Chapter 4 The Electrochemical Activity of CELD Ceria Structures

4.1 Introduction, Methods, and Background

4.1.1 A.C. Impedance Spectroscopy (ACIS) Introduction

Any good device design philosophy seeks to identify the area(s) of worst performance and address the appropriate issues. In this way, maximum gains can be efficiently accomplished. As fuel cells involve electrochemical reactions and current flow, both inherently rate-related, the primary inhibiting process is referred to as the "rate-limiting step."

A.C. Impedance Spectroscopy (ACIS) is an invaluable tool for this effort, as it is able to separate relevant processes, such as oxygen ion conduction and electrochemical surface reaction rates, as well as elucidate their associated impedances. Processes are distinguished by probing in the frequency domain, where differing characteristic relaxation frequencies are expected for each process. In brief, a small voltage perturbation is applied to a cell, and the phase-shifted current response is recorded, from which the impedance can be ascertained. A detailed treatment of ACIS as an electrochemical analysis tool can be found in references [94, 97]. For the purposes of this chapter, three basic impedance responses need to be known. As an aid, the complex impedances (*Z*) of a resistor and a capacitor are given below, where *R* is resistance, *C* is capacitance, ω is frequency, and *j* is $\sqrt{-1}$.



Fig. 4.1. A representative Nyquist plot for a PLD film of SDC deposited on single crystal YSZ, on top of which is laid 5-35 μm Pt strip patterns. The equivalent circuit for such a spectra is also given. These data and the equivalent circuit are taken with permission from [1].

$$Z_{resistor} = R \tag{4.1}$$

$$Z_{capacitor} = \frac{1}{j\omega c}$$
(4.2)

Most often, the complex impedances obtained via ACIS are represented as Nyquist plots, where the positive real component is plotted on the x-axis, and the negative imaginary component is plotted on the y-axis. These plots are parametric with frequency, where data points on the right hand side of the plots are the lower frequencies, and those on the left hand side are higher frequencies. For a purely resistive process, with no associated capacitance (or, with a capacitance that cannot be resolved within experimental limitations), there will be no imaginary component, so the impedance will simply be a point on the x-axis (Eqn. 4.1). For a non-diffusion-related, resistive process with an associated capacitance, a semi-circular, symmetric arc manifests in the Nyquist plot, owing to the frequency dependence of the capacitive impedance (see Eqn. 4.2). This case is shown in Fig. 4.1 for a YSZ substrate with SDC layers on either side of it, deposited by PLD, and on top of which is a 5-35 μ m Pt strip pattern. These data are taken with permission from [1]. Each arc that manifests indicates one resistive process; hence, in Fig. 4.1, there is exactly one process that is probed. The resistance of such a process is easily extracted from the Nyquist representation of the complex impedance—it is simply the breadth, or diameter, of the arc on the real (x) axis, or ~16 Ω cm² for the process in Fig. 4.1. This "ohmic offset" is subtracted for ease of comparison for all subsequent plots. Also note that the arc is offset from the origin—this means that the resistive process is in series with a simple resistor. Its origin is the electronic resistance of the oxygen ions in the supporting YSZ substrate. Finally, for a diffusion-related, resistive process, a half tear-drop shaped arc manifests, with a near 45° angled feature at higher frequencies.

Equivalent circuits (with *R* and *C* elements, among others) are used to represent experimentally measured spectra. As an example, the physically-derived equivalent circuit for the spectra in Fig. 4.1 is shown as an inset. This derivation can be quite complicated, however, these equivalent circuits are not unique, meaning there are essentially an infinite number of equivalent circuits that accurately map to a given measured spectrum. To alleviate (but not eliminate, necessarily) this concern, the work in this chapter employs a physically-derived model to establish the equivalent circuit (see ref [26]).

The strategy used here is to correlate the processes measured via ACIS to the physical geometry of the cell. The reason this is useful is because ACIS probes the most

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resistive process for the least resistive serial pathway—this allows the rate-limiting step to be identified. This is done by probing the evolution (or lack, thereof) of ACIS spectra with surrounding atmospheric partial pressure changes and geometric changes. An example of altering the cell's geometry is as follows: if it appears that the rate-limiting process is related to the migration of oxygen ions from point A to point B, then the physical distance from A to B could be doubled, and the impedance response measured again to see if it follows suit. Once a robust correlation is established, systematic architectural changes can be made to maximize electrochemical activity. In addition, the response of the CELD coatings will be compared with that of PLD films deposited on identical substrates.

A quick note on notation is necessary. Electrode impedances (or resistances) that have been normalized by the total deposited area are given as \tilde{Z} (or \tilde{R}), whereas impedances (or resistances) that have been normalized by the projected area of the exposed SDC surface are given as \tilde{Z}^* (or \tilde{R}^*). Accordingly, a resistance value extracted from the Nyquist plots is referred to as an ASR, or area-specific resistance.

4.1.2 Experimental Approach

This chapter is concerned with the evaluation of the ceria-based, template-free HSA microstructures discussed in Chapter 3 as a suitable anode candidate, shown schematically in Fig. 4.2d. To do so, symmetric cells are constructed, where identical electrode configurations exist on both sides of a single-crystal YSZ supporting substrate.

The first two porous metal networks mentioned in Chapter 3, namely platinum strips and nickel anti-dot films, are used as conducting substrates during CELD and

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current collectors during ACIS probing. Recall that the 3PB, 2PB, and metal/YSZ areas are well-defined for both metal networks. The reader is referred to Chapter 3 for detailed characteristics of these current collectors, as the ones used here are identical.

Three different cell configurations are examined, listed here with increasing complexity.

- *Metal-exposed configuration*: this configuration is the model configuration explored in [1], where a PLD SDC layer is situated underneath Pt patterns.
 Both the metal network and the PLD SDC under-layer are fractionally parts of the total exposed surface area, as in Fig. 4.2a.
- Metal-embedded configuration: PLD/CELD coatings are overlaid onto metal networks on YSZ as in Fig. 4.2b and c. Fig. 4.3 shows SEM images comparing a PLD top-layer (4.3ab) and a CELD top-layer (4.3cd).
- Metal-sandwich configuration: first, a dense, 1 µm thick PLD layer is deposited onto a bare YSZ substrate; second, the porous, metal network is laid down as before; and third, PLD/CELD top-layer coatings are overlaid onto both the metal and exposed PLD-SDC, as in Fig. 4.2d and e.

The CELD HSA coatings are deposited with the Sm-doped electrolyte solution and at 0.8 mA cm⁻², a la Chapter 3. The PLD films are deposited at 300 mJ and 5 mtorr pO_2 , at a substrate temperature of ~650 °C. These samples were provided by Dr. William Chueh and Dr. Yong Hao, and the details of the PLD film deposition procedure can be found elsewhere [1, 31].

Once made, the cells are evaluated in a symmetric gas configuration, meaning the same atmospheric conditions (e.g., flow rate, partial pressures) are experienced on both



Fig. 4.2. Schematics showing surface reaction locations for two-phase boundary (2PB), mixed ionic-electronic conducting substrates (a); PLD (b) and CELD (c) embedding Pt strips; and PLD (d) and CELD (e) sandwich configurations. In (b) and (c) electronic conduction across the deposited layer that lies on top of the metal is inhibited and the field lines are accordingly confined to the nominal 3PB region; in (d) and (e), the same inhibition exists as in (b) and (c), but the field lines are free to readjust themselves to accommodate the newly available underside of the metal. The left column is PLD films, and the right column is CELD coatings. The rows indicate identical configurations.

sides of the YSZ substrate. The primary reason for this is convenience—no sealing is required, and the gas delivery system is simpler.

The electrochemical characterization system consisted of a vertical furnace tube reactor system, through which gas was continually flowed at a total flow rate of ~101 sccm, controlled by MKS PR 400 controllers and MKS mass-flo controllers. Three gas lines were used to achieve specific hydrogen and water partial pressures: a dry, pure hydrogen line; a dry, pure argon line; and a humidified 0.1% hydrogen in argon line. Humidification was achieved by passing the 0.1% H₂ in Ar line through a variable



Fig. 4.3. SEM images showing PLD top-layer (a and b) and CELD top-layer (c and d) metal-embedded configurations. Depositions are performed at the standard conditions given in the corresponding text.

temperature bubbler. Impedance data were collected using a Solartron 1260A frequency response analyzer at zero bias with a 20 mV perturbation amplitude via an in-house Labview program. Four platinum wires were used to minimize inductance loops. Platinum was chosen for its inertness in oxidative/reductive atmospheres.

4.1.3 System Precedence

Previous detailed work has been reported on an analogous, symmetric cell configuration consisting of PLD thin film SDC on YSZ substrates overlaid with lithographically patterned metal current collectors, as in Fig. 4.2a [1, 26, 31-32].

In those experiments, only one semi-circular arc was manifested (see Fig. 4.1), and was unambiguously determined to be related to the SDC|gas interface. This necessarily means that for this model system, the surface reaction that occurs at the SDC|gas interface is rate-limiting. This simple system is used to provide insight into interpretation of the following data obtained for more complex systems, namely those given schematically in Fig. 4.2.

4.2 Arc Identification: PLD Films vs. CELD Coatings

4.2.1 Representative Spectra

A representative sampling of ACIS spectra taken from metal-embedded cells (Fig. 4.2b and c) under identical conditions is shown in the Nyquist plot of Fig. 4.4. The three cells shown are PLD embedding platinum strips (open circles), CELD embedding platinum strips (open triangles), and CELD embedding a nickel anti-dot film (open squares). Each sample was probed in different gas environments, an example of which is shown for the CELD embedding a nickel anti-dot film in Fig. 4.5. As indicated by the notation, the impedance is normalized by the total deposited area, irrespective of the metal network geometry. Significantly, all spectra of the embedded metal geometry exhibited two similar arcs, even though the SDC deposition techniques are different, and, in the CELD case, different metal networks are used. Recall that frequency is swept from low to high, which is right to left in the Nyquist plots; accordingly, the arc on the right-hand side is referred to as the LF (low frequency) arc, and the arc on the left is the HF (high frequency) arc. From these spectra, it is evident that PLD films have larger LF arcs than the CELD coatings. Also, the HF arc is similarly sized for the PLD/Pt strip and CELD/Pt strip samples, but is slightly smaller for the CELD/Ni anti-dot sample.



Fig. 4.4. (a) Representative Nyquist plots exhibiting the two arc behavior for PLD embedding 5-5 μm Pt strips (open circles), CELD embedding 5-5 μm Pt strips (open triangles), and HSA CELD embedding a Ni anti-dot network with 1.4 μm pores (open squares); (b) a magnified view of the CELD/Pt strips' LF arc; (c) a magnified view of the CELD/Ni anti-dot network's LF arc. Solid lines are the results from the fits to the equivalent circuit shown as an inset in (a); and the dotted lines are simulations of the arcs as a guide to the eyes. The normalization is the entire deposited area for all three cases here.



Fig. 4.5. Representative hydrogen (a) and water (b) partial pressure dependence of a Ni anti-dot-embedded CELD sample. The anti-dot pores are 1.4 μm and the CELD is deposited at the HSA conditions. The HF arc is relatively static with partial pressure changes, whereas the LF arc strongly depends on the gas atmosphere. The normalization is the entire deposited area. The plots in (c) and (d) are magnified views of the LF arcs in (a) and (b), respectively.

Analogously, a representative sampling of ACIS spectra taken from metalsandwich cells under identical conditions is shown in the Nyquist plot of Fig. 4.6, again with the resistance normalized by the total deposited area. The two samples shown here are PLD sandwiching platinum strips (c.f. Fig. 4.2d; seen in Fig. 4.6 as open squares), and CELD sandwiching platinum strips (c.f. Fig. 4.2e; seen in Fig. 4.6 as open triangles). Only one arc can be seen for both PLD- and CELD-platinum sandwich samples, which manifests at lower frequencies. Although the sandwich configuration has a more complex fabrication, the response is simpler, so it is considered first in the analysis below.



Fig. 4.6. Representative Nyquist plot of a PLD/Pt strips sandwich (open squares); and a CELD/Pt strips sandwich (open triangles). In both cases, there is only one arc. Solid lines are the results from the fits to the equivalent circuit from Fig. 4.1. The normalization is the entire deposited area.

4.2.2 Origin of the Single Arc in the Metal-Sandwich Configuration

Recall that the sandwich configuration for both PLD and CELD samples yields a single impedance arc (c.f. Fig. 4.6). Also recall that the model system of a SDC PLD film with Pt strips exposed yields a single arc (c.f. Fig. 4.1). The hydrogen gas dependence of the resistance values from these three samples are compared in Fig. 4.7—namely, the PLD/Pt strips-exposed configuration (black squares), the PLD/Pt strips-sandwich configuration (blue triangles).



Fig. 4.7. Hydrogen partial pressure dependence of the solitary arc resistance values for PLD/Pt strips exposed (black squares), PLD/Pt strips sandwich (red circles), and CELD/Pt strips sandwich (blue triangles) configurations. The normalization is the projected area of the exposed ceria surface. Solid lines are guides to the eyes.

Both the absolute values and gas dependence of the ASRs for each sample are comparable. This strongly suggests that the single arc in the model PLD/Pt strips exposed system is the same as the single arc in the PLD and CELD/Pt strips sandwich configurations. Consequently, it can be concluded that this arc is due to the interface between the SDC surface and the surrounding gas, for each sample compared in Fig. 4.7.

One notable peculiarity remains, however. When CELD is used as the top coating in a platinum-sandwich configuration, the absolute ASR values of the SDC|gas arc do not decrease as would be expected from the higher surface area accessed by the HSA CELD coating. Upon *ex situ* SEM analysis of the CELD/Pt sandwich sample, it can be seen that the CELD coating on the exposed SDC only slightly enhances the surface area, in



Fig. 4.8. SEM images of a CELD/Pt strip-sandwich configuration after testing at 650 °C for ~24 hours: (a) the top-layer CELD does not significantly enhance the surface area over the exposed PLD SDC regions, where some cracking is observed; (b) highly angled view of the phenomena in (a); and (c) the deposit lying on top of the Pt strips appears disconnected from the deposit on the exposed SDC regions, and can be seen here uncovering the Pt strip altogether.

contrast with CELD coatings on YSZ (compare Figure 4.8ab to Figure 4.2cd). Also seen in Figure 4.8, the part of the CELD coating that lies on top of the metal network appears disconnected from the coating on top of the SDC. This is likely due to the volume reduction that inevitably happens when electrochemically deposited oxide material is annealed—this adverse effect is exacerbated for thicker samples like the one shown here. The CELD deposits on Pt/YSZ surfaces also exhibit this behavior, but restricted to a small area in the vicinity of the liquid electrolyte meniscus. A break of this fashion is tantamount to completely nullifying the activity of the SDC above the metal, as no continuous pathway for oxygen ions exists. Furthermore, non-trivial cracking in the first PLD layer is observed when the second layer is deposited via CELD, but not PLD. This could be due to thin film stresses induced by a slight lattice expansion, arising from the reduction of Ce^{4+} to Ce^{3+} in the underlying SDC PLD layer during the cathodic electrochemical deposition. These factors undoubtedly affect the measured ASR for CELD/metal-embedded samples.

4.2.3 Origin of the HF Arc in Embedded Metal Configurations

Now consider only the HF arc for the metal-embedded configurations shown in Fig. 4.4. Analogously to the previous section, the hydrogen partial pressure dependence of the HF ASR values extracted from the Nyquist plots is shown in Fig. 4.9 for the same three samples from Fig. 4.4—namely, PLD/Pt strips-embedded (black open squares), CELD/Pt strips-embedded (blue open triangles), and CELD/Ni anti-dot-embedded (red open circles) configurations. Note the nearly flat response of the metal-embedded configurations' HF ASRs to changing hydrogen partial pressure. This is true regardless of deposition technique or the metal network underneath. The water dependence is similarly weak (not shown). The apparent lack of partial pressure and fabrication technique dependence of the HF arc suggests a configurational origin, one that is shared between PLD and CELD samples. To further investigate the origin of the HF arc, embedded Pt strip samples of large pattern sizes are analyzed.

Four exotic platinum patterns are utilized to tease out robust dependencies related to the HF arc—50-100 μ m, 50-500 μ m, 50-900 μ m, and 50-1300 μ m. When the metal spacing is increased beyond 100 μ m, the HF ASR values show appreciable hydrogen/water partial pressure dependence, eventually exhibiting equal but opposite

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Fig. 4.9. Hydrogen partial pressure dependence of the HF arc resistance values for PLD/Pt strips-embedded (black open squares), CELD/Pt strips-embedded (blue open triangles), and CELD/Ni anti-dot-embedded (red open circles) configurations. The normalization is the projected area of the exposed ceria surface. Solid lines are guides to the eyes.

slopes in the log-log plots of Fig. 4.10a and b. This suggests that the HF arc is an electron-related process, as the electronic carrier concentration is oxygen partial pressure dependent [27, 31, 94]. For the same pattern sizes, the ASRs also show a strong relationship to the nominal 3PB length and lateral metal spacing (Fig. 4.10c and d). These dependencies, like the oxygen partial pressure dependence, decrease in intensity as the pattern sizes are made smaller. Also of note is the fact that these HF arcs are decidedly semi-circular, as opposed to half tear-drop shaped, suggesting that neither oxygen ion nor electron diffusion are rate limiting, even on length scales approaching millimeters. These data imply the SDC-metal interface as the origin of the HF arc.



Fig. 4.10. HF resistance water (a) and hydrogen (b) partial pressure dependence of PLD embedding Pt strips of large pattern sizes taken at 650 °C; deviation from an explicit oxygen partial pressure dependence can be seen in the smaller patterns. HF resistance three-phase boundary (c) and metal spacing width (d) dependencies are shown for the same samples as in (a) and (b); again, deviation from the strong dependencies can be seen for the smaller pattern sizes. Solid lines are guides to the eyes.

Consider the SEM image in Fig. 4.3b and the corresponding schematic in Fig. 4.2b. SDC deposited via PLD on top of single-crystal YSZ produces epitaxial, singlecrystal growth [1, 31]. However, SDC deposited via PLD on top of the platinum strips is polycrystalline and columnar. The columns are oriented perpendicular to the platinum surface, which would cause in-plane electronic migration to be highly resistive. This forces the electron migration paths from a surface reaction site that lies above YSZ, where they are generated, to the nominal 3PB region (see Fig. 4.2b). The coalescence of the field lines to the sides of a 200 nm thick platinum strip manifests as an additional arc at higher frequencies. Electrons that are generated directly above the metal are not restricted in this way, since they only have to travel along the columns' length to access the metal.

CELD samples also exhibit a HF arc, indicating that a similar restriction occurs, albeit for a different reason. Figure 4.11a shows a TEM image of a CELD deposit on top of a platinum surface, which has been annealed at 650 °C for 2 hours in air. Across the entire metal surface, a layer approximately 10 nm thick of dense SDC can be seen. Above this initial layer, sheets and needles of SDC randomly intersect with one another on both the metal and YSZ areas. However, gaseous hydrogen evolution occurs on the metal surface during CELD, making the deposit more porous on the metal than on the YSZ (c.f. Chapter 3). This is schematically shown in Figure 4.2c and confirmed by TEM imaging—a partial view of the inevitable voids above the metal area can be seen in a matrix of SDC in Figure 4.11a. Similar to the PLD case, lateral electronic migration is particularly resistive through the SDC that lies on the metal. An analogous restricting



Fig. 4.11. TEM images of an annealed (650 °C in ambient air for 2 hours) CELD SDC deposit on a Pt surface, showing the continuous 10 nm thick layer, off of which tortuous nanosheets/needles grow, but with significant voids, particularly above the Pt surface (a) and in the 3PB regions (b). The slight texturing in the SDC deposit is FIB damage incurred during the lift-out process. Images obtained with assistance from Carol Garland, Caltech.

effect occurs for the electronic field lines in the CELD deposits, producing the familiar HF arc. This effect is possibly further exacerbated by an incomplete CELD coating, particularly in the immediate region surrounding the 3PB. Figure 4.9b shows such a void, whose effect would be to reduce the accessible SDC|metal interface even more.

Consistent with this picture, the absolute value difference of the HF ASRs for the CELD/Pt strips-embedded and CELD/Ni anti-dot-embedded samples (see Fig. 4.9) can be explained by their respective metal network thickness difference. The Pt strips are 200 nm thick, whereas the Ni anti-dot network is 400 nm thick.

This electronic pathway restriction theory is confirmed by the metal-sandwich configuration impedance response, namely that the deleterious HF arc disappears and the remaining, lone arc is identical to the single arc of the PLD/Pt strips exposed configuration. The disappearance of the HF arc can be explained as follows. Although the electronic migration through the SDC above the metal areas for both the PLD and CELD top layers is highly resistive, the presence of a PLD SDC under-layer allows the electronic field lines to be redistributed to the entirety of the underside of the metal, shown schematically in Fig. 4.2d and e.

4.2.4 Origin of the LF Arc in Embedded Metal Configurations

Consider now the LF ASRs of the metal-embedded configurations (c.f. Fig. 4.2c and d), whose hydrogen partial pressure dependencies are shown in Fig. 4.12—specifically, the PLD/Pt strips-embedded (black squares), the CELD/Pt strips-embedded (blue triangles), and the CELD/Ni anti-dot-embedded (red circles) configurations are compared. Also included is the data for the single arc in the PLD/Pt strips exposed model system (green upside-down triangles). Comparing the PLD/Pt strips exposed data to the PLD/Pt strips-embedded data, the absolute values and dependencies are almost identical. According to [1], this is within an expected level of variation for the same surface-dominated process. From this comparison, a confident connection can be made between the single arc in metal-exposed configurations and the LF arc in metal-embedded configurations—their origins are from the same surface-dominated, SDC|gas interfacial resistive process.

The context is now complete for understanding the LF arc behavior of CELD/metal-embedded samples. Using Fig. 4.12 as a guide, it can be seen that both the CELD/Pt strips-embedded and CELD/Ni anti-dot-embedded samples exhibit similar hydrogen gas dependencies as the PLD/Pt strips-embedded sample. However, their absolute values are 25 - 50x smaller. Taking the gas dependence similarity to be an indication that the LF arc for the CELD/metal-embedded samples is also surface-related, a simple surface area argument can explain the absolute value difference between these



Fig. 4.12. Hydrogen partial pressure dependence of the LF arc resistance values for PLD/Pt stripsembedded (black squares), CELD/Pt strips-embedded (blue triangles), and CELD/Ni anti-dotembedded (red circles) configurations. Also for comparison, the single arc gas dependence for the PLD/Pt strips exposed configuration is shown (green upside-down triangles). The normalization is the projected area of the exposed ceria surface. Solid lines are guides to the eyes.

samples. Indeed, Fig. 4.3a and c show a surface area increase on that order obtained per projected area when using CELD as the top coating. Despite the overall microstructural similarity in the CELD deposits, there is some sample-to-sample surface area variation, which manifests itself as the difference in ASRs between the two CELD samples. These observations establish the LF arc in CELD/metal-embedded configurations to be the SDC|gas interface.

4.3 The SDC|Gas Interface Arc: A Closer Look

The following is a brief summary of the results from Section 4.2. It was determined that the single arc that manifested for the metal-sandwich configurations and the LF arc for the metal-embedded configurations are both due to the SDC|gas interface. Hereafter, this arc is referred to as the "SDC|gas interface arc." This arc is scrutinized in greater detail in this section, with the goal of reducing its associated ASR. Because of the undesirable ASR increase that occurs when utilizing the CELD/metal-sandwich configuration, this section utilizes the CELD/metal-embedded configuration, despite the presence of the HF arc. The SDC|gas interface arc is taken to accurately represent the potential for CELD as a fabrication method for producing highly active electrode structures, and, as such, is the only arc examined from here on out. The rest of the chapter is organized by the metal network that is used.

4.3.1 Platinum Strips

Four experimental parameters are varied to ascertain their effect on the SDC|gas interfacial ASR. For each, the gas dependence of the ASR is evaluated, and an attempt to correlate the observed behavior to the deposit geometry via SEM is made. The impedance is normalized by the projected area of the exposed SDC surface.

1. Platinum pattern size effect: 5-5 μm vs. 20-20 μm.

Undoped HSA ceria is deposited on two platinum pattern sizes, 5-5 μ m and 20-20 μ m. Their interfacial reaction resistance gas dependencies are shown in Fig. 4.13, where it can be seen that the 5-5 μ m pattern ASR absolute values are 2 – 3*x* smaller than their 20-20 μm counterpart. Examining the SEM images in Fig. 4.14 reveals a stark difference between the total deposition coverage for the two pattern sizes. Both patterns have qualitatively similar deposition on the platinum strip portion of the substrate, but the 20-20 μm pattern only has disconnected, island-like growth on the exposed YSZ portion of the substrate. In contrast, the 5-5 μm pattern has well-connected, HSA growth on seemingly all portions of the substrate, platinum and YSZ alike. Despite the fact that both patterns have nominally 50% platinum and 50% YSZ exposed surfaces, the lack of quality deposition on the YSZ portions lying greater than a few microns away from the base generating metal portions of the substrate causes a decrease in performance. This defines a lateral metal spacing limitation; consequently, only patterns with feature sizes equivalent to (or below, for the nickel anti-dot films) 5-5 μm are subsequently used.



Fig. 4.13. Water (a) and hydrogen (b) partial pressure dependencies of the SDC|gas interfacial ASR for 5-5 μm (squares) and 20-20 μm (circles) CELD/Pt strips-embedded samples deposited for 10 minutes with the undoped electrolyte.



Fig. 4.14. SEM images of the samples probed in Figure 4.13: (a) and (b) are top-down views of the 20-20 μm sample; (c) and (d) are angled views of the 5-5 μm sample. The inset in (b) is an isolated HSA ceria growth in the center of a 20 μm wide YSZ region, pictured in low magnification in the rest of (b).

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2. CELD deposition time effect: 5 vs. 10 (vs. 20) min.

Both CELD undoped and Sm-doped HSA ceria microstructures are evaluated at different deposition times—5 and 10 minutes for the undoped ceria, and 5, 10, and 20 minutes for the Sm-doped ceria.

Figure 4.15 shows the gas dependencies for undoped ceria deposited for 5 and 10 minutes. The only real difference is under water partial pressure change, where the 5 minute sample exhibits a sharper slope. Comparing SEM images for the two samples at equal magnification shows a slight qualitative decrease in apparent surface area for the 10 minute sample (Fig. 4.16). The deposit that lies on top of the platinum strips in the 10 minute sample has less wispy features than that grown on the YSZ surfaces, and as compared to all areas of the deposit grown for 5 minutes. This observation holds true for multiple samples and multiple configurations—prolonged depositions tend to reduce the apparent surface area of the coatings grown on metal surfaces.

Analogously, Figure 4.17 shows the partial pressure dependencies for Sm-doped ceria deposited for 5, 10, and 20 minutes. Similarly to the undoped comparison, the ASRs are essentially the same, although the 10 minute sample performed slightly better in water. The SEM images in Figure 4.18 show a slight deposition coverage increase in going from 5 to 10 minutes of deposition, and the familiar chunky morphology is observed for the 20 minute sample. Recall from Chapter 3 that the deposition rate for Sm-doped ceria is slower than that of undoped ceria. 5 minutes of Sm-doped ceria CELD is not enough to cover the sample with the HSA morphology, hence its higher ASRs as compared to the 10 minute sample. Just like the undoped case, however, chunky coatings over the platinum areas due to prolonged deposition times also increase the ASR.

These results indicate an optimal deposition time—approximately 5 minutes for undoped ceria and approximately 10 minutes for Sm-doped ceria.



Fig. 4.15. Water (a) and hydrogen (b) partial pressure dependencies of the SDC|gas interfacial ASR for 5 minute (squares) and 10 minute (circles) depositions for 5-5 μm CELD/Pt strips-embedded samples with the undoped electrolyte.



Fig. 4.16. SEM images of the undoped samples probed in Fig. 4.15: (a) a 5 minute deposition on a 5-5 μm pattern; (b) a 10 minute deposition on a 5-5 μm pattern.



Fig. 4.17. Water (a) and hydrogen (b) partial pressure dependencies of the SDC|gas interfacial ASR for 5 minute (squares), 10 minute (circles), and 20 minute (triangles) depositions for 5-5 μm CELD/Pt strips-embedded samples with the doped electrolyte.



Fig. 4.18. SEM images of the doped samples probed in Fig. 4.17: (a) a 5 minute deposition on a 5-5 μ m pattern; (b) a 10 minute deposition on a 5-5 μ m pattern; and (c) a 20 minute deposition on a 5-5 μ m pattern.

3. Cation doping effect: undoped vs. Sm-doped ceria.

The doping effect for samples deposited for 5 minutes can be seen in Figure 4.19. There appears to be little to no impact introduced by samarium doping. Considering the similarities in microstructure seen in Figure 4.20, and the short distance charged species must travel, this result is not surprising. Indeed, samarium is not expected to aid the surface reaction kinetics much, and is instead introduced to increase the oxygen vacancy concentration, as in Eqn. 1.5. Conversely, there is a difference in the performance of undoped and Sm-doped samples deposited for 10 minutes, as seen in Figure 4.21, but judging from the SEM images of Figure 4.22, it is likely that this difference is due to slight surface area differences, rather than surface reaction kinetics. Similar to the preceding section, the deposition rate difference between the undoped and Sm-doped samples appears to be the primary culprit here.

Despite the minimal difference for samples deposited for 5 minutes, Sm-doped ceria is preferred over undoped, if for no other reason than compatibility with a Sm-doped ceria electrolyte solution.



Fig. 4.19. Water (a) and hydrogen (b) partial pressure dependencies of the SDC|gas interfacial ASR for undoped (squares) and doped (circles) electrolyte depositions for 5 minutes for 5-5 µm CELD/Pt strips-embedded samples.

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Fig. 4.20. SEM images of the 5 minute deposition, 5-5 µm pattern samples probed in Fig. 4.19: (a) with the undoped electrolyte; and (b) with the doped electrolyte.



Fig. 4.21. Water (a) and hydrogen (b) partial pressure dependencies of the SDC|gas interfacial ASR for undoped (squares) and doped (circles) electrolyte depositions for 10 minutes for 5-5 µm CELD/Pt strips-



Fig. 4.22. SEM images of the 10 minute deposition, 5-5 μm pattern samples probed in Fig. 4.21: (a) with the undoped electrolyte; and (b) with the doped electrolyte.

4. Consecutive deposition effect: 5 vs. 5+5 minutes.

Section 3.3.2 outlined the high temperature behavior of the HSA coatings. Therein, undesirable cracking issues were defined, and subsequent depositions were investigated as a possibility to "healing" cracks induced either by the deposition process itself, or a later annealing step. To assess the electrochemical activity impact of consecutive depositions on a single sample, a Sm-doped sample deposited for 5 minutes was subjected to an annealing step at 600 °C for 10 hours. The un-cracked, as-deposited morphology is shown in Fig. 4.24a, and the cracked, as-annealed morphology is shown in Fig. 4.24a, and the cracked, as-annealed morphology is shown in Fig. 4.24b. The sample was then probed for the first time via ACIS. Immediately following the testing step, a second 5 minute deposition was performed on the same sample, pictured in Fig. 4.24c. Then, the sample was probed for the second time via ACIS, and is pictured in its final post-second-testing state in Fig. 4.24d.

As can be seen in Figure 4.23, there is practically no change in activity between the 5 and 5+5 minute samples. This is a telling result, indicating that cracking in the HSA morphology is not a significant concern. Fig. 4.24cd exhibits the expected deposition in the former cracks of the sample, yet no impact on the ASR is detected. Although cracking seems intuitively counterproductive, the cracking observed in these samples is on a length scale so as to not prevent the migration of charged species. In fact, in-plane cracking propagated perpendicularly to the length of the platinum strips will not impact movement of charged species in the same perpendicular direction, as is the case for this electrode configuration. If there was significant in-plane cracking along the length of the platinum strips, then there would be an insurmountable barrier for oxygen ions to traverse, in order to access surface reaction sites on top of the metal strips.

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From a different perspective, the possibility exists to create even more surface area by consecutive depositions due to concentration on the cracked areas. For this reason, and because it is now known to not have an adverse effect, consecutive depositions are still pursued in practice.



Fig. 4.23. Water (a) and hydrogen (b) partial pressure dependencies of the SDC|gas interfacial ASR for a 5-5 μm CELD/Pt strips-embedded sample that underwent two consecutive 5 minute depositions, with a high temperature step in between: the first 5 minute deposition (squares) and the second 5 minute deposition, referred to as 5+5 minute (circles), with the doped electrolyte are shown.



Fig. 4.24. Chronological SEM images of the 5-5 μm pattern sample probed in Fig. 4.23: (a) the asdeposited, un-cracked morphology after the first 5 minute deposition; (b) the cracked morphology after annealing at 600 °C for 10 hours in air; (c) the as-deposited morphology after the second 5 minute deposition, healing the cracks; and (d) the cracked morphology post-testing for the second time.

The following is a summary of the insights gained from the above experiments. First, the furthest non-conducting surface distance away from the base electrogenerating metal features should not exceed 3 microns. Prolonged depositions tend to lead to chunky, lower surface area coatings on the metal portions of the substrate. This motivates a reduction in the exposed metal area fraction, but is limited in practice by thermal stability of micro-/nano-sized metal features. 5 minute depositions are preferred for undoped samples, and 10 minute depositions are preferred for Sm-doped samples—the difference is due to the deposition rate influence of cation doping. Sm-doped samples are preferred due to their inherent transport properties, but surface kinetics do not appear to be impacted at all. Healing cracks by consecutive depositions does not harm the electrode activity, but could lead to a further enhancement of surface area; also, cracking does not appear to be a critical concern in this electrode configuration.

Using the trends with partial pressures, these data can be extrapolated to 97% H₂, 3% H₂O, at 650 °C. The best samples give SDC|gas interfacial ASRs in the range $1.3 - 3.7 \text{ m}\Omega \text{ cm}^2$, far below the state-of-the-art at the time of this writing [24-25].

4.3.2 Nickel Anti-Dot Films

Two experimental parameters are investigated for the CELD/Ni anti-dot-embedded configuration, analogous to the treatment of platinum strip samples given above.

1. CELD deposition time effect: 5 vs. 10 vs. 20 + 2.5 minutes.

The SDC|gas interfacial ASRs of three nickel anti-dot samples are compared in Fig. 4.26, with different depositions times—namely, 5 + 2.5 minutes, 10 + 2.5 minutes, and 20 + 2.5 minutes samples. A 2.5 minute consecutive deposition is used in all three cases. Not much difference can be discerned from the partial pressure dependence plot, although there is a slight ranking under changing pH₂O, with the 10 minute besting the 5 minute and 20 minute samples, in that order. A microstructure investigation revealed some offsetting issues.

All three samples suffer from asymmetric deposition on what should be identical sides of the cell. This is due to an experimental shortcoming. When a sample is dipped into the liquid electrolyte (c.f. Fig. 3.2), one side of the cell is directly facing the counter electrode, whereas the other is facing away from it. The side facing the counter electrode

experiences faster deposition rates than the side facing away. This is shown in Fig. 4.25, where each row of images is a different sample, and the first three images of the first column, i.e., 4.25a, c, and e, represent the side facing away from the counter electrode, and the first three images of the second column, i.e., 4.25b, d, and f, represent the side directly facing the counter electrode. Clear deposition maturity differences can be seen between the two sides of each sample. Longer deposition times develop slat-like growth on top of the original HSA morphology, seen in Fig. 4.25d, f, and h; however, in-between the slats lay ideal HSA morphology (Fig. 4.25g). The 20 minute sample even sees HSA growth on top of the slats, although the slats begin to warp and fold, disconnecting themselves from the underlying layer (Fig. 4.25h).

These features notwithstanding, the critical characteristic that appears to dominate the ultimate performance is overall coverage. The 5 minute sample left innumerable micro-sized regions devoid of the HSA morphology, as in Fig. 4.25a. The 20 minute sample had large areas completely uncovered by any deposit, HSA or not. The 10 minute sample, on the other hand, was the most consistently covered over large and small scales with the desired morphology, and consequently exhibits the best performance. Neither cracking nor slat-growth inhibits performance as much as basic coverage issues.



Fig. 4.25. SEM images of the doped Ni anti-dot samples probed in Fig. 4.26: the first row is the 5 + 2.5 minute sample, where (a) is taken from the side facing away from the counter electrode and (b) is from the side facing toward it; the second row is the 10 + 2.5 minute sample, where (c) is the side facing away, (d) is the side facing toward; and the third row is the 20 + 2.5 minute sample, where (e) is the side facing away, (f) is the side facing toward. (g) is the morphology lying in between the slats in (d); and (h) shows overgrown slats disconnecting from the substrate from (f).



Fig. 4.26. Water (a) and hydrogen (b) partial pressure dependencies of the SDC|gas interfacial ASR for CELD/Ni anti-dot-embedded samples deposited with the doped electrolyte for 5 + 2.5 minutes (squares), 10 + 2.5 minutes (circles), and 20 + 2.5 minutes (triangles). The initial PS bead size was 2 μ m and etched to 1.4 μ m.

2. CELD morphology effect: planar vs. HSA(1) and HSA(2).

As discussed in Chapter 3, both HSA and planar film morphologies are possible with CELD ceria. These are compared in Fig. 4.28. There is a clear difference in activity, owing to the surface area difference between HSA samples (see Fig. 4.27ab, HSA(1) and 4.27cd, HSA(2)) and planar samples (see Fig. 4.27ef). Sample-to-sample variability is again seen here in the two HSA samples. This difference appears to correlate well with morphological differences apparent in the SEM images of Fig. 4.27.



Fig. 4.27. Post-testing SEM images of the doped Ni anti-dot samples probed in Fig. 4.28: the first row is HSA(1), deposited for 10 + 2.5 minutes; the second row is HSA(2), deposited for 10 + 2.5 minutes; and the third row is the planar sample, deposited with the doped + H₂O₂ electrolyte at -0.55 V vs. SCE for 0.5 + 0.5 minutes.



Fig. 4.28. Water (a) and hydrogen (b) partial pressure dependencies of the SDC|gas interfacial ASR for CELD/Ni anti-dot-embedded samples deposited with the doped electrolyte for 10 + 2.5 minutes at 0.8 mA cm⁻² (HSA (1), squares), 10 + 2.5 minutes at 0.8 mA cm⁻² (HSA (2), circles), and with the doped + H₂O₂ electrolyte for 0.5 + 0.5 minutes at -0.55 V vs. SCE (triangles). The initial PS bead size in each case was 2 μ m and etched to 1.3-1.4 μ m.

In summary, consistent HSA coverage is critical, and some sample-to-sample variation exists. The deposition time should be long enough to cover the anti-dot network, but not so long that slat-like growth begins, which effectively covers portions of the enhanced surface area.

Extrapolating the best CELD/Ni anti-dot-embedded configuration data to 97% H₂, 3% H₂O, and 650 °C, the best LF ASR is 6.8 m Ω cm².

It should be stressed that to make use of these promising results, the issues associated with the CELD/metal-sandwich configuration need to be alleviated. The reader should keep in mind that a HF arc still exists for the results presented in the preceding section.