

Low Temperature Gd doped CeO₂ Nano-Layer Electrolytes for Solid Oxide Fuel Cells

Patrick Willson^a Dr. Vasantha Amarakoon^b and Dr. Walter Schulze^b

^aMaterials Science Undergraduate Research Assistant, Alfred University, 2 Pine Street Alfred New York 14802

^bSchool of Engineering, Alfred University, 2 Pine Street Alfred New York 14802

Submitted September 30, 2005

Abstract

Gd doped CeO₂ is a candidate material for high temperature solid oxide fuel cells (SOFC) due to its high ionic conductivity at intermediate temperatures (~450-600°C). Electronic conduction of CeO₂ under low O₂ pressure limits its use in SOFC's due to the reduction of Ce⁺⁴ to Ce⁺³. Electron trapping at interfaces may provide a method of overcoming this limitation. This study investigates the sol gel chemical synthesis preparation and characterization of thin film SiO₂/CeO₂/SiO₂ nanocomposites spun coat on fused silica. Soda lime silicate and silicon substrates were also employed to enhance the results of some characterization techniques. The SiO₂ material in this study was doped with manganese and cobalt in equivalent amounts to achieve 3 and 9mol% p-type doping. Tetraethyloxysilane and cerium acetyl acetate hydrate precursor materials were used to spin coat alternate layers of amorphous SiO₂ and nanostructured CeO₂ under 10,000 grade clean room conditions. A conventional sintering technique was used for densification at 900°C. Optical microscopy, x-ray diffraction, TGA/DTA, Zygo optical interferometry, ellipsometry, and ESEM/EDS were used to determine the effect of processing parameters on the fabrication and development of SiO₂/CeO₂ nanocomposite thin films. Electrical characterization is currently being performed as part of Willson's senior thesis to be submitted to the Materials Science Department at Alfred University in December 2005. The main purpose of this study is to develop a new electrolyte material to increase the efficiency of solid oxide fuel cell technology with the overall goal of decreasing emissions from today's combustion engines. Many of the processing parameters in this study have not been optimized up to this point, and future work may be necessary to enhance the capabilities of this nanocomposite.

Introduction

Solid oxide fuel cell technology requires a fuel and oxidizing agent for continuous generation of electrical current. The fuel and oxidizing agent are supplied to opposite sides of the electrolyte material known as the anode and cathode respectively. In SOFC's oxygen ions are supplied to the cathode and move through the electrolyte to the anode where a chemical reaction is induced.⁶ The chemical reaction results in a direct conversion of chemical energy to electrical current which in turn allows electrons to flow from the anode to the cathode through an external circuit. This current is utilized to supply a device with power.

Solid oxide fuel cell electrolytes require materials capable of high ionic conductivity and low electronic conductivity. Zirconia based electrolytes have been the most extensively studied materials for ionic conduction in recent years due to their entirely ionic conduction mechanism at temperatures greater than 700°C. The main reason for paucity in solid oxide fuel cell development associated with stabilized zirconia based electrolytes is the high temperature required for the onset of ionic conduction.⁶ The temperature range >700°C is associated with high thermal expansion mismatch which in turn causes major compatibility problems between the electrolyte and electrode materials. To overcome the thermal expansion problem new electrolyte materials that exhibit ionic conduction at lower temperatures have received increasing attention.

In this case Gd doped Ceria has been chosen for study due to its high ionic conductivity as compared to other fluorite structures doped with aliovalent and divalent cations. Incorporation of Gd into Ceria has been shown to increase the ionic conduction by decreasing the activation energy barrier required for oxide ion movement in the lattice.⁸ At 600°C ceria doped with 20mol% Gd has been shown to exhibit an ionic conductivity of 0.035 S cm⁻¹, as compared to 0.005 S cm⁻¹ for Zirconia.³ Gd doped CeO₂ has been extensively studied as an electrolyte material in solid oxide fuel cell technology and it has been found to offer a highly efficient method for electrical current generation under high oxygen partial pressures. The problem with ceria is that when the electrolyte is subjected to partial pressure of oxygen typically associated with the anode side of a fuel cell its electronic contribution to the overall conductivity increases. This increase in electronic conduction, due to the reduction of Ce⁴⁺ to a Ce³⁺ state, shorts out the electrolyte resulting in failure of the electrolyte material.⁶

To prevent this problem sol gel processing has been incorporated in the development of thin film SiO₂/CeO₂/SiO₂ composite structures. It has been theorized that an electron depletion region can be developed by coating a Gd doped Ceria thin film on upper and lower surfaces with a p-type amorphous silica layer. This coating will impose a depletion region into the ceria layer on both sides resulting in electron trapping at the interfaces. That ultimately ends in a decrease in the electronic contribution to conduction. This paper consists of the materials development, spin coat deposition, and materials analysis portion of the research. An extensive electrical analysis is currently being performed as part of senior thesis research and will be reported in December 2005.

Experimental Procedure and Discussion

An extensive literature search was performed to gain a basic knowledge of the sol-gel materials available for SiO₂ and CeO₂ thin film fabrication. For the deposition of amorphous silica thin films tetraethyloxysilane was the most extensively used

organometallic. This sol-gel processes proceeds as a catalyzed hydrolysis-condensation reaction that forms a final gelled product.^{1,7} For this project it was determined that ideally a 100nm dense film of p-type silica would be necessary to develop a depletion region extending into the ceria layer. The dopants used in this experiment were manganese, and cobalt obtained by dissolution of manganese nitrate hexahydrate, and cobalt nitrate hexahydrate in the TEOS solution. Antimony ethoxide was also tested as a potential dopant but wasn't used due to precipitation problems when adding it to solution. Before processing the films the final solutions were double filtered using a syringe driven filtration method capable of filtering out particles larger than 30nm.

Extensive information on the formation of ceria thin films through successive layering to a thickness of 30-100nm utilizing the spin coating technique could not be located at the time of this research. Information on films prepared by spin coating and other methods, varying in thickness from 100-600nm, was readily available and this information was considered in the development of the cerium acetyl acetonate hydrate solution (CAAH) for this application.

The first trial solutions developed to produce the ceria thin films were through sol-gel preparation of a cerium nitrate precursor solution. These solutions exhibited poor wettability when they were used to spin coat ceria layers on TEOS. Many experiments were performed in attempt to enhance the wetting behavior of the cerium nitrate solutions on TEOS. None of these conditions seemed to enhance the wetting capabilities of the nitrate solutions.

It was then determined that cerium acetyl acetonate hydrate could be a possible precursor material. A .1M CAAH stock solution was prepared through a mechanical mixing process in which 3.7g CAAH was added to 66.3g ethanol and mixed for 24 hours. The gadolinium nitrate dopant was added to the stock solutions to achieve 10 and 20mol% solutions. These solutions were mechanically mixed for 24hours and double syringe filtered to prevent contamination. The cerium acetyl acetonate hydrate solution showed complete wetting when spun on TEOS.

During preparation for the spin coating process a literature search was performed to determine typical spin coat parameters that could be used for this study. These parameters were used as the baseline for the spin coating process. From zygo surface analysis and optical imaging of samples processed at multiple spin speeds, accelerations, and dwell times the best parameters for deposition of stock TEOS were found. These parameters resulted in a uniform film. Some waviness is apparent when spinning TEOS under the current parameters, but the resulting surface topography has been deemed acceptable for the current study. Films constructed from multiple layers of CAAH have been deemed important to achieve a dense film. The spin coating parameters necessary to achieve 30-100nm dense ceria films through multiple layer deposition have been determined to be 1 sec acceleration to 6000rpm with a 30 second dwell and 10 second deceleration. The CAAH films where heat treated on a hot plate at 250°C between applications.

Thermal analysis was performed to determine total weight loss and regions of endothermic and exothermic reactions that occur when firing TEOS and CAAH materials. From the thermal gravimetric analysis (TGA) performed on TEOS powders it was found that a 23% weight loss occurs during sintering to 900°C. Note that this weight

loss does not include the evaporation of alcohol and water that occurs during the gellation process.

Prism couple, environmental scanning electron microscopy, and ellipsometry analysis were attempted to determine the thickness of the CAAH and TEOS films. Prism couple analysis was not applicable due to the constraints on measurements of film thickness of less than 300nm. These measurements were verified using ESEM imaging of eight and ten layer CAAH samples. Electron dispersion spectroscopy was performed to verify the composition of the thin films. These results verified the presence of cerium and the gadolinium dopant in the gadolinium doped ceria thin film. Due to resolution issues associated with nano layers only very small peaks of cerium and gadolinium are apparent.

X-ray diffraction was performed on the fired CAAH and TEOS powders. This analysis provided information concluding that the CAAH solution after being fired to 900°C forms the cubic fluorite structure and is in the preferred Ce⁴⁺ oxidation state. The TEOS powder exhibits an amorphous hump that is associated with fused silica in the amorphous state.

From the literature available concerning ceria and SiO₂ thin films it was determined that dull densification of the thin films could be achieved by firing at a rate of 1°C/min to 900°C and holding for 1Hr. Thin film x-ray diffraction is scheduled and will be submitted as part of Willson's thesis in December.

Conclusion

During the study some very positive steps have been made in the development of p-type SiO₂ and Gd doped ceria thin films for solid oxide fuel cell nanocomposite electrolytes. This study proves the potential use of cerium acetyl acetonate hydrate, and tetraethylorthosilicate as precursor solutions for sol gel processing of nanocomposite thin films to be utilized in the spin coating process. Optical imaging has been used to show the suitable wettability of the CAAH solution on a TEOS thin film. Zygo surface analysis has provided the information necessary to adjust parameters allowing the investigator to determine acceptable spin parameters used to achieve final sample thin films with a surface roughness average of 2-3nm. TGA and DTA data have provided information used to determine the weight loss and solidification points of the materials tested. Ellipsometry and environmental scanning electron micrographs have provide the measurement tools necessary to determine the thickness vs. coatings relationship of the CAAH solution. Through qualitative analysis techniques including electron dispersion spectroscopy and x-ray diffraction the presence of the optimal composition and microstructural configurations have been verified.

At this point in the study there is still a significant amount of work being performed to verify the potential use of the nanocomposite developed. New solutions are being mixed and samples are being prepared for multiple tests. Thin film x-ray diffraction will be performed on a ten layer sample of 20mol% Gd doped CeO₂ to verify that after doping the ideal stoichiometric configuration (cubic fluorite structure) is maintained. EDS analysis on a 9mol% p-type SiO₂ thin film will be performed to verify the presence of the cobalt and manganese dopant cations, and EDS of the Gd doped ceria layer will be provided. TGA and DTA analysis will be performed on the TEOS and CAAH stock solutions. The X-ray scanning microprobe is also being used to develop

thickness profiles based on compositional changes throughout the thickness of 10 and 6 layer CAAH samples. A statistical design is being developed to analyze the electrical testing that is being performed on the samples. The electrical tests consist of high temperature vs. resistance measurements to develop Arrhenius plots that will be used to determine the activation energy of different conduction mechanisms. Alternating current impedance analysis will also be conducted under multiple partial pressures of oxygen to determine the effect of oxygen partial pressure on standard 60nm and 100nm ceria thin films as compared to the nanocomposite structures. Microwave sintering is also being considered as a means of densification to eliminate extensive firing cycles. A full report including the electrical analysis results will be submitted to the Center for Environmental and Energy Research upon completion of Willson's thesis in December 2005.

Acknowledgements

There are many that deserve credit for their help in making this study a success thus far. First of all I would like to thank the Center for Environmental and Energy Research for their generous funding. I would also like to thank the many professors that have given me direction. A special thanks to my advisors Dr. Vasantha Amarakoon and Dr. Walter Schulze for their guidance and confidence in my work on this project. I would also like to thank the crew in McMahan 218 and to a good friend Gerry Wynick for help evaluating samples in the environmental scanning electron microscope, and x-ray scanning microprobe.

References

- 1) Akhtar, Masyood. "Factors Controlling The Sol Gel Conversion in TEOS." Alfred University Doctoral Thesis, Alfred NY (1984): 9-15.
- 2) A. Tschope, S. Kilassonia, R. Birringer, "The Grain Boundary Effect in Heavily Doped Cerium Oxide," Solid State Ionics 173 (2004) 57-61
- 3) Chen, L., C.I. Chen, D.X. Huang, Y. Lin, X. Chen, and A.J. Jacobson. "High Temperature electrical conductivity of epitaxial Gd-doped CeO₂ thin films." Solid State Ionics (2004). Science Direct. Scholes Library, Alfred, NY.
- 4) Chen, L., C.I. Chen, X. Chen, W. Donner, S.W. Liu, Y. Lin, D.X. Huang, and A.J. Jacobson. "Electrical properties of a highly oriented, textured thin film of the ionic conductor Gd:CeO₂ on (0001) MgO." Applied Physics Letters 83 (2003): 4737-4739. Scholes Library, Alfred, NY. 25 Feb.-Mar. 2005.
- 5) G. Balazs, R. Glass, "AC Impedance Studies of Rare Earth Oxide Doped Ceria," Solid State Ionics 76 (1995) 155-162
- 6) Petterson, Jeffrey. "Effect of electron trapping on electronic conduction in Cerium Oxide/ Aluminum Composites." Alfred University Doctoral Thesis, Alfred NY (2003).
- 7) Wright, John D., and Sommerdijk Nico. Sol-Gel Materials Chemistry and Applications. London: Taylor and Francis Books Ltd., 2003. 16-31.
- 8) Zhang, T.S, J. MA, S.H. Chan, P. Hing, and J.A. Kilner. "Intermediate-temperature ionic conductivity of ceria-based solid solutions as a function of gadolinia and silica contents." Solid State Sciences 6 (2004): 565-572. Science Direct. Scholes Library, Alfred, NY.