Tunability and Electrical Properties of Yttria-doped-ceria Films Fabricated via Atomic Layer Deposition

R. Sparks
Department of Chemical Engineering
Carnegie Mellon University
rsparks@andrew.cmu.edu
G. Jursich
Department of Bioengineering
Department of Chemistry
University of Illinois at Chicago
jursich@uic.edu
A. Zdunek
Department of Chemical Engineering
University of Illinois at Chicago
zdunek@uic.edu
J. Rossero
Department of Chemical Engineering
University of Illinois at Chicago
jrosse2@uic.edu
C. Takoudis
Department of Chemical Engineering
Department of Bioengineering
University of Illinois at Chicago
takoudis@uic.edu

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Abstract:

Current Solid Oxide Fuel Cell (SOFC) designs have operating temperatures between 800-1000°C.[1] Reducing this temperature to 500-600°C would allow efficient utilization in varied applications.[2] Yttria Doped Ceria (YDC) films show high ionic conductivity when used as fuel cell electrolytes in lower temperature ranges.[3] This investigation shows that stoichiometric tunability of YDC film composition can be achieved through Atomic Layer Deposition (ALD). Film resistivity at room temperature is measured using a custom four-point probe sensor. Controlling doping and thickness allows fabrication of electrolytes with high ionic conductivities.

Introduction:

Automobile emissions are one the biggest contributors to environmental pollution[4]. SOFC's have been considered as a clean replacement for gasoline engines in automobiles, but current technology limits their widespread use.[5] One ongoing issue with SOFC's is that the electrolyte layer separating the anode and cathode is currently operated between 800-1000°C. Previous results suggest that YDC films demonstrate higher ionic conductivity at lower temperatures with 20.2-34 %Y[6 7] concentration and thinner YDC coats.[8] It is possible to achieve precise film compositions and thickness control using ALD.[9]

ALD functions by exposing a substrate to repeated pulses of a precursor gas containing a rare earth metal (RE) followed by a separate pulse of an oxidizing gas. Both gases undergo self-limiting reactions with the –OH tails on the substrate surface. Inert nitrogen gas is used to purge the chamber between pulses and as a carrier gas for the metal precursors and water. The chamber is evacuated by a vacuum pump that maintains pressures of 180 mTorr. The precursor gas bonds to the –OH tails on the substrate. After exposure to the oxidizing gas, the RE contained in the precursor remains bound on the surface with replenished –OH tails to produce the next RE layer. This cycle is repeated until the desired thickness and composition are achieved.[10] Precursor gases can be alternated to produce a film with multiple RE components. The optimum temperature for ALD deposition of ceria and yttria tends to be between 250 and 300 °C.[11] The experiments presented here were conducted at 260 °C. Previous research has demonstrated consistent film growth rates using similar ALD operating characteristics when using tris(methylcyclopentadienyl)-yttrium(III) and tetrakis (2,2,6,6-tetra-methyl-3,5-heptanedionato)cerium(IV) precursors for Y and Ce.[12]

Ce^{4+} in thin films has also been observed reducing to Ce^{3+} [13], increasing unwanted electrical conductivity.[14] Ytrria stabilizes Ce in the Ce^{4+} state to enable continued conductivity by meshing with the Ce lattice structure[15] and increasing oxygen presence in structural vacancies.[16 17] To the best of our knowledge, these properties have not been applied to the challenges of SOFC design. Further investigation is needed before YDC films can enter widespread use as fuel cell electrolytes.

Experimental:

YDC films were deposited on p-type Si (1 0 0) substrates using ALD. A custom ALD instrument (Figure 1) produced all films. Tris(isopropyl-cyclopentadienyl)cerium and Tris(isopropyl-cyclopentadienyl)yttrium (Air-Liquide USA) precursors were used. Film composition was controlled by changing the ALD cycle ratio $Y_{Cycle}/(Ce_{Cycle}+Y_{Cycle})$ and

film thickness was controlled by increasing the total number of ALD cycles. The reaction chamber was maintained at 180 mTorr and 260 °C. Precursors and feed lines were heated to ensure gas did not condense on the reactor manifold before deposition on the surface. Water was used as the oxidizer. The water was kept in an ice bath at 0 °C. Nitrogen from Airgas was used to purge the reactor chamber between pulses and act as a carrying gas for water and the precursors.

YDC sample films were analyzed using X-Ray Photoelectron Spectroscopy (XPS) to determine sample composition. YDC film resistivity was measured using a custom setup. Film thickness was measured using a J.A. Woollam Co. M-44 spectral ellipsometry instrument. A custom 4-point probe for measuring film resistivity was made using a sample stage consisting of 4 Pt wires thread through holes in an acrylic base (Figure 2). The wires were pulled taut and then epoxied into place using high temperature epoxy. The ALD sample was placed face down on the exposed Pt wires. An additional prototype was made using polyethylene as the base material. In addition, a sample stage consisting of 4 Pt wires and a Si wafer with a 100nm thick SiO_2 layer ALD film produced by thermal oxidation on top of a ceramic base was designed for future use (Figure 3). This will provide a smooth nonconductive surface for resistance measurements. Note that the wires in both the acrylic and polyethylene designs are not as straight or flat as required for the final model.

Film resistivity was measured using a QuadTech 7600 Precision LCR Meter Model B four terminal instrument. The instrument was calibrated according to the procedure listed in the instruction manual. Electrical leads with low (<1 Ω) ohmic resistances were connected to the instrument and to unsheathed conductive wires. The calibration was confirmed on several resistors of known resistances. The plastic sample holders described above were tested using the LCR instrument to design the interface between the instrument and the target sample.

Results:

YDC samples were deposited using ALD cycle ratios of 2:1, 1:1, 1:4 (Y:Ce) to determine tunability of the ALD process. In addition, 20% YDC samples (ALD ratio 1:4) with thicknesses between 6-28 nm were deposited to determine optimal operating procedures for the LCR instrument. Previous reports indicate that the growth rate of ceria on silicon substrates is ~1.4Å/cycle.[18] The deposition of yttria on ceria also has a linear dependence between the number of cycles and similar growth rate of ~1.4Å/cycle (Figure 4). It was found that yttria films show stoichiometric tunability with variation of the ALD cycle ratio (Figure 5). XPS spectra of an as-deposited YDC 20% sample (Figure 6) shows that the as-deposited films contain both Ce^{+4} and Ce^{+3}. The film consists of 77 % Ce^{+4} based on analysis performed using the method proposed by Pfau and Schierbaum.[19]

Film resistance was analyzed using the acrylic holder at room temperature (Figure 2). The 6-28 nm 20%Y YDC films were used to determine the optimal settings for the LCR instrument. Adding additional weight to the sample caused the electrical leads to measure the resistance of the substrate and not the film, giving inconsistent results. Subsequent experiments did not use any additional weight. As seen in Figures 7 and 8, low frequencies (100-200 Hz) produced the most accurate results because the current most resembles DC current in that range. The LCR instrument is not capable of supplying DC current, but it can add DC bias to AC current to create more stable resistance measurement

conditions. External DC bias was not necessary since all tests were carried out at high voltage (1-5 V) where the effects of electrical instability are less pronounced. Repeated trials demonstrated that the average resistance across different voltages (Figure 7) converged on a single point. In addition, the choice of voltage had little impact on the reported resistance when in the high voltage range.

The influence of the atomic concentration of yttium in the sample on the sheet resistance was analyzed and presented in figure 8. Little difference in sheet resistance was observed between films of 20 and 30 %Y. This is expected since both concentrations are close to the 20.2-34 %Y range indicating high resistance. Analysis of as-deposited and annealed films also indicates that there is little difference between the two types. Other research indicates that annealing does change resistance when measured at higher temperatures.[20]

Reported resistance for the thin films presented in this paper was comparable to analysis performed on ~0.5 cm thick 20 % Y YDC films.[21] This result cannot be directly compared to our findings as it was taken at 75 or 150 °C. Given that heating the samples tends to decrease resistance, this indicates that our samples are less resistive than the 0.5 cm thick samples.

Conclusion:

YDC thin films can be grown via ALD using $Ce(iprcp)_3$, $Y(iprcp)_3$ and water as precursors. The thickness of the deposited films was highly uniform across all samples and can be controlled by increasing the total number of ALD cycles. The ALD cycle ratio can be changed to accurately change the composition of the film indicating high tunability of the process. Film resistivity measurement at 3 V and 150 Hz was found to be the most suitable settings for taking measurements using the LCR instrument. The film resistivity method and sample holder design is now ready for future use in characterizing samples. In addition, a resistance measurement platform has been designed for future resistance experiments at high temperature (>500 °C).

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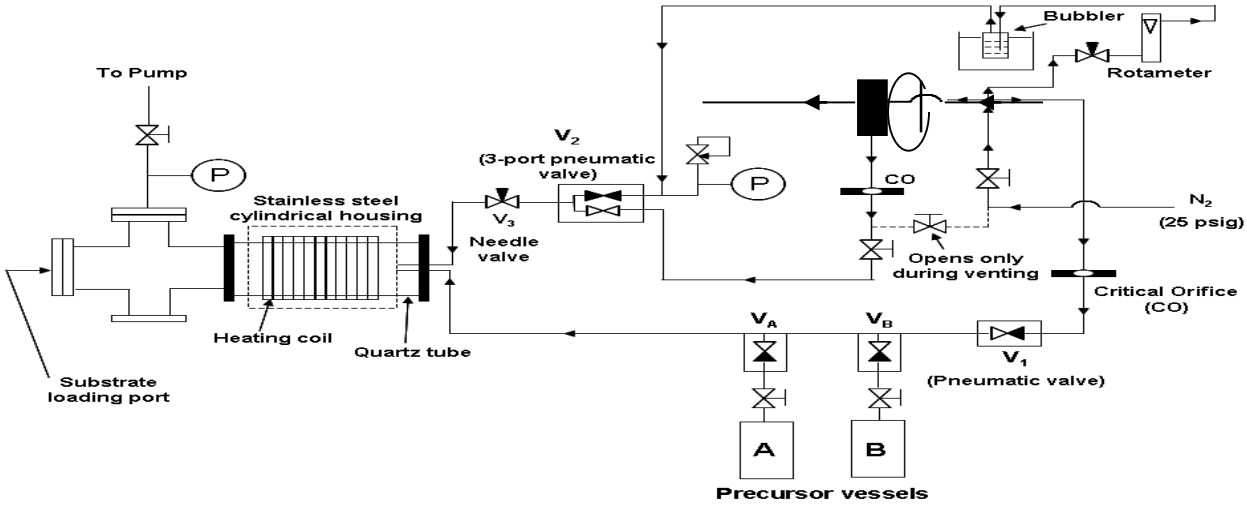

Figure 1: Schematic of ALD instrument

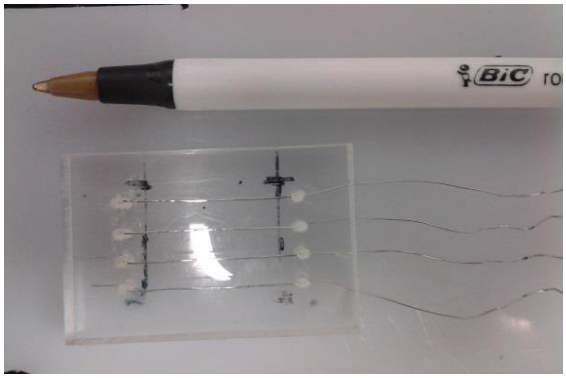

Figure 2: Acrylic model of resistivity measurement holder. Pen is shown for size comparison.

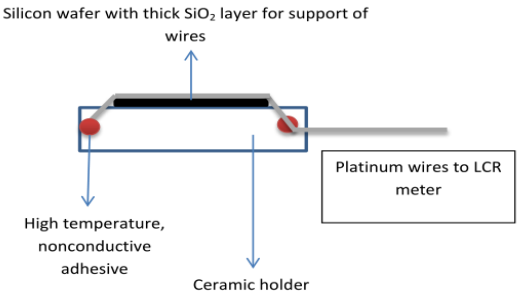

Figure 3: Schematic of resistivity measurement holder. Note that no thin film sample is shown in this schematic.

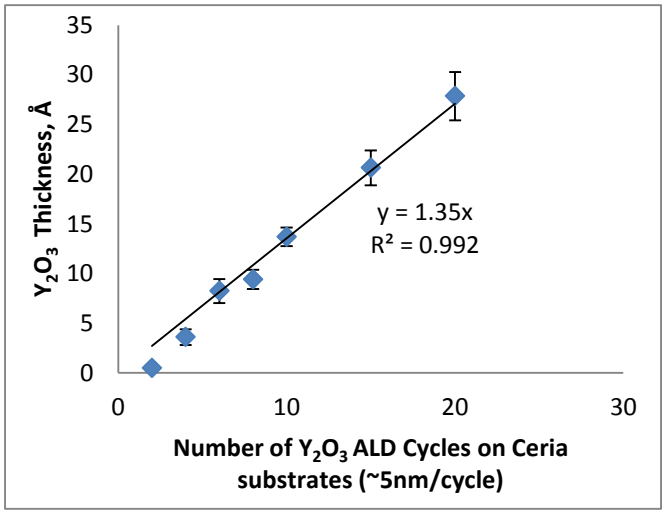

Figure 4: variation of Yttria films thickness with the number of ALD cycle. Yttria films were deposited on ~5nm thick ceria substrates

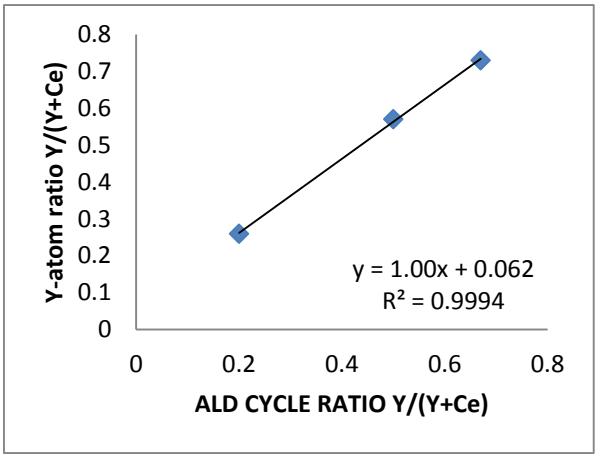

Figure 5: Chart demonstrating ALD tunability. Note the wide range of Y% shown in the chart.

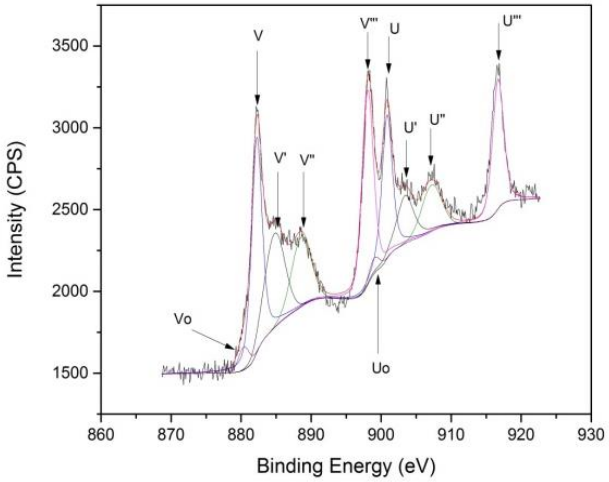

Figure 6: Ce-3d XPS spectra for an as-deposited YDC film with an ALD cycle ratio of 1:4 (Y:Ce). U and V marking indicate peaks used for the Pfau-Schierbaum method.

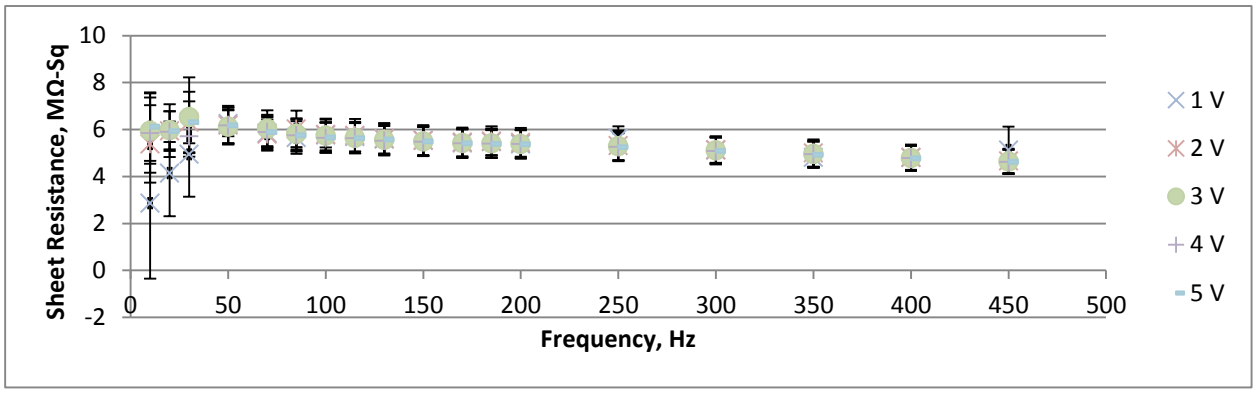

Figure 7: Frequency vs. Sheet resistance of 28 nm thick annealed 20% YDC sample at different frequencies and voltages. Note that the average readings for different voltages tend to cluster together.

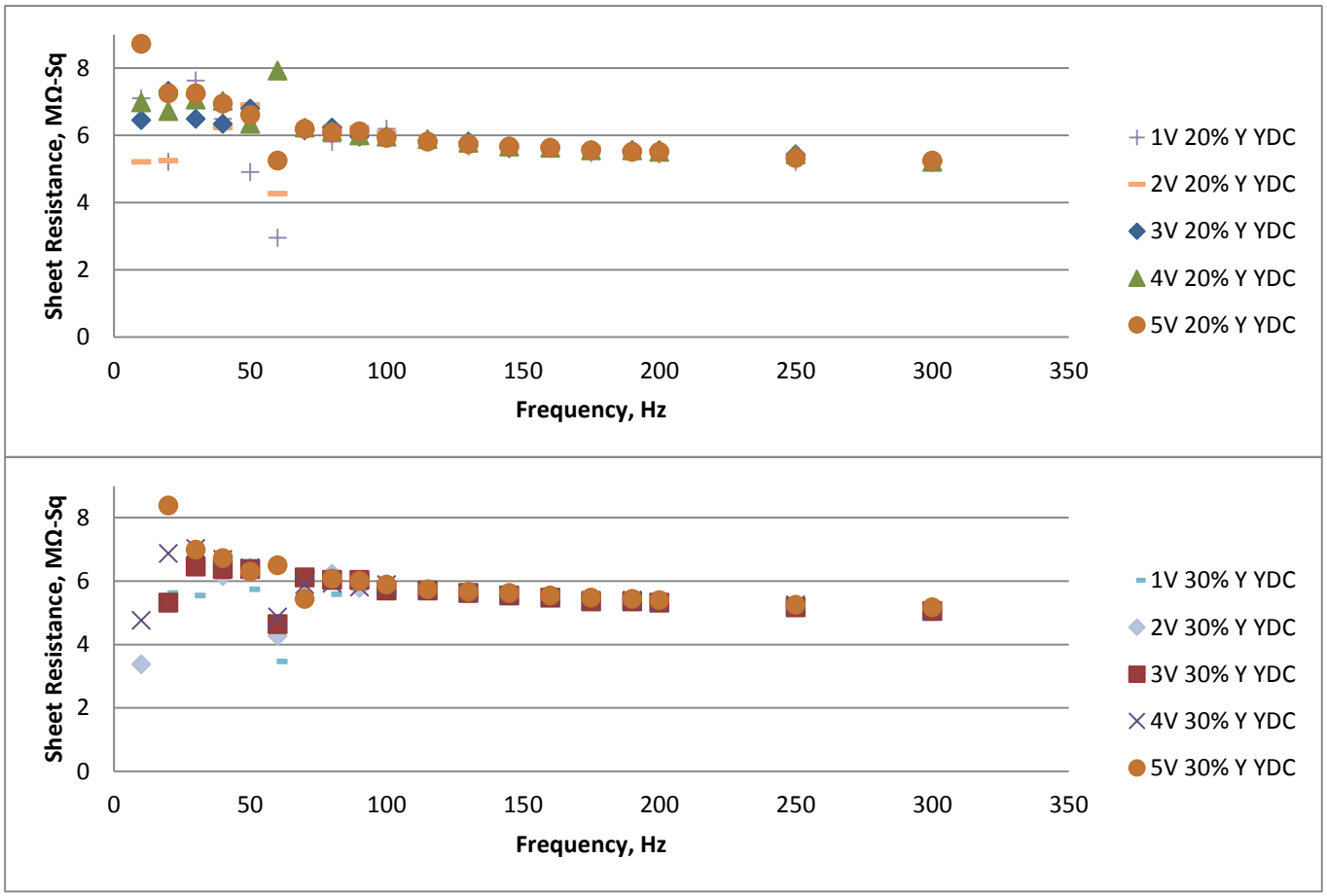

Figure 8:Comparison of frequency vs. sheet resistance for 20 and 30 % YDC films.

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