

Atomic Layer Deposition of Cerium Oxide for Potential Use in Solid Oxide Fuel Cells

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## Abstract

With the growing need for sustainable energy, solid oxide fuel cells are an attractive alternative for power generation since they are efficient and environmentally friendly. However, required high operating temperatures limit their widespread use. (There are two ways of reducing the operative temperature, one is making the electrolyte thinner and the other one is looking for new materials that have better transport properties. In this case, CeO<sub>2</sub> is considered a new material since the one used so far is YSZ yttrium stabilized zirconia) By making the cell's electrolytes thin films, it is possible to lower the operating temperatures. One technique for making thin films (with good qualities as pinhole free, good conformality and film thickness control) is atomic layer deposition, also known as ALD, which uses alternating saturative surface reactions. In this study, the atomic layer deposition of cerium oxide was studied for potential use in solid oxide fuel cells as the electrolyte and anode. The optimum precursor temperature was found to be 130 °C and the water pulse length was found to be 55 msec. The ALD window, which is the temperature range of ideal ALD growth, was determined to be from 210 to 280 °C, the surface was saturated when at least four plugs of precursor pulses was used in the procedure, and the growth was linear at 1.2 Å/cycle.

## Key Words

Atomic Layer Deposition, Solid Oxide Fuel, Cerium Oxide

## Introduction

With the rising need for sustainable energy, fuel cells are an attractive alternative for power generation and are now becoming practical for wide spread use. Fuel cells are generally characterized by the material that the electrolyte is made of. Examples include alkaline fuel cells, PEM fuel cells, and solid oxide fuel cells[1]. With no nitrogen oxides, sulfur oxides, or hydrocarbon emissions, very little CO<sub>2</sub> emissions, high efficiency, and fuel flexibility, solid oxide fuels cells are a sustainable power source for high power applications[2]. However, solid oxide fuel cells have very high operating temperatures- in the range of 800 to 1000 °C. The high operating temperatures forces the cells to have long heat up and cool down periods, and the materials that a cell can be made of is currently limited since the thermal expansion coefficients for cell layers must be close[3].

There are three parts of a solid oxide fuel cell- the anode, the cathode, and the electrolyte which is made of a solid inorganic oxide. As seen in Fig. 1, the fuel, which (also can be pure hydrogen) is a hydrocarbon such as methane, biogas, or landfill gas, enters at the anode. The fuel is reformed into hydrogen and carbon monoxide either at the anode or before entering the cell. On the cathode side, air containing oxygen enters, and oxygen is reduced to oxygen ions which then travel though the electrolyte. Once the ions reach the anode, they react with the fuel to produce carbon dioxide and water. The electrons move from the anode to the cathode through an external circuit where they can perform electrical work[2].

There are two ways to lower operating temperatures. The first is to change the materials that the electrolyte is made of to a material with a lower ion resistivity, and the second is to decrease the thickness of the cell's electrolyte which lowers the ion resistivity[3]. A way to decrease the thickness of the electrolyte is by making the components of the cell out of thin films. There are multiple ways of creating thin films including physical vapor deposition which is a purely physical process, and chemical vapor deposition, a chemical process frequently used in the semi-conductor industry. Chemical vapor deposition includes atomic layer deposition which is a technique for creating thin films with control down to the atomic level [4].

There are many benefits of using atomic layer deposition over other thin film manufacturing techniques. ALD (atomic layer deposition) creates highly uniform and pinhole-free films, and the process is

reproducible. Another benefit is that the reaction is self-limiting- once all of the saturation sites are filled, the reaction is complete which means that the exact stoichiometric ratios do not need to be known. The film thickness is also easily controlled by the number of cycles[5]. Atomic layer deposition is also insensitive to small temperature changes during the process when operating in the ALD window which is the temperature range in which ALD behavior is nearly ideal. Below this range, condensation or incomplete reactions may occur and above this range decomposition or desorption may occur[4].

ALD creates films by using alternating saturative surface reactions between a precursor, a coreactant, and the surface. The process is cyclic with each cycle containing four steps. The first step is to pulse the first precursor into the reactor using an inert carrier gas, and the precursor saturates the surface. Once enough time has been allowed for all sites to be filled, the first purge takes place. In this step, an inert gas is pulsed through the reactor to remove the excess of the precursor so it does not react with the coreactant in the vapor phase. Once the reactor has been evacuated, the coreactant is pulsed into the chamber where it reacts with the surface to complete the first monolayer. To finish the cycle, the reactor is purged again. Cycles are preformed until the film is at the desired thickness[5]. This process can be viewed in Fig. 2.

In this study, atomic layer deposition was used to create cerium oxide for use in solid oxide fuel cells as the anode and electrolyte. Cerium oxide is a valid replacement for yttrium doped zirconium (better known as YSZ), which is currently used as the electrolyte in solid oxide fuel cells, because the ion permeability of cerium oxide is higher at lower temperatures than YSZ (you can add here some previous references about the ALD of CeO<sub>2</sub> using ALD and other precursors). The precursor being used was tris(i-propylcyclopentadienyl)cerium and the coreactant was water. Tris(i-propylcyclopentadienyl) cerium was used because it reacts with water (if you add the other studies, you can add here: contraire of other Cerium precursors with  $\beta$ -diketonates ligands and put the reference where it says that these kind of precursors only react with ozone). The goals were to find the optimal ALD conditions for the growth of cerium oxide including the ALD window, the saturation curve, and the linear growth dependence.

## Materials and Methods

The custom-built hot wall reactor was brought to 0.18 Torr by a vacuum pump and was brought to the desired temperature by a heating coil that surrounded the quartz tube that held the sample. The system contained three precursor's vessels and deionized water in an ice bath as the coreactant. The ice was replaced daily to ensure that the amount of water pulsed into the reactor was the same for each experiment run. Nitrogen gas was the carrier gas and the purge gas for the system.

A pulse time of 55 msec of water followed by a purge time of 22 s was used for all experiments for finding the ALD window, the saturation curve, and the linear growth. (you can add: In order to avoid cold spots in the flow pattern, the temperature was increased as follows) The temperature of the precursor was set at 130 °C, the precursor valve at 140 °C, the precursor leg at 150°C, and the manifold at 155 °C for all experiments. 130 °C was chosen as the precursor temperature because above that temperature an excess of precursor was entering the reactor chamber and condensing on the wall and below 130 °C the vapor pressure of tris(i-propylcyclopentadienyl cerium) decreases too low for deposition. Each experiment for finding the ALD window used the condition of fifty cycles made of six plugs of precursor pulsing per cycle.

After deposition, the substrates' thicknesses were measured by a spectral ellipsometer (JA Woollam Co., Inc. model M-44).

For each experiment, the substrate was a 1cm x1 cm silicon wafer cleaned by standard RCA-1 treatment. The native silicon oxide layer was reduced to 8 to 10Å using two percent hydrofluoric acid solution. The substrates were washed in ultrapure deionized water and dried with nitrogen gas.

## Results and Discussion

At first, a precursor temperature of 140 °C was used which yielded high growth rates as seen in Fig. 3. It was determined that there was excess precursor in the reactor due to the darkening of the quartz tube that contained the sample during deposition as one can see in Fig. 4. To prevent precursor from being wasted, the precursor temperature was reduced to 130 °C, and condensation of the sample onto the quartz tube's wall no longer occurred.

Experiments were continued with a precursor temperature of 130 °C, a reactor temperature of 250 °C, and a water pulse of 50 msec which yielded that results seen in Fig. 5. It was discovered that not every water pulse was being delivered which explained the inconsistencies in the data points. The time of the water pulse was increased to 55 msec to ensure at all experiments were repeatable.

To find the ALD window, for each experiment, the conditions described above in the Materials and Methods section were used. As seen in Figure 6, the ALD window was found to reach 280 °C. Above this temperature, decomposition of the precursor occurred which allowed other molecules to adhere to the surface of the substrate with yields a higher growth rate. The lower limit of the ALD window was found to be 210 °C below this temperature condensation and high variability of the thickness occurred.

For the experiments that were used to determine that saturation curve, the conditions described in the Materials and Methods section were used. The reactor was at a temperature of 250 °C, and each experiment consisted of 50 cycles. As seen in Fig. 7, at four plugs of precursor pulse and higher, the growth rate per cycle is constant. When less than four plugs of precursor pulsing was used, the growth rate was very low and yielded results that were immeasurable when less than 100 cycles were used.

Cerium oxide was deposited at various thicknesses by varying the number of cycles between 10 and 400 cycles using five plugs of precursor pulsing and the conditions as described in the Materials and Methods section of this paper. The growth followed a linear trend with a growth of 1.2 Å/cycle as seen in Fig. 8. The coefficient of linear determination is 0.9954 which indicates that the process is extremely linear.

## Conclusions

In this study, the optimum atomic layer deposition conditions were found. The precursor temperature was found to be 130 °C and the optimum water pulse length 55 msec for atomic layer deposition of cerium oxide. In this study, ALD window was determined to be 210-280 °C, whereas in previous studies, it was indicated that the ALD window did not exist for this system[6]. When the number of plugs of precursor pulsing was varied, it was determined that deposition occurs optimally at four plugs of precursor pulsing and higher. It was also determined that atomic layer deposition of cerium oxide follows a linear trend with an average growth rate of 1.2 Å/cycle. This is comparable to work using the same precursor and plasma enhanced atomic layer deposition which gave a growth rate of 0.35 Å/cycle[7]. Future work involves using this information to create yttrium doped cerium films for use as the electrolyte and nickel doped cerium films for use as the anode in solid oxide fuel cells.

## Acknowledgements

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(I think you should add here AirLiquide for providing the precursor, we can ask professor Takoudis in the afternoon)

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## Figures

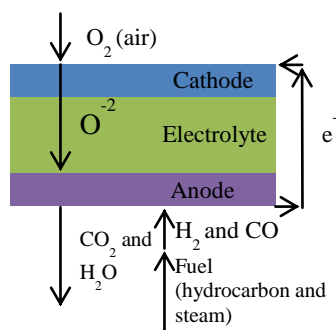


Fig. 1: Fuel is fed to the anode of the solid oxide fuel cell where it is reformed to hydrogen and carbon monoxide while oxygen is feed to the cathode. Electrons provided from the half-cell oxidation reaction at the anode travel through an external electrical circuit to the cathode to reduce oxygen to oxygen ions which flow through the electrolyte.

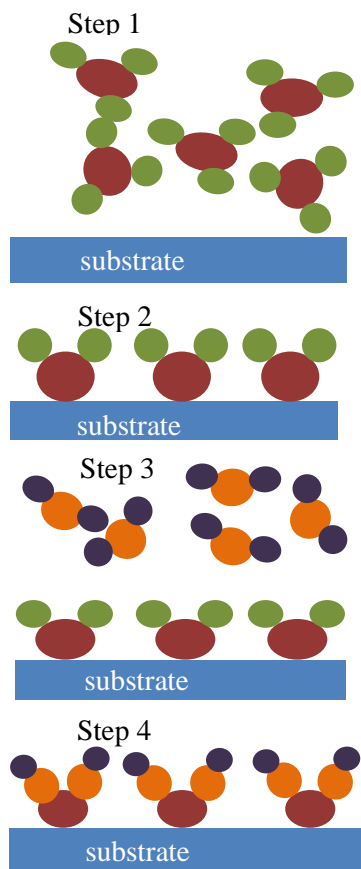


Fig. 2: A single cycle of atomic layer deposition: the introduction of the precursor, the purging of the precursor, the introduction of the coreactant, and the purging of the coreactant and the byproducts.

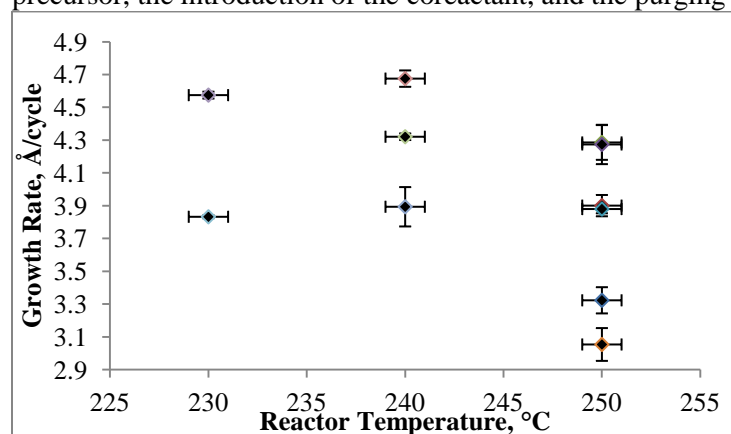


Figure 3: Growth Rate of Cerium Oxide with a precursor temperature of 140 °C for a time of 30 cycles.

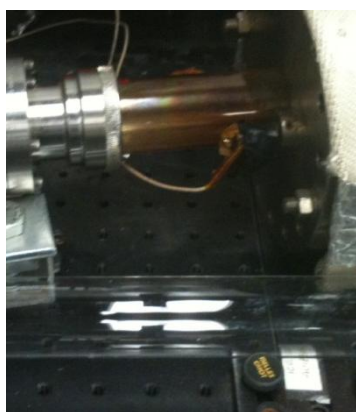


Fig. 4: The dark purple color of the glass tube, which was caused by the condensing of precursor, indicated that excess precursor was being used in the experiments. The original appearance of the cylinder can be seen in the tube sitting below the reactor.

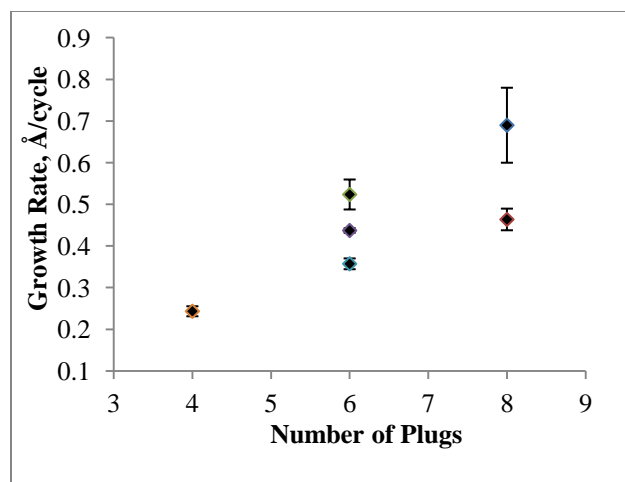


Fig. 5: Results of experiments performed with a precursor temperature of 130 °C, a reactor temperature of 250 °C, and a water pulse of 50 msec. The inconsistencies in the data points were caused by misfires of the water pulse. The length of the water pulse was increased to 55 msec which stabilized the growth rate.

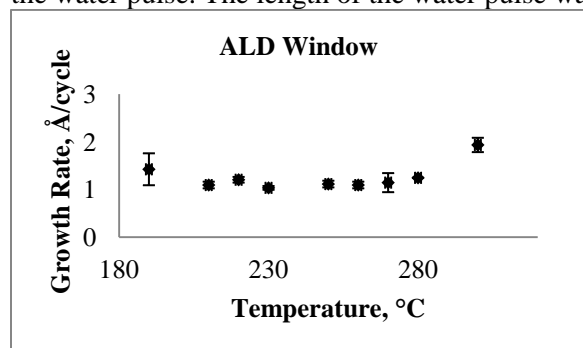


Fig. 6: The data collected for finding the ALD window. Decomposition occurs above 280 °C which gives an increased growth rate.

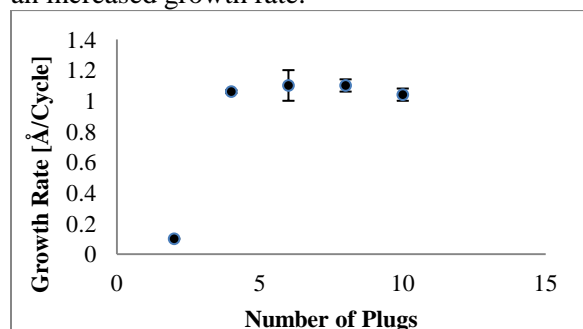


Fig. 7: The saturation curve of the atomic layer deposition of cerium oxide with a precursor temperature of 130 °C, a reactor temperature of 250 °C, a water pulse of 55 msec, and 50 cycles. At four plugs of precursor pulse, the growth rate of cerium oxide stabilizes.

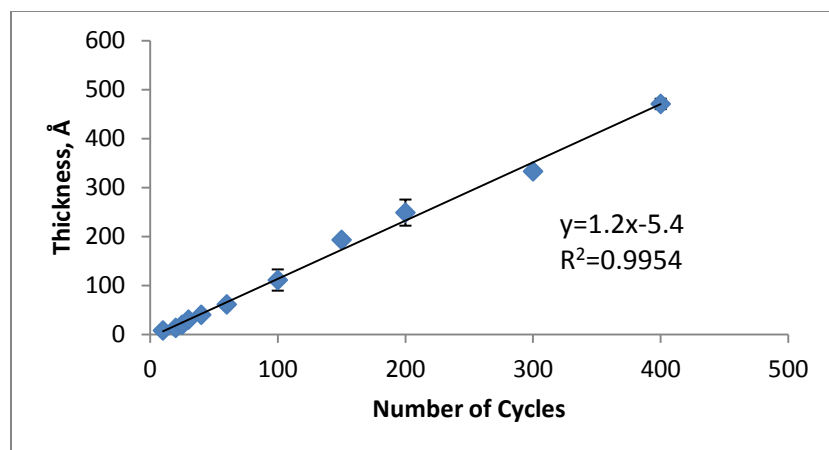


Fig. 8: The linear dependence of the atomic layer deposition of cerium oxide with a precursor temperature of 130 °C, a reactor temperature of 250°C, a water pulse of 55msec, and 5 plugs of precursor pulsing. The growth fits a linear trend with a growth rate of 1.2 Å/cycle and a coefficient of linear determination of 0.9954.