Advances in Solid Oxide Fuel Cells and Electronic Ceramics

Ceramic Engineering and Science Proceedings
Volume 36, Issue 3, 2015

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The American Ceramic Society

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A Collection of Papers Presented at the 39th International Conference on Advanced Ceramics and Composites
January 25–30, 2015
Daytona Beach, Florida

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

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

ISBN: 978-1-119-21149-5
ISSN: 0196-6219

Printed in the United States of America.

10 9 8 7 6 5 4 3 2 1

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Preface

The 12th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science, and Technology and a Focused Session: Single Crystalline Materials for Electrical, Optical and Medical Applications were held during the 39th International Conference and Exposition on Advanced Ceramics and Composites in Daytona Beach, FL, January 25–30, 2015. These symposia 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 and single crystal materials for electronic applications. This CESP issue contains 18 papers submitted by authors of these two symposia for inclusion in the meeting proceedings.

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 following members of the international organizing committee at various stages were instrumental in making this symposium and focused session a great success.

- 12 International Symposium on SOCFs: Vincenzo Esposito, Tatsumi Ishihara, Ruey-Yi Lee, Nguyen Minh, Mogens Mogensen, Prabhakar Singh, Federico Smeacetto, Jeffry Stevenson, Toshio Suzuki, and Sascha Kuhn
- Single Crystalline Materials: Noboru Ichinose, Robert Feigelson, Richard Moncorgé, Reinhard Uecker, Alain Largeteau, Mauro Tonelli

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 and single crystal materials.

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Introduction

This CESP issue consists of papers that were submitted and approved for the proceedings of the 39th International Conference on Advanced Ceramics and Composites (ICACC), held January 25–30, 2015 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 Engineering Ceramics Division (ECD) of The American Ceramic Society (ACerS) since 1977.

The 39th ICACC hosted more than 1,000 attendees from 40 countries and over 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 2015 conference was organized into the following 21 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	12th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science, and Technology
Symposium 4	Armor Ceramics: Challenges and New Developments
Symposium 5	Next Generation Bioceramics and Biocomposites
Symposium 6	Advanced Materials and Technologies for Energy Generation and Rechargeable Energy Storage
Symposium 7	9th International Symposium on Nanostructured Materials and Nanocomposites
Symposium 8	9th International Symposium on Advanced Processing & Manufacturing Technologies for Structural & Multifunctional Materials and Systems (APMT), In Honor of Prof. Stuart Hampshire

Symposium 9	Porous Ceramics: Novel Developments and Applications
Symposium 10	Virtual Materials (Computational) Design and Ceramic Genome
Symposium 11	Advanced Materials and Innovative Processing ideas for the Industrial Root Technology
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, Chemically Bonded Ceramics, Eco-friendly and Sustainable Materials
Focused Session 2	Advanced Ceramic Materials and Processing for Photonics and Energy
Focused Session 3	Materials Diagnostics and Structural Health Monitoring of Ceramic Components and Systems
Focused Session 4	Additive Manufacturing and 3D Printing Technologies
Focused Session 5	Single Crystalline Materials for Electrical, Optical and Medical Applications
Focused Session 6	Field Assisted Sintering and Related Phenomena at High Temperatures
Special Session	2nd European Union-USA Engineering Ceramics Summit
Special Session	4th Global Young Investigators Forum

The proceedings papers from this conference are published in the below seven issues of the 2015 CESP; Volume 36, Issues 2-8, as listed below.

- Mechanical Properties and Performance of Engineering Ceramics and Composites X, CESP Volume 36, Issue 2 (includes papers from Symposium 1)
- Advances in Solid Oxide Fuel Cells and Electronic Ceramics, CESP Volume 36, Issue 3 (includes papers from Symposium 3 and Focused Session 5)
- Advances in Ceramic Armor XI, CESP Volume 36, Issue 4 (includes papers from Symposium 4)
- Advances in Bioceramics and Porous Ceramics VIII, CESP Volume 36, Issue 5 (includes papers from Symposia 5 and 9)
- Advanced Processing and Manufacturing Technologies for Nanostructured and Multifunctional Materials II, CESP Volume 36, Issue 6 (includes papers from Symposia 7 and 8 and Focused Sessions 4 and 6)
- Ceramic Materials for Energy Applications V, CESP Volume 36, Issue 7 (includes papers from Symposia 6 and 13 and Focused Session 2)
- Developments in Strategic Ceramic Materials, CESP Volume 36, Issue 8 (includes papers from Symposia 2, 10, 11, and 12; from Focused Sessions 1 and 3); the European-USA Engineering Ceramics Summit; and the 4th Annual Global Young Investigator Forum

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 Jubilee Celebration of the 40th International Conference on Advanced Ceramics and Composites (http://www.ceramics.org/daytona2016) January 24-29, 2016 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.

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Volume Editors
July 2015

Solid Oxide Fuel Cells

EFFECTS OF TiO_2 ADDITION ON MICROSTRUCTURE AND IONIC CONDUCTIVITY OF GADOLINIA-DOPED CERIA SOLID ELECTROLYTE

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ABSTRACT

Ceria containing trivalent rare-earth is a solid electrolyte with higher ionic conductivity than the yttria fully-stabilized zirconia standard ionic conductor. This feature turns these ceria-based ionic conductors promising materials for application in solid oxide fuel cells operating at intermediate temperatures (500-700ºC). One of the most utilized approaches to optimize the electrical conductivity and other properties of these materials is the introduction of a second additive. In this work, ceria-20 mol% gadolinia with additions of TiO_2 was prepared by solid state reaction. The main purpose was to investigate the effects of the additive on densification, microstructure and electrical conductivity of the solid electrolyte. Sintered pellets were characterized by evaluating apparent density, X-ray diffraction, Raman spectroscopy, scanning electron microscopy, and electrical conductivity by impedance spectroscopy. The additive was found to influence all studied properties. Increase of densification was obtained with TiO_2 addition. This additive promotes increase of the blocking of charge carriers at the grain boundaries due to solute exsolution and formation of the pyrochlore $Gd_2Ti_2O_7$ phase at grain boundaries for contents in excess of the solubility limit.

INTRODUCTION

Polycrystalline ceramics based on cerium dioxide have attracted much attention over the last decades from both theoretical and experimental point of views, due to their wide range of applications. Some of the well know applications of cerium-based ceramics are as catalysts for chemical reactions [1], mechanical polishing media in microelectronics [2], as gas sensor [3], as solid electrolyte and electrode in solid oxide fuel cells [4], luminescent material [5] and as ultraviolet filter and blocker [6,7].

Additives in cerium dioxide have been used for changing a specific property. The addition of trivalent rare earth, for example, results in a substantial increase of the ionic conductivity. The highest increase of the ionic conductivity in cerium dioxide based solid solutions has been obtained with samarium and gadolinium. The ionic conductivity of Gd-doped ceria at 800ºC is similar to that of yttria-stabilized zirconia at 1000ºC [8]. Thus, these solid solutions have been considered for possible application in solid oxide fuel cells operating at intermediate temperatures (600-800ºC) [8].

Other additives to cerium oxide ceramics have been considered to aid the sintering process allowing for increasing the sinterability of this material along with a better microstructural design and control. Few reports may be found concerning the addition of TiO_2 to doped ceria ceramics, probably because the partial substitution of Ce^{4+} for Ti^{4+} do not change the concentration of oxygen vacancies. Consequently, no influence of this additive on the ionic conductivity is expected. Jurado [9] showed that titanium oxide addition do gadolinia-doped ceria introduces a low resistivity intergranular phase, thereby the blocking of charge carriers at the grain boundaries is reduced. Cutler [10] and Pikalova [11] observed an increased densification of doped ceria with this additive. The latter also observed that a pirochlore phase with composition $Gd_2Ti_2O_7$ was formed depending on the content of TiO_2.

In this work, the effects of TiO_2 on the densification, microstructure and ionic conductivity of gadolinia-doped ceria was investigated, for additive contents below and above its solubility limit.

EXPERIMENTAL

$Ce_{0.8}Gd_{0.2}O_{2-\delta}$, CGO (>99.5%, Fuel Cell Materials) and TiO_2 (99.95%, Alfa Aesar) were used as starting materials. Solid solutions containing 1, 2.5 and 5 mol% TiO_2 were prepared by solid state reaction. The starting materials were first dried in an oven. Afterwards they were mixed in alcoholic medium in the stoichiometric proportions. After drying, the mixtures were pressed into discs of 10 mm diameter and 2-3 mm thickness. Sintering was performed in a box type furnace (Lindberg BlueM) heating at a rate of 3 ºC.min^{-1} up to 1100ºC and at 5 ºC.min^{-1} from 1100 to 1500ºC with 3 h holding time. For comparison purposes, specimens without the additive were also prepared under the same experimental conditions.

Characterization of the sintered specimens was carried out by density measurements using the immersion method. The porosity of the sintered materials was estimated according to ASTM C20-00. The phases were characterized by Raman spectroscopy (Renishaw, InVia Raman Microscope) with a He-Ne laser with 633 nm wavelength in the 200-800 cm^{-1} spectral range. The microstructure of polished and thermally etched surfaces was evaluated by scanning electron microscopy (Philips, XL30) with secondary electrons. The electrical conductivity was determined by impedance spectroscopy measurements (HP 4192A) in the 5 Hz-13 MHz frequency range. Silver was used as electrode material.

RESULTS AND DISCUSSION

All sintered specimens attained high density values as shown in Table 1. Addition of TiO_2 allowed for increasing further the density, turning negligible the apparent porosity.

Table 1. Values of relative density and apparent porosity of sintered specimens.

Material	Relative density (%)	Porosity (%)
CGO	97.5	0.1
CGO + 1% TiO_2	99.8	~ 0
CGO + 2.5% TiO_2	98.7	~ 0
CGO + 5% TiO_2	~ 100	~ 0

The linear shrinkage up to 1500ºC (not shown here) is similar for both specimens (with and without titanium oxide) and amounts 23%. In addition, the additive does not change the initial temperature of shrinkage.

Figure 1 shows Raman spectra of the investigated specimens.

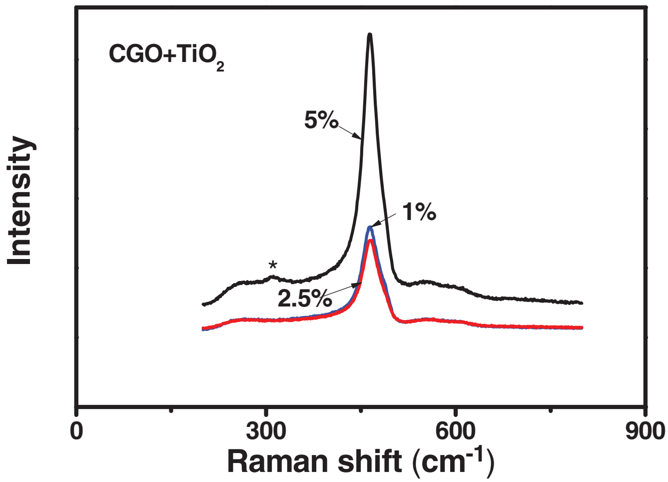

Figure 1. Raman spectra of sintered specimens containing TiO_2.

The Raman spectra consist of a predominant band centered at 465 cm^{-1} attributed to the triple degenerated F_{2g} mode of the fluorite lattice. Low intensity Raman bands at 550 and 650 cm^{-1} are usually assigned to the extrinsic oxygen vacancies created by partial substitutions [12]. In the Raman spectrum of the specimen containing 5 mol% TiO_2, other low intensity band at ~ 312 cm^{-1} is observed (indicated by *). This band is ascribed to $Gd_2Ti_2O_7$ phase, which displays about six allowed Raman modes [13]. This result evidences then the formation of the pirochlore phase in specimens with 5 mol% TiO_2. Moreover, the formation of this crystalline secondary phase reveals that when the concentration of the additive exceeds the solubility limit in the ceria matrix, it induces the exsolution of the dopant (gadolinium) from the solid solution. It is worth noting that no other phase than the cubic fluorite characteristic of ceria was detected by conventional X-ray diffraction measurements, possibly due to the experimental limitations of that technique.

Figure 2 shows a scanning electron microscopy micrograph (a) and an impedance spectroscopy diagram of the base material after sintering at 1500ºC for 3 h.