAL
NASA Glenn Research Center

Mihails Kusnezoff
Fraunhofer IKTS

Introduction

This issue of the Ceramic Engineering and Science Proceedings (CESP) is one of nine issues that has been published based on manuscripts submitted and approved for the proceedings of the 37th International Conference on Advanced Ceramics and Composites (ICACC), held January 27–February 1, 2013 in Daytona Beach, Florida. ICACC is the most prominent international meeting in the area of advanced structural, functional, and nanoscopic ceramics, composites, and other emerging ceramic materials and technologies. This prestigious conference has been organized by The American Ceramic Society's (ACerS) Engineering Ceramics Division (ECD) since 1977.

The 37th ICACC hosted more than 1,000 attendees from 40 countries and approximately 800 presentations. The topics ranged from ceramic nanomaterials to structural reliability of ceramic components which demonstrated the linkage between materials science developments at the atomic level and macro level structural applications. Papers addressed material, model, and component development and investigated the interrelations between the processing, properties, and microstructure of ceramic materials.

The conference was organized into the following 19 symposia and sessions:

Symposium 1	Mechanical Behavior and Performance of Ceramics and Composites
Symposium 2	Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications
Symposium 3	10th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science, and Technology
Symposium 4	Armor Ceramics
Symposium 5	Next Generation Bioceramics
Symposium 6	International Symposium on Ceramics for Electric Energy Generation, Storage, and Distribution
Symposium 7	7th International Symposium on Nanostructured Materials and Nanocomposites: Development and Applications

Symposium 8	7th International Symposium on Advanced Processing & Manufacturing Technologies for Structural & Multifunctional Materials and Systems (APMT)
Symposium 9	Porous Ceramics: Novel Developments and Applications
Symposium 10	Virtual Materials (Computational) Design and Ceramic Genome
Symposium 11	Next Generation Technologies for Innovative Surface Coatings
Symposium 12	Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nanolaminated Ternary Carbides and Nitrides (MAX Phases)
Symposium 13	Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy
Focused Session 1	Geopolymers and Chemically Bonded Ceramics
Focused Session 2	Thermal Management Materials and Technologies
Focused Session 3	Nanomaterials for Sensing Applications
Focused Session 4	Advanced Ceramic Materials and Processing for Photonics and Energy
Special Session	Engineering Ceramics Summit of the Americas
Special Session	2nd Global Young Investigators Forum

The proceedings papers from this conference are published in the below nine issues of the 2013 CESP; Volume 34, Issues 2–10:

- Mechanical Properties and Performance of Engineering Ceramics and Composites VIII, CESP Volume 34, Issue 2 (includes papers from Symposium 1)
- Advanced Ceramic Coatings and Materials for Extreme Environments III, Volume 34, Issue 3 (includes papers from Symposia 2 and 11)
- Advances in Solid Oxide Fuel Cells IX, CESP Volume 34, Issue 4 (includes papers from Symposium 3)
- Advances in Ceramic Armor IX, CESP Volume 34, Issue 5 (includes papers from Symposium 4)
- Advances in Bioceramics and Porous Ceramics VI, CESP Volume 34, Issue 6 (includes papers from Symposia 5 and 9)
- Nanostructured Materials and Nanotechnology VII, CESP Volume 34, Issue 7 (includes papers from Symposium 7 and FS3)
- Advanced Processing and Manufacturing Technologies for Structural and Multi functional Materials VII, CESP Volume 34, Issue 8 (includes papers from Symposium 8)
- Ceramic Materials for Energy Applications III, CESP Volume 34, Issue 9 (includes papers from Symposia 6, 13, and FS4)
- Developments in Strategic Materials and Computational Design IV, CESP Volume 34, Issue 10 (includes papers from Symposium 10 and 12 and from Focused Sessions 1 and 2)

The organization of the Daytona Beach meeting and the publication of these proceedings were possible thanks to the professional staff of ACerS and the tireless dedication of many ECD members. We would especially like to express our sincere thanks to the symposia organizers, session chairs, presenters and conference attendees, for their efforts and enthusiastic participation in the vibrant and cutting-edge conference.

ACerS and the ECD invite you to attend the 38th International Conference on Advanced Ceramics and Composites (http://www.ceramics.org/daytona2014) January 26-31, 2014 in Daytona Beach, Florida.

To purchase additional CESP issues as well as other ceramic publications, visit the ACerS-Wiley Publications home page at www.wiley.com/go/ceramics.

SOSHU KIRIHARA, *Osaka University, Japan*
SUJANTO WIDJAJA, *Corning Incorporated, USA*

Volume Editors
August 2013

Contents

DEVELOPMENT OF A PORTABLE PROPANE DRIVEN 300 W SOFC-SYSTEM

Andreas Lindermeir, Ralph-Uwe Dietrich, and Christian Szepanski
Clausthaler Umwelttechnik Institut GmbH (CUTEC)
Clausthal-Zellerfeld, Germany

ABSTRACT

Portable power generation is expected to be an early and attractive market for the commercialization of SOFC-systems. The competition in this market is strong at costs per kilowatt, but weak in terms of electrical efficiency and fuel flexibility. Propane is considered as attractive fuel because of its decentralized availability and easy adaptability to other well-established hydrocarbons, such as camping gas, LPG or natural gas.

The Lower Saxony SOFC Research Cluster was initiated as network project to bundle the local industrial and research activities on SOFC technology. Goal is the development of a stand-alone power supply demonstrator on the basis of currently available SOFC stack technology. Electrolyte supported cells are deployed because to their good stability and robustness. Possible application areas are engine-independent power generation for recreational vehicles or off-grid power supply of cabins and boats. Further potential markets are industrial applications with a continuous demand for reliable power, e.g. traffic management, measuring systems and off-grid sensors and surveillance equipment. To cover the technical requirements of those applications, the SOFC system should provide the following features:

- propane as fuel,
- net system electrical power ≥ 300 We,
- net system efficiency ≥ 35 %,
- compact mass and volume,
- time to full load ≤ 4 hours.

Anode offgas recycle in conjunction with a combined afterburner/reforming-unit in counter flow configuration is used for high efficient fuel gas processing without complex water treatment. All main components are in a planar design and stacked to reduce thermal losses and permit a compact set-up.

INTRODUCTION

The Lower Saxony research cluster consists of 5 institutes from the universities of Braunschweig, Hannover, Clausthal, and the University of Applied Sciences Osnabrück and 9 industrial partners. The project is aimed to introduce innovations in component- and system development by an interdisciplinary team of researchers. The consortium adopted the planar design of the SOFC stack to the other high-temperature components like reformer, stack, heat exchanger and afterburner, thus enabling a compact system setup with a high degree of integration. All units are placed on top or below the stack and rigid pipe connections are avoided whenever possible to minimize space requirements and reduce thermal stresses during the heat-up and cool-down phase. In addition, arrangement and connection of the process units has to consider pressure drop and limitations concerning fabrication and system assembly. The high degree of thermal integration in conjunction with the internal recycle of anode offgas promises an electrical system net efficiency above 35 %. That would be remarkable for a small scale system in the power range < 500 W.

BASIC BLACK BOX CONSIDERATIONS

Prior to the detailed system design and the component specifications, a simple interactive black box model was used to prove the general feasibility of the system concept approach at different boundary conditions (see Figure 1). The Staxera Mk200 stack is equipped with 30 ESC4 cells of H.C. Starck Ceramics and has a rated power output of 700 W_e at a fuel utilization (FU) of 75 %, if operated with a H_2/N_2 mixture of 40/60 Vol.-%[1]. For the basic considerations a performance drop of about 5 % was estimated if syngas from propane reforming was used instead of the H_2/N_2 mixture, resulting in 665 W gross electrical power output. Assuming an electrical gross system efficiency of 60 % the necessary C_3H_8 input is 1,108 W (corresponding 0.022 g/s, HHV). The black box model considers heat losses via the outer system casing by calculating the convective heat flux under the assumption of a flow velocity of the ambient air of v = 0.25 m/s. The heat transfer coefficient α was estimated by

$$\alpha = 2 + 12 \cdot v^{0.5} \tag{1}$$

The heat loss is 300 W for a surface temperature of 50 °C and an area of 1.5 m^2. The system offgas temperature was calculated by closing the energy balance. The offgas temperature is 121 °C for a cathode air flow rate of 1.2931 g/s (corresponding 60 l_N/min). The cathode air blower causes mainly the parasitic electrical demand of the BoP components. Overall, BoP power demand has to be less than 270 W_e to obtain the demanded electrical net system efficiency of 35 %. For that case, an electrical net power output of 390 W results. Thus, the initial performance goals seem feasible.

Nevertheless, these figures emphasize the impact of heat loss via the surface for small SOFC systems. 27 % of the supplied energy are lost in terms of waste heat at 50 °C surface temperature; 480 W is the convective heat loss at 65 °C surface temperature and the overall energy balance no longer agrees. Additional energy supply would be required to maintain a self-sustaining operation. These simple considerations illustrate the basic necessity of a high degree of thermal integration and the need for internal usage of heat fluxes, what has to be taken into account from the beginning of system design.

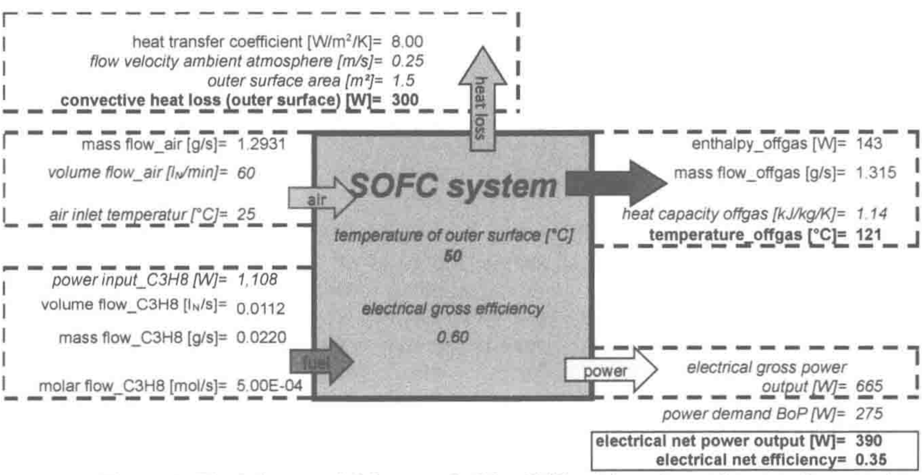

Figure 1. Black box model for proof of feasibility (given input data are formatted italic)

SYSTEM CONCEPT

Figure 2 shows a simplified process flow diagram of the proposed system. Propane and anode offgas (AOG) are fed to the reformer. The AOG contains H_2O, CO_2 and heat from the electrochemical oxidation of the H_2 and CO on the SOFC anode. That is used for endothermic steam- and dry-reforming of the propane. The reformer provides the fuel gas for the SOFC stack. The remaining part of the AOG is fed together with the cathode exhaust air to the afterburner for additional heat generation. Heat is used to maintain the endothermic reformer reactions and for cathode air pre heating to about 650 °C, before entering the stack.

Hot anode offgas recycling is a challenging task and no commercial hardware solution is currently available for the desired flow range. Thus, a piston pump was proposed and developed for AOG recycle. Intercooling of the anode offgas cannot be fully avoided due to the temperature limitations of the compressor bearings and seals. Thus, reheating the compressed AOG with the hot AOG from the anode exit using a tube-in-tube heat exchanger seems to be a reasonable compromise.

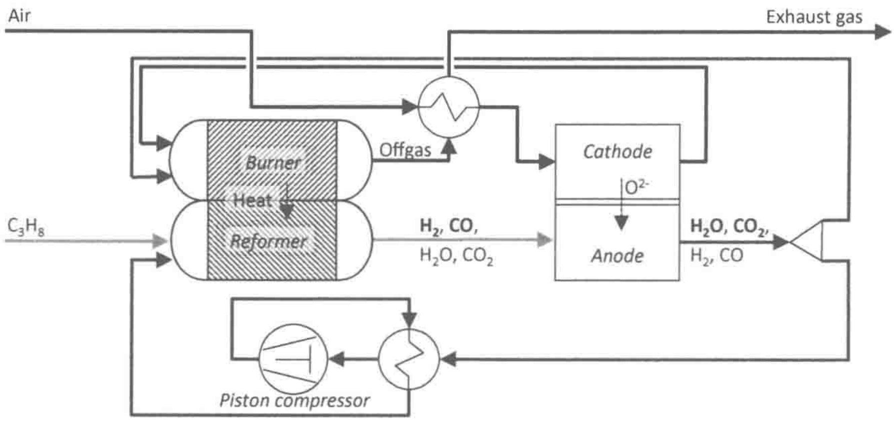

Figure 2. Process flow diagram of the propane SOFC system with anode offgas recycle

The lower limit of the AOG recycle rate is determined by the carbon formation boundary in the reformer for the given temperature. It is shown in previous tests that the oxygen to carbon ratio at the reformer inlet $(O/C)_{Ref}$ (Equation 2) is the key figure with respect to carbon formation[2].

$$\left(\frac{O}{C}\right)_{Ref} = \frac{\dot{n}_{H_2O} + \dot{n}_{CO_2}}{3 \cdot \dot{n}_{C_3H_8}} \quad (2)$$

The parameter $(O/C)_{Ref}$ corresponds to the steam to carbon ratio S/C, well known for steam reforming reactions. Equation 3 and 4 show the strong endothermy of the reforming reactions taken place:

dry-reforming: $C_3H_8 + 3\ CO_2 \rightarrow 6\ CO + 4\ H_2 \qquad \Delta_R^{298}H = 622.1$ kJ/mol (3)

steam-reforming: $C_3H_8 + 3\ H_2O \rightarrow 3\ CO + 7\ H_2 \qquad \Delta_R^{298}H = 498.6$ kJ/mol (4)

Figure 3 shows the equilibrium reformate composition at different temperatures based on stationary process flow sheet simulations (ChemCAD®). The flow rate ratio of AOG to propane has been kept constant at a calculated $(O/C)_{Ref}$ of 1.82. Hydrocarbon conversion is almost complete for reforming temperatures above 700 °C. The fraction of H_2 and CO is greater than 60 Vol.-%. Soot formation is inhibited above 720 °C for the distinct operation conditions.

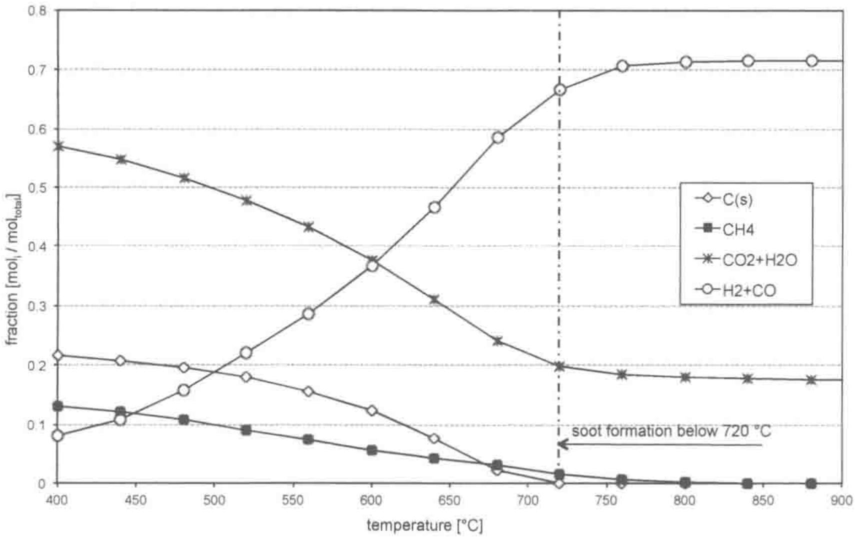

Figure 3. Reformate composition for combined steam-/dry-reforming of propane at different equilibrium temperatures, $(O/C)_{Ref} = 1.82$

While the reformer and burner can be considered as Gibbs reactors (delivering thermodynamic equilibrium values), the flow sheet simulation of the overall process requires the implementation of a confirmed stack characteristic. Key figures for the stack are power output, fuel utilization and electrochemical efficiency at the desired operation point. Thus, a Staxera Mk200/ESC4 stack was evaluated in a stack-test-bench with different fuel gas compositions and throughputs. Figure 4 shows the measured U/I-curves, Table 1 summarizes the stack performance data for the different operation points.

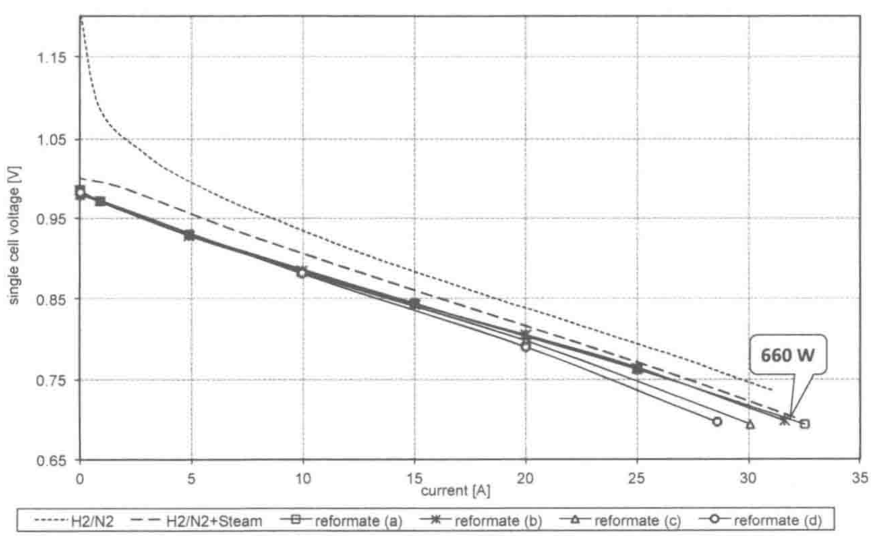

Figure 4. Single cell U/I-curves, Mk200/ESC4 stack, 850 °C stack temperature