Development of Novel Thin Film Electrolyte Materials for Intermediate Temperature Solid Oxide Fuel Cells

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Abstract

Solid oxide fuel cells (SOFCs) are electrochemical devices that convert chemical energy into electricity using ion-conducting oxide ceramics as electrolytes. Two new electrolyte materials, (1) gadolinia-doped ceria coated with yttria-stabilized zirconia thin films (a three-layer electrolyte) and (2) thin films of gadolinium-doped barium zirconate (a proton conductor), have been developed which have the potential to lower SOFC operating temperatures. Pulsed laser deposition (KrF; 0.5-2 J/cm^2) was used to deposit these materials as thin films on suitable substrates in a 20-200 mTorr oxygen environment. The crystalline structure of these films was confirmed to be cubic by X-ray diffraction and their thickness determined by transmission spectroscopy.

Keywords: Solid oxide fuel cells (SOFCs), Yttria-stabilized zirconia (YSZ), Gadolinia-doped ceria (CGO), Gadolinium-doped barium zirconate (BZG)

Introduction

We are currently in the midst of a transition to sources of energy that are more efficient, more sustainable, and better for the environment than the sources currently used. Since the world's energy demand is met primarily by fossil fuels, their depletion is becoming a concern. The current methods used to extract energy from fossil fuels, specifically combustion, are extremely inefficient and produce large amounts of greenhouse gases and other pollutants. After centuries of burning fossil fuels, the long-term negative effects on the environment have been realized. Thus, alternative energy sources are needed that will meet increasing demand without the disastrous effects of the most widely used sources today. Solid oxide fuel cells (SOFCs) are one possible solution to these challenges.

SOFCs are electrochemical conversion devices that produce electricity directly from the oxidation of a fuel, freeing them from the efficiency constraints that apply to combustion. The electrolytes used in SOFCs are ion-conducting oxides of two types: oxygen ion conducting oxides and proton conducting oxides. In the former, oxygen ions diffuse through the electrolyte from the cathode to the anode where they electrochemically oxidize the fuel. In the latter, oxidation of the fuel produces protons, which diffuse through the electrolyte from the anode to the cathode where they combine with oxygen from air to form water. The best electrolytes for use in SOFCs are those that have a high oxygen ion or proton conductivity. SOFCs present

a viable and attractive bridging technology in the global shift from energy production based on fossil fuels towards cleaner sources due to their greater efficiency and ability to utilize various fuels. SOFCs can usher in this transition by making more efficient use of fossil fuels widely available now and by utilizing more environmentally friendly sources such as hydrogen in the future. They can be used for energy production on several scales, ranging from large-scale on-site energy production such as the fuel cell stacks employed by Bloom Energy to smaller applications such as cars that run on natural gas. While fuel cells are more expensive now than other methods of extracting energy from fossil fuels (such as combustion), their superior efficiency makes them an attractive alternative and is the biggest motivator for continued research in the field.

Unfortunately, currently available ceramic electrolytes require very high temperatures (800-1000°C) in order to conduct ions. These temperatures present challenges in the design of fuel cells, especially regarding the materials used to hold and integrate the fuel cells in high power stacks [1]. Materials that can withstand these high temperatures tend to be costly. High temperatures also necessitate a start-up time before the fuel cell becomes fully operational and able to produce a current that can be used to perform work. Current research efforts are focused on reducing the operating temperatures of SOFCs by creating ceramics that have high ion conductivity in the intermediate temperature range (500-750°C) [2]. This could potentially lower operating costs of SOFCs, thereby encouraging their use. Accordingly, we pursued in this project the fabrication of two new electrolyte materials that have the potential to allow SOFCs to operate at reduced temperatures. First, we explored the synthesis of a novel three-layer electrolyte comprising gadolinia-doped ceria (CGO) coated on both sides with yttria-stabilized zirconia (YSZ) thin films. Second, we began development of the proton conductor gadolinium-doped barium zirconate (BZG) in the form of thin films.

Gadolinia-doped ceria (CGO) has been shown to exhibit high oxygen ion conductivity at relatively low temperatures [3,4]. However, in the temperature range of 500-750°C, CGO also conducts electrons [5]. This effectively shorts out the fuel cell and is the major reason why CGO has not been widely adopted over the current standard, yttria-stabilized zirconia (YSZ). In this project, we attempted to solve this problem by applying a very thin layer of YSZ to both sides of the CGO electrolyte and creating a triple layer YSZ/CGO/YSZ electrolyte that does not exhibit

electron conductivity. Unfortunately, this will also decrease the oxygen ion conductivity of the material. Nevertheless, our goal was to determine an optimal thickness that will prevent the flow of electrons through the ceramic and at the same time allow reasonable ionic conduction in the intermediate temperature range.

In parallel with the development of the triple layer YSZ/CGO/YSZ electrolyte, we also investigated the fabrication of the promising proton conductor gadolinium-doped barium zirconate (BZG). Recently, numerical simulations of proton transport in this material have predicted proton conductivity higher than those of the most commonly used electrolyte materials [6]. In this project we attempted to fabricate this material in the form of thin films, of which there have been virtually no reports in the literature to date.

Experimental

Both fabrication efforts in this project involve the use of the technique called as pulsed laser deposition (PLD). This method of thin film fabrication passes a laser beam through a quartz window of a vacuum chamber to strike a rotating target. This creates a plasma plume, originating from the target and ejecting material from the target surface, which then strikes a rotating, heated substrate. The ions, neutral species, and particles adhere to the substrate and form a thin film. The deposition rate of the film can be increased by increasing the laser energy density. The pressure of the background gas, if one is used, also alters the deposition rate and permits reactive synthesis. Figure 1 shows a schematic of the PLD system used in this project.

Figure 1. Schematic diagram of pulsed laser deposition (PLD)
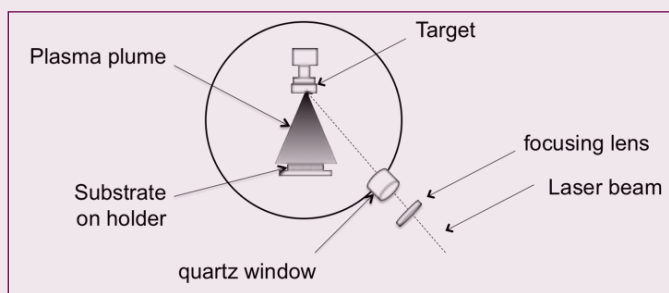
system. The system allows for controlled variation of substrate temperature, pressure of any background gasses, and laser energy density.

Pulsed Laser Deposition of Yttria-Stabilized Zirconia (YSZ) Thin Films

Thin-films of YSZ were deposited on both sides of CGO substrates using PLD. A KrF excimer laser (248 nm) and commercial 8 mol. % yttria-stabilized zirconia targets were employed. The thicknesses of the resulting films were controlled by varying the number of pulses during deposition and using laser energy densities in the 0.5-2 J/cm^2 range. In order to achieve desired oxide stoichiometry, deposition was carried out in an oxygen atmosphere at pressures of 20-200 mTorr. The temperature of the substrate was kept constant at 680°C. Film thicknesses were then measured using transmission spectroscopy and the crystalline structures determined using X-ray diffraction (XRD).

In order to determine the best parameters for YSZ deposition, films were first grown on double-sided silicon substrates. Substrate temperature, O_2 partial pressure, laser energy density, and the number of laser pulses were varied in order to obtain accurate calibration of YSZ deposition rates, which were then used to grow YSZ films with precise thickness control on the CGO substrates.

Pulsed Laser Deposition of Gadolinium-doped Barium Zirconate (BZG) Thin Films

Because the commercial cost of BZG targets is prohibitively high, we generated our own BZG targets for PLD thin films. This was achieved by mixing $BaZrO_3$ and Gd_2O_3 powders at various concentrations. The obtained targets were then placed in a hydraulic press, compressed at a pressure of 2800 psi, and subsequently annealed at 1600°C in air for 24 hours. The temperature in the furnace was initially 450°C and increased
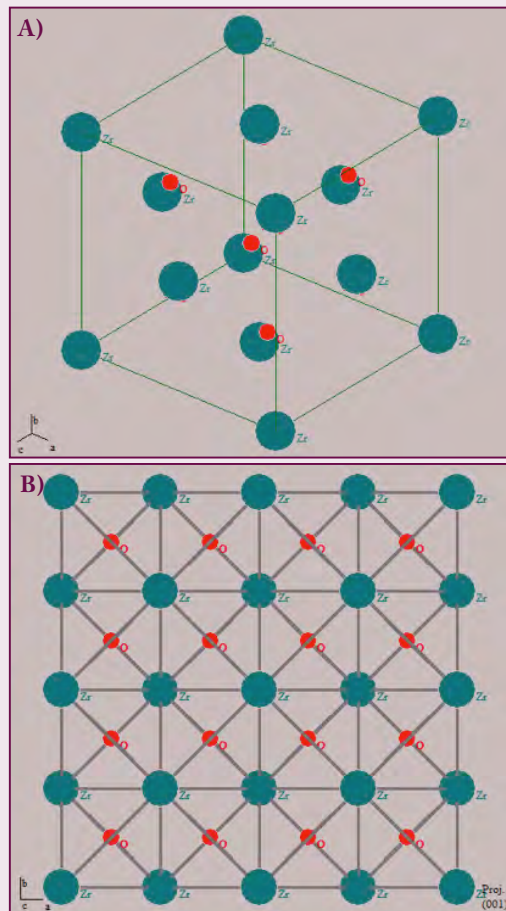

Figure 2. (A) Unit cell of cubic zirconia. (B) (100) projection of the crystal structure of cubic zirconia, as it should be featured in the material stabilized using the addition of yttria (i.e., YSZ). Both generated using Powder Cell.

at a rate of 120°C per hour. It took 9.5 hours for the furnace to reach 1600°C. The furnace was then cooled at the same rate. Figure 8 shows the resulting sintered target 21.8 mm in diameter. The annealing temperature and time were reduced for future targets. These targets were then laser ablated using the same PLD system described previously, also in an O_2 environment but with pressures ranging from 40 to 200 mTorr. Thin films were deposited first on silicon substrates and then on various other materials suitable for electrochemical and electrical characterization. Transmission spectroscopy was used to measure the film thicknesses and XRD to investigate their crystal structures.

Results and Discussion

We used a GUI based program called Powder Cell to explore crystal structures and calculate powder diffraction patterns [7]. Figure 2 shows the atomic structure of cubic zirconia visualized using Powder Cell. Zirconia, which can also crystallize in monoclinic or tetragonal configurations, is stabilized by the addition of yttria. The cubic configuration is the desired crystal structure because it conducts oxygen ions more efficiently than alternative configurations. Powder Cell was also used to calculate the X-ray diffraction pattern for yttria-stabilized zirconia (YSZ), shown in Figure 3a. The crystal data used to create this X-ray diffraction pattern were obtained from the American Mineralogist Crystal Structure Database [8]. This calculated pattern will be used for comparison to the pattern measured using XRD.

Figure 3b shows the XRD pattern obtained on the film deposited on a silicon substrate by ablating our YSZ target at an energy density of ~1.87 J/cm² and an O_2 pressure of 200 mTorr. The silicon substrate was kept at a temperature of 680°C and 24,000 laser pulses were used. The main peaks observed in the XRD pattern of our film correspond to the (111), (200), (220), and (311) reflections of the cubic zirconia structure and agree with the predicted diffraction pattern from Powder Cell for a unit cell with 5.070 Å. This indicates successful deposition of a cubic YSZ film. From the interference fringes of the transmission spectroscopy data obtained on the same film shown in Figure 5, film thickness was found to be 1.59 ± 0.01 mm. This thickness information allowed us to determine the deposition rate of YSZ for the deposition parameters employed. This deposition rate was found to be 0.066 ± 0.004 nm/pulse. The presence of large particulates on the film as shown by several micrographs of the film suggests that using lower energy densities would enhance film quality.

This deposition process was repeated at energy densities of ~0.64 J/cm² and ~0.76 J/cm² with all other variables held constant. The resulting deposition rates were 0.021 ± 0.0004 nm/pulse and 0.040 ± 0.0004 nm/pulse, respectively. Figure 6 shows the deposition rate as a function of laser energy density. The line is not a fit and should not be interpreted as
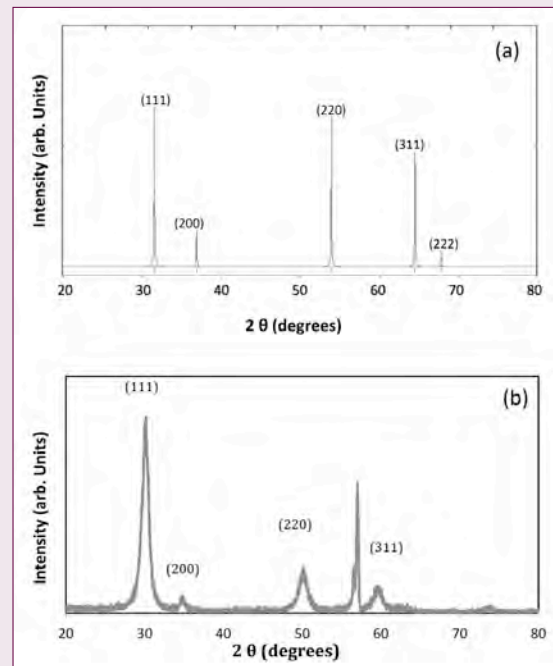

Figure 3. (a) Calculated XRD pattern of cubic zirconia from PowderCell, which serves as a reference for any XRD measurements taken of the YSZ films produced. (b) XRD pattern obtained from a nominal YSZ film deposited with an energy density of 1.87 J/cm², at a temperature of 680°C and an O_2 background pressure of 200 mTorr. The large peak at 58° is due to the silicon substrate.
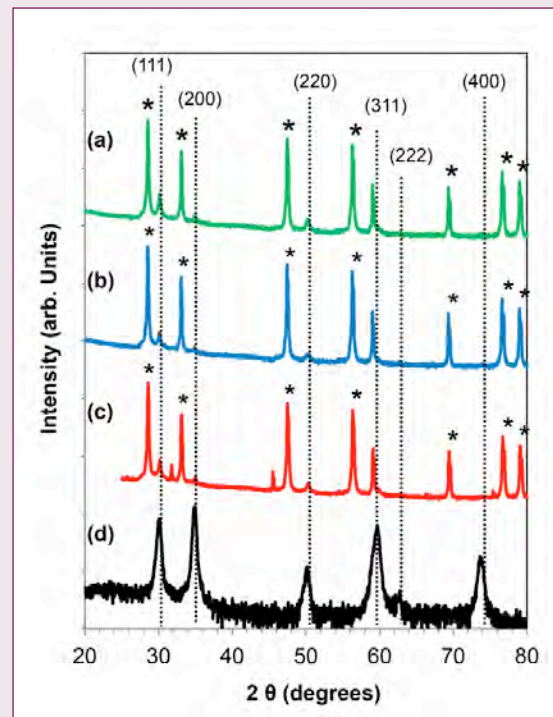

Figure 4. XRD pattern obtained from YSZ deposition of various thicknesses on CGO substrates at various O_2 pressures. (a) 250 nm at 20 mTorr. (b) 120 nm at 200 mTorr. (c) 250 nm at 200 mTorr. (d) Thick film on Si.

interpolation or extrapolation of the data. It is only meant to show the general trend of the data. We were not able to determine with confidence the uncertainty associated with our deposition rates and energy density. However, typical pulsed laser deposition experiments using our geometry usually yield film thickness variations of the order of 10%. Fluctuations in energy density in our experiment are also usually of the order of 10%. The error bars in the data shown in Fig. 6 reflect these uncertainties in our data. Micrographs of these films showed improved film quality with fewer particulates. Knowledge of the effect of energy density on the resulting film thickness allows for straightforward determination of which parameters to use for a particular YSZ thickness when YSZ is to be deposited on the CGO substrates. YSZ films were deposited at 20 to 200 mTorr O_2 on both sides of a CGO substrate heated to 800°C with an approximate laser energy density of 0.5 J/cm^2 and an appropriate number of laser pulses to give 290, 250, and 80 nm films. The resulting X-ray diffraction pattern shown in Figure 4 confirms that the cubic form of YSZ was indeed deposited.

The ionic conductivity of the CGO/YSZ samples was tested by our collaborators in Brazil using electrochemical spectroscopy (EIS). Figure 7 shows the resulting conductivity data, which is an order of magnitude lower than that of YSZ. Both the temperature control and the current measurement of the EIS system have precision better than 0.1%, resulting in error bars smaller than the points used to represent the data.

Targets of BZG were used to deposit films first on silicon to repeat the procedure for determining the deposition rate. XRD was again used to characterize the crystal structure of the deposited BZG. Figure 9 shows XRD data from three BZG samples of various dopant (Gd_2O_3) concentration. Two of the films were amorphous, as indicated by the broad peak, while the 15% film contained both crystalline and amorphous phases. Electrochemical impedance spectroscopy was carried out on

samples deposited using the same parameters on platinum substrates. Due to the mismatch between the coefficients of thermal expansion for the substrates and the BZG, the films were cracked. This resulted in a much lower measured value for ionic conductivity than was expected. To reduce the amount of thermal stress in the films, a substrate with a similar thermal expansion coefficient is needed. Niobium is a suitable candidate as it is used for ionic conductivity testing and its thermal expansion coefficient is almost identical to that of barium zirconate. Depositions on niobium substrates will be performed in future work.

Conclusions

The goal of this research was to generate a more thorough understanding of the deposition process of YSZ. This understanding allowed for the deposition of very thin films of YSZ on CGO substrates in order to block electron conduction in this important electroceramic. We have shown that PLD is suitable for the deposition of cubic YSZ in thicknesses around 1 micron. We have also shown that energy densities around 1.87 J/cm^2 are apparently too high as they lead to a large amount of particulate material on the films.

The ionic conductivity of our YSZ/CGO electrolyte was found to be lower than industry standard bulk YSZ. We believe that this is most likely the result of the loss of available ions for conduction due to their being trapped in the interface between YSZ and CGO or other defective areas in the YSZ itself. Further optimization of the deposition and the parameters used should correct this.

PLD targets of $BaZrO_3$ and Gd_2O_3 powders were processed as described previously to create 10%, 15%, and 20% Gd_2O_3 targets. Films were then deposited on various substrates at 50 mTorr, 100 mTorr, and 200 mTorr and XRD was used to determine crystal structure. An XRD analysis
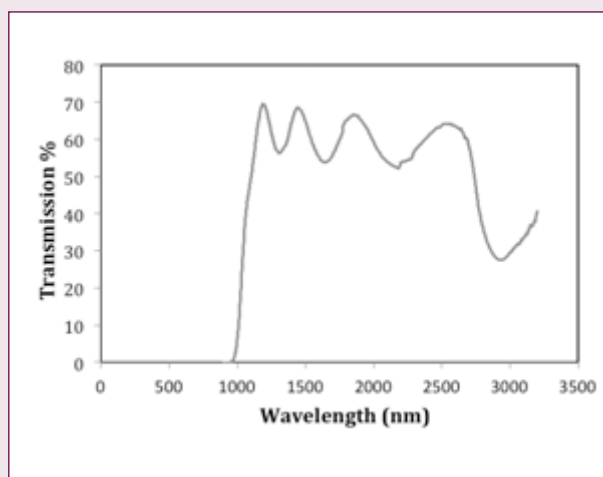
Figure 5. Transmission spectroscopy data of one YSZ film. The interference fringes lead to an estimated film thickness of approximately 1.59 microns.
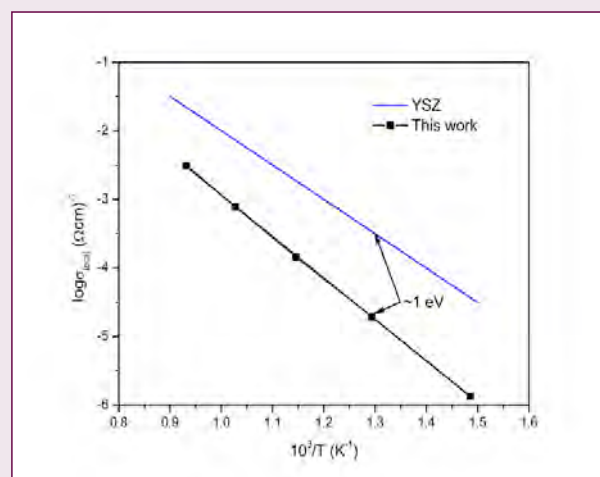
Figure 6. The deposition rate of YSZ at various laser energy densities for an O_2 pressure of 200 mTorr. The line is not a fit and only shows the general trend of the data.
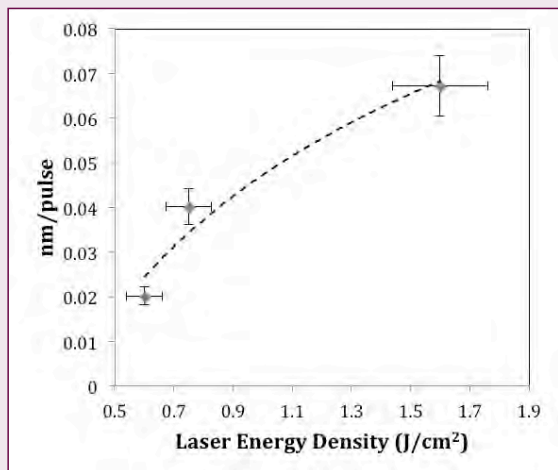
Figure 7. Resulting ionic conductivity of YSZ/CGO/YSZ structure as a function of reciprocal temperature.
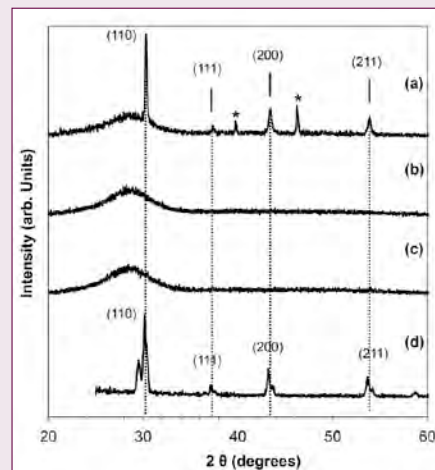

Figure 9. XRD data for three BZG films with (a) 15% , (b) 10%, and (c) 5% Gd_2O_3 concentration and one target for reference (d). The 15% film shows a cubic crystal structure as desired.

showed that cubic BZG was indeed deposited. However, the thermal stress present in the samples resulted in cracking in the films, which negatively affected the ionic conductivity as measured using electrochemical impedance spectroscopy. To attempt to overcome this, niobium will be tested as a substrate in future experiments.

Figure 8. Target produced by mixing BZO3 and Gd2O3 powders, pressing, and subsequent annealing at 1600 °C for 24 h.

In this research we have explored the fabrication of both gadolinium-doped ceria coated with yttria-stabilized zirconia thin films and thin films of gadolinium-doped barium zirconate using pulsed laser deposition. The results presented indicate that PLD is a suitable method for the fabrication of both of these materials. We anticipate that solid oxide fuel cells based on BZG and multilayer YSZ/CGO/YSZ structures will improve the range of applicability for efficient, clean, and economically viable fuel cell energy conversion.

Acknowledgments

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