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Investigation of Nano-ceria Catalyst Infiltration of Solid Oxide Fuel Cell (SOFC) Electrodes Using Bio-Inspired Catechol Surfactants

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Investigation of Nano-ceria Catalyst Infiltration of Solid Oxide Fuel Cell (SOFC) Electrodes Using Bio-Inspired Catechol Surfactants

Ozcan Ozmen

Dissertation submitted

to the Statler College of Engineering and Mineral Resources

At West Virginia University

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ABSTRACT

Investigation of Nano-ceria Catalyst Infiltration of Solid Oxide Fuel Cell

(SOFC) Electrodes Using Bio-Inspired Catechol Surfactants

Ozcan Ozmen

Development of solid oxide fuel cell (SOFC) electrodes with nano-structured grains can show enhanced power density with high catalytic activity owing to the higher surface area to volume ratio of the particles. However, the addition of nano-particles during the conventional electrode manufacturing process causes inevitable structural changes due to the coarsening of nano-particles at sintering temperatures. Wet impregnation/ infiltration methods are a practical and well-utilized method to form nanoparticles within the porous electrode microstructure of solid oxide fuel cells (SOFC) which requires relatively low calcination temperatures. Critical factors that impact the reduction of the electrode polarization using the nano-catalyst impregnation strategy include catalyst loading, decoration type, and volumetric distribution homogeneity through the porous electrode microstructure. These can mostly be tuned by performing repetitive infiltration cycles followed by a co-firing step after each cycle for calcination. This labor and time-intensive method continues until the desired nano-catalyst loading is achieved. The factors that may degrade the performance as inter-particle interactions, pore-clogging, and/or inhomogeneous deposition result in gas diffusion related to rapid cell voltage degradation issues.

The objective of this work is to investigate organic electrode modifiers to enhance nano-catalyst infiltration efficiency and uniformity within a commercial nickel oxide (NiO)/ yttria stabilized zirconia (YSZ) anode support and lanthanum strontium manganite (LSM)/YSZ cathode systems. The aim is to reduce the process to minimal processing steps while increasing both the performance and stability of the SOFC by decorating the nano-catalyst deposition. In this study, nano-CeO₂, ceria, was used as a redox catalyst system and efficiently inserted throughout both porous SOFCs electrodes simultaneously by using a bio-inspired surfactant-assisted infiltration protocol. The process includes the initial modification of the electrode pore walls with a catechol-based surfactant film, i.e., poly-dopamine (pDA), poly epinephrine (pNE) or other alternative surfactants from the catechol family. The nano-ceria layer is then deposited uniformly over the bio-template surfactant layer during a single submersion of the SOFC into a cerium salt solution. Voltage-current-power curves and impedance spectroscopy were used to characterize the electrochemical performance of the impregnated anode-supported SOFC button cells. The end-goal of the work was to develop an infiltration protocol that performs boosted initial power density (performance) with high-stability by mitigating the nano-catalyst coarsening. The infiltrated cells displayed up to 35% reduction in polarization over the baseline cell with high electrochemical stability during 300 hours of testing at 750°C.

The catechol surfactant deposition kinetics and the degree of polymerization of the surfactants on planar substrates were investigated. The adhered catechol thickness was fitted to

exponentially decreasing function of time. The growth of the fired ceria particles over the pNE coated substrates showed that the growth of ceria particles can be both by forming new nuclei or growing over the existing nuclei.

DISCLAIMER

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Dedication

I dedicate this dissertation to my beloved parents, who have been the source of my strength. Your words made me stronger, better, and more fulfilled than I could have ever imagined...

to my mentors, friends, both near and far, my sister and brother who shared their words of advice and encouragement to finish this journey and touched my heart...

to my little nephew, Uras Celik whom we have never met in person yet due to my hectic Ph.D. workload. If you read these lines one day, just so you know that many memories will have been treasured; I promise...

“Science is the most reliable guide for civilization, for life, for success in the world.”

Mustafa Kemal Ataturk

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This thesis becomes a reality after countless pages of reading, hours of discussion, and endless times of failure/success sequences.

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Chapter 1 : Introduction and the Statement of Problem

1.1. Statement of Problem

The wet nano-catalyst infiltration (or impregnation) of porous Solid Oxide Fuel Cell (SOFC) electrodes is a recognized, cost-effective process to enhance electrochemical performance. The known impregnation methods include pipetting aqueous salt solutions onto the SOFC electrodes, which are then followed by multiple co-firing steps for calcination. These series of processes are replicated until the desired catalyst loading level achieved. The studies in the literature usually demonstrate initial enhanced electrocatalytic activity, boosted performance due to extending the triple phase boundary (TPB) length. However, apart from being a time-consuming and labor-intensive method, these infiltrated cells may suffer from long-term stability issues. One reason for the unstable nature of the nanoparticles is the multiple infiltration cycles and co-firing step between these cycles. The multiple infiltration cycles of diluted metal salt solutions may control the deposition amount between the steps; however, infiltration over the already formed nano-catalyst particles (from the previous step) may cause inhomogeneous deposition throughout the inner electrode surface. Besides, during the precursor drying stage inside the electrode, the solution is subjected to 3-D segregation where the dried gel is located at the edges and/or in the near-surface region. Lower co-firing temperatures help to form nano-particles. In contrast, poorly decorated highly and connected nano-particle networks lead to the reduction of overall surface energy by agglomeration and particle growth (Oswald Ripening) at an operating temperature which is higher than the co-firing temperatures. Agglomerated nano-particles lead to catalytic deactivation and gas-starvation issues due to pore-clogging.

By utilizing an innovative method, three-dimensional segregation during the drying process can be avoided by precipitating the metal ions and attaching them to the inner electrode surface. With a homogenous and controlled nano-catalyst decoration throughout the electrode inner surface, coarsening related drawbacks can be minimized. Hence the process will result in a lower electrode overpotential, enhanced power density, and enhanced long-term stability with a simplified and cost-effective infiltration protocol.

1.2. Goals of Research

The end-goals of this research are to develop impregnation/infiltration protocol(s) that can enhance the nano-catalyst decoration for highly stable infiltrated fuel cells using bio-inspired surfactants. The objectives of this research are:

- Adapting and tuning the catechol-based surfactant protocol to the three-dimensional networks of SOFC electrodes.
- Better understanding the effect of the catalyst network on the initial and the long-term stability of the fuel cells. This includes selecting process parameters and methods to adjust the microstructures and properties.
- Investigating the parameters to control the film thickness of the catechol film adhered to planar substrates.
- Investigating the chelating mechanism of the cerium precursor on to the catechol coated planar substrates. Monitoring the effect of nano-catalyst microstructure and decoration as a function of various conditions.
- Observing the change in surface morphology of cerium oxide formation of the fired samples as a function of pNE and cerium nitrate immersion times.

- Investigating alternative surfactants with similar chemical structure and comparing the infiltrated fuel cell properties and microstructure.

Chapter 2 : Literature Review

Over the past decades, there has been an increased demand for energy along with exceptionally efficient and environmentally friendly sources of electricity. Traditional fossil fuel conversion to energy is known to be an inefficient and polluting process. Fuel cells are one promising system to substitute for the direct combustion of fossil fuels in that sense. Fuel cells are known to convert chemicals (in the gas, liquid, or solid phase) directly to electricity with very little thermal or electrical loss. Fuel cell systems can also be practical where there is no access to the public grid or as a replacement of uninterruptible power supplies (UPS) for power generation [1, 2].

Fuel cells convert the various chemical forms to electricity through an electrochemical reaction. The most basic fuel cell reaction is based on the oxidation of hydrogen to form water. Eq.1 shows the net electrochemical reaction in a fuel cell system [1].

Fuel cells vary according to their efficiency, operating temperature, and electrochemical reaction, but mainly they are classified based on the electrolyte and fuel type. Figure 2.1 shows a brief introduction of the anode feed, cathode feed, exhaust chemistry, electrolyte material, operating temperature, and electrochemical reaction for each of the main fuel cell types: alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC) proton exchange membrane fuel cell (PEMFC) and solid oxide fuel cell (SOFC) [2] .

Figure 2.1. A schematic representation of the different fuel cell types [2].

2.1. Alkaline Fuel Cell (AFC)

One type of low-temperature fuel cell is called the alkaline fuel cell (AFC) which was one of the modern fuel cells developed in the 1960s to provide onboard electric power for the Apollo space vehicle[3]. The electrolyte, potassium hydroxide (KOH)-water solution, allows for the migration of hydroxyl ions (OH⁻) from the cathode to the anode side. The migrating OH⁻ groups react with hydrogen gas to form H₂O and 2e⁻. The AFC's operate below 100 °C with a low cost. The electrical efficiency of AFC is around 60 % (>80% combined heat and power –CHP-). Mostly, nickel is used as the catalyst for the cathode and anode electrodes[4]. Despite the relatively low catalyst cost, they are incredibly intolerant to carbon dioxide. The presence of CO₂ in the air shortens the lifetime of AFCs through the conversion of potassium hydroxide (KOH) to potassium carbonate (K₂CO₃), which affects the conductivity, and hence, the overall cell performance. In that sense, purified air or oxygen must be used to increase the operational life of AFCs. All in all, the

need of CO₂-free hydrogen and air increases the cost and storage issues that affect the practicality of AFCs.

2.2. Proton Exchange Membrane Fuel Cell (PEMFC)

PEMCs are low-temperature fuel cells that usually operate between 60-100°C. They were first invented by GE in the 1960s to be used by the U.S. Navy [1]. The fluorinated sulfonic acid polymer or a similar polymer is used as the hydrogen (or proton) electrolyte, but these electrolytes block the flow of electron and reactant transport. The electrochemical reaction occurs at the cathode electrode, where oxygen gas meets the hydrogen ions, and electrons pass through the external circuit and generate electricity. PEMFC systems can be stationary and compact, and they typically require low maintenance. Thus, the adaptation of PEMFC through road vehicles is a very promising application area [4]. Since a non-corrosive solid electrolyte is used, it is safe to handle. They are semi-tolerant to CO₂, and atmospheric air can also be purged [1]. However, they are intolerant to hydrogen impurities such as more than 50 ppm CO and sulfur. In the case of hydrocarbon fuel usage, extensive fuel processing systems must be used. A working temperature above 100°C vaporizes the water within the cell architecture causing dehydration of the membrane, which leads to a reduction in the proton conductivity of the membrane. In a cost perspective, platinum is used as the catalyst, and the solid polymer membrane is relatively expensive, as well. The electrical efficiency of PEMFC is between 40-50 %, and the output power can be as high as 250 kW. The main application area is for light electric vehicles and portable electronic equipment.

2.3. Phosphoric Acid Fuel Cell (PAFC)

Phosphoric acid fuel cells (PAFC) use liquid phosphoric acid (H_3PO_4) within a silicon carbide matrix as the electrolyte and carbon paper electrodes. PAFCs can only operate at the range of 150-220°C since the charge carrier (H^+) conduction is very low at lower temperatures. Water forms at the cathode electrode with the presence of a platinum catalyst[4]. PAFCs can tolerate up to 30% CO_2 ; therefore, these fuel cells may use air directly from the atmosphere as for PEMFCs. While working at a medium temperature, they can use the waste heat for co-generation. The electrolyte has lower volatility and long-term stability. However, carbon monoxide (CO) generation from steam reforming poisons the cell. Also, the liquid electrolyte is corrosive at average temperatures, so safety and handling problems arise. The entry of water to the system can dilute the electrolyte acid concentration, which may cause performance degradation [1]. PAFCs are an expensive system to manufacture due to the need for finely dispersed platinum catalyst coating the electrode. The development of PAFC had slowed down after peak research of PEFC over the decades that were thought to have a better cost potential.

2.4. Molten Carbonate Fuel Cell (MCFC)

The first working MCFC was built in the 1960s by the US Navy. Molten carbonate fuel cells are based on the use of an electrolyte composed of a mixture of lithium and potassium carbonate. This fuel cell architecture runs with circulating carbonate ions (CO_3^{2-}) from the cathode to the anode[1]. The molten carbonate fuel cell requires high-temperature to function. Typically, the working temperature is around 650°C. They require carbon dioxide and oxygen as the oxidant. In the MCFC, the reaction at the anode electrode occurs between hydrogen fuel and the carbonate ion, which react to form carbon dioxide, water, and electrons.

MCFCs are currently used for natural gas and coal-based power plants in the electrical utility, industrial military, and marine applications. MCFCs may be directly fueled with hydrogen and carbon monoxide, natural gas, and propane[4]. At the high operating temperatures, the MCFC anode and cathode are Ni and nickel oxide, respectively, and are adequate to promote the reaction. A benefit for MCFCs is that there is no requirement for an expensive noble catalyst which gives the cost effectiveness of the system. Also, MCFCs are capable of internal reforming which provides a high-level capability for fuel flexibility. MCFC stacks also show a tolerance to sulfur which is typically present in many fossil fuel sources. The main challenge for MCFCs is that they include a very corrosive mobile electrolyte that may potentially result in handling and safety issues. Also, CO₂ flow is required at the cathode side, which is usually recycled from anode exhaust to form a carbonate ion [3].

2.5. Solid Oxide Fuel Cell (SOFC)

The gradual increase of energy demand of the world pursues efficient, economic, and environmentally-friendly electric generators. Solid oxide fuel cells (SOFCs) are one promising system that arises among other fuel cell technologies in many respects. SOFC systems operate at high temperatures up to 600 to 1000°C due to technical requirements [5]. Hence high operating temperature produces a byproduct of heat for co-generation. The efficiency of an SOFC system can reach up 70 % with additional heat recovery [6]. First SOFC, operating at 1000°C, was built by Baur and Preis [6]. The components that were used are Fe or C as an anode, 10 wt. % MgO-ZrO₂ or 15 wt. % Y₂O₃-ZrO₂ as electrolyte and Fe₃O₄ as a cathode. After decades of development, a wide range of electrodes and electrolyte compositions have been utilized to decrease the overall

resistance, operating temperature, catalytic activity, and stability. Recently, the main requirements and design are reviewed by Keegan C. Wincevich et al., and A. Boudghene Stambouli et al. [5, 6].

An SOFC consists of two electrodes, an anode and a cathode sandwich that are manufactured as a porous network to allow gas diffusion through a few micron thick active area. The electrolyte, the middle component, is required to be a dense, oxygen ion-conductive ceramic layer. As structural components, interconnects are used to complete the circuit through the anode to the cathode, and a sealant is used to provide hermetic tightness between the manifold and the electrode surface. Figure 2.2 illustrates the general mechanism of the SOFC based on the simplest fuel system. Fed hydrogen oxidizes with the oxygen ions in the anode electrode, which generates free electrons and water vapor (or other oxidized by-products, such as CO/CO₂ for hydrocarbon fuels).

Figure 2.2. Concept diagram of SOFC based on oxygen-ion conductors using H₂ as fuel [6].

The fuel cell performance is limited by three factors: 1) transportation of charge related to ohmic losses, 2) gas starvation/transport of ions related mass transport losses and 3) catalytic deactivation of the electrodes. Ohmic and mass-transport limitations have been overcome by engineering the fuel cell designs and geometry. To minimize the ohmic and polarization resistance, the current path in the components must be as short as possible. So, the cell components must be manufactured as thin layers. Moreover, to reduce the mass transportation losses, the design must provide good, homogeneous access for the reacting gasses [7]. Solid oxide fuel cell stacks are categorized based on their shapes: the seal-less tubular design, segmented-cell-in-series design, the monolithic design, and the flat-plate design as schematically shown in Figure 2.3.b. [8]. Tubular design (Figure 2.3.a) was first proposed by Westinghouse in the 1950s, and the first seal-less design was launched in 1980 [9]. The main feature of the sealless tubular design is the stack does not need a sealing component under gas flow. Moreover, each cell is built over one thick ceramic support which gives a uniform thermal expansion coefficient that prevents thermal cyclic cracking. However, due to the form factor and thickness of the support, the current travels a longer path. This long current path in the electrodes results in high cell resistance and losses. The support tube also causes the rate limiting step of gas diffusion through the tube which affects the performance. Manufacturing techniques such as electrochemical vapor deposition (EVD), slurry coating or plasma spraying processes increase the cost of tubular SOFC [10]. The segmented-cell-in-series design is a modified tubular design which was proposed in the 1960s. Short-cylinder cells are joined together with interconnecting materials. The interconnect also acts as a sealant between the anode and the cathode. Like the seal-less tubular SOFC, the segmented-cell-in-series design improves mechanical durability. The system offers improved stack efficiency. However, above five cells in series, it is reported that the power output diminishes in airflow series. Planar SOFC

designs (Figure 2.3. c, d) were also utilized well over time. Feasible designs such as monolithic SOFCs offer great potential and advantages due to the high active surface area. It was demonstrated only in the laboratory scale due to the difficulty of fabrication at the commercial scale [9]. The most utilized stack design among the current architectures is the flat plate SOFC design. Flat plate design consists of thick planar plates usually rectangular or circular (button type). This design shows higher power densities relative to the tubular designs. Planar SOFC's are usually fabricated by tape casting, screen printing or tape calendaring. Those simple fabrication routes increase the feasibility and cost-effectiveness of the stack. Also, thin manufacturing minimizes the ohmic and electrical resistance of the system.

Figure 2.3. SOFC stack designs: (a) Seal-less tubular design, (b) Segmented-Cell-in-Series design (c) Monolithic design (d) Flat-plate design [8].

Another categorization is based on the thickest functional component, which adequately supports the cell. Figure 2.4 illustrates different SOFC designs based on the support component [11]. Usually, the support component of the cell is manufactured in a few hundred microns to provide mechanical rigidity. Moreover, in tubular SOFC designs, a thick ceramic isolator houses the fuel cell components. By giving the advantage of inertness and low thermal expansion coefficient, it is preferred for ceramic-based fuel cells. Owing to very small electrical loss, interconnect metal plates also are preferred as the supporting component. Both electrodes and electrolyte can be deposited or printed as very thin layers onto the interconnect metal in metal-supported SOFCs.

Figure 2.4. SOFC's based on the support component (a) electrolyte (b) anode (c) cathode (d) metal (interconnect) supported SOFC designs [11].

The third factor that affects the fuel cell performance, the catalytic deactivation overtime at elevated temperature, can be overcome by materials selection. Generally, the cathode electrode

is referred to as the air or oxygen electrode where oxygen in the air reacts with the electrons and becomes oxygen ions. The reduction reaction of oxygen is given in Eq. 2.2.

The main material selection requirements for cathode materials are high electrical conductivity and ionic conductivity, good catalytic activity for oxygen reduction and high stability in an oxidizing environment at working temperatures. The cathode electrode materials are generally perovskite or related structures. Among the many candidates have been studied by the researchers, the lanthanum-based cathode (LSM= $\text{La}_x\text{Sr}_{(1-x)}\text{MnO}_3$) is the most popular material for high-temperature SOFC's owing to the good stability with yttria stabilized zirconia (YSZ= $\text{Y}_x\text{Zr}_{(1-x)}\text{O}_2$) electrolyte [5]. For low-temperature cells, LSF= $\text{La}_x\text{Sr}_{(1-x)}\text{FeO}_3$ ($x \sim 0.8$), LSCF = $\text{La}_{(1-x)}\text{Sr}_x\text{Fe}_y\text{Co}_{(1-y)}\text{O}_3$ ($x \sim 0.4$, $y \sim 0.2$) and strontium based (SSC= $\text{Sm}_x\text{Sr}_{(1-x)}\text{CoO}_3$ ($x \sim 0.5$)) perovskite cathodes are substituted due to the low conductivity of LSM cathode . Depending on the electrical/ionic properties, the electrochemical phase boundary may vary. For instance, LSM is a poor ionic conducting cathode material and is often compensated by mixing with an ionic conducting phase, such as yttria-stabilized zirconia (YSZ). Here, the electrochemical reaction takes place at the triple-phase boundary (termed as TPB or 3PB), which is the point of contact of the electronic conductor, oxygen ion conductor, and oxygen gas (Figure 2.5.a and b). For the mixed ionic-electronic conducting (MIEC) systems, such as LSCF, the double-phase boundary (DPB, or 2PB) dominates at the point of contact to the MIEC and air [12] as shown in Figure 2.5.c. Cathodes are usually manufactured thin and porous to increase the diffusion and the phase boundary points,

Figure 2.5. Reaction pathways of oxygen reduction (a) and (b) for electronically conductive systems mixed with electrolyte material (YSZ), (c) for MIEC systems. Modified from [11].

The electrolyte, the middle layer, is made up of a dense metal oxide (ceramic) containing a population of oxygen vacancies that allow for only O^{2-} charge carriers to pass from the cathode to anode electrode due to the concentration gradient. So, as a rule of thumb, an electrolyte material must be electronically insulating (high ohmic resistance) but ionically conductive, chemically stable in both oxidizing and reducing atmospheres and gas-tight hence free of porosity. Yttria stabilized zirconia (YSZ) and pure or gadolinium doped ceria (GDC) are the most popular electrolyte materials owing to their excellent properties. Defect chemistry of these compounds can be written in Kröger-Vink notation. As shown in Eq. 2.3 and Eq. 2.4, doping with a lower valent cation is compensated by oxygen vacancies due to the charge neutrality principle [13].

Moreover, cerium oxide has a unique oxygen ion conductivity and oxygen storage capacity by dual oxidation states of Ce^{+3} and Ce^{+4} . It is reported that this switching mechanism is driven by downsizing the ceria crystallite size. Moreover, the oxygen partial pressure also promotes this

mechanism. As a result, oxygen vacancies are created in the lattice, represented by Eq. 2.5 [14]. It should be noted that electrolyte ionic conductivity primarily determines the operating temperature of the whole SOFC.

The second electrode, the anode, is referred to as the fuel electrode where the hydrogen gas or hydrocarbon fuel is fed. Mostly anodes are made as of a ceramic-metal composite, called cermet to meet the physical and chemical criteria. Major design requirements for the anode is that it must be electrically and ionically conductive for electron and ion flow and highly electrocatalytic active to break hydrogen and/or carbon bonds in the fuel. When hydrogen is fed, the oxidation reaction of hydrogen at the anode side is given in Eq. 2.6. Carbon monoxide (CO) and hydrocarbons (CH₄) can also be purged to the anode electrode for electron or hydrogen generation. At elevated temperature, it is applicable to oxidize CO to CO₂ and complete the circuit (Eq. 2.7), or with the water gas shift reaction, hydrogen can be generated (Eq. 2.8). Since direct oxidation of CH₄ is not being performed yet, steam forming reactions (Eq. 2.8 and Eq. 2.9) allow hydrogen generation to be achieved [15].

At the anode site, electrochemical reactions are also driven by 2PB, for MIEC, and 3PB, for the composite matrix. Although the mechanism of H₂ oxidation and H₂O reduction is

controversial, adsorption/desorption, surface diffusion, and charge-transfer reactions take place at these sites [12]. For the Ni/YSZ anode system, the schematics of the proposed mechanisms are illustrated in Figure 2.6. Adsorption and dissociation of H_2 into H^+ ions on the Ni surface resulting in water formation on the surfaces and through bulk Ni and YSZ is shown in Figure 2.6.a. In Figure 2.6.b, the migration of O^{2-} or OH^- from the YSZ to the Ni along the surface, which results in water formation on the Ni, is visualized. The third proposed mechanism is shown in Figure 2.6.c, where the water formation takes place at the surface of YSZ and the electron transport, occurs at the surface of YSZ and through the Ni. For MIEC electrocatalysts, the reaction is extended to the entire ceramic/gas interface (2PB) with the surface reaction being rate-determining.

Figure 2.6. Reaction pathways of hydrogen dissociation and H_2O formation [12].

Nickel is the most common and cost-effective electrocatalyst that reduces the hydrogen to protons. It also provides excellent electrical conductivity at the SOFC working temperature [11]. To improve the ionic conductivity of the electrode and extend the triple-phase boundary, the YSZ phase is usually mixed into the anode composition proportionally. This also helps to match the thermal expansion coefficient to the YSZ electrolyte. One drawback of Ni/YSZ cermet composite structure is the close melting temperature of nickel (1455°C) relative to the anode fabrication temperature (~1400°C). In that sense, nickel oxide is more preferred for processing of the anode owing to its high melting temperature (1955 °C). Both phases contribute to the Ni/YSZ anode during the operation due to the reduction process of NiO to Ni metal under the H₂ environment. The anode structure is designed to have 20-40% porosity to facilitate gas transport. Figure 2.7 displays the scanning electron microscope (SEM) image of an anode-supported cell composed of porous Ni/YSZ anode, YSZ electrolyte, and porous LSM/YSZ cathode. Despite the benefits of the nickel-based anodes, this cell architecture encounters a series of problems, including a mismatch of thermal expansion coefficients to certain electrolytes and hydrocarbon fuels/impurities poisoning. In that sense, replacing nickel with a more resistant copper reduces the carbon formation to bring fuel flexibility. Lanthanum-based perovskite anodes, $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$, $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{M}_y\text{O}_3$ (M=Mn, Fe, Co, Ni), $\text{La}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ –LST– are also alternatively used compositions for stability benefits [5].

Figure 2.7. SEM anode supported cell [16].

Solid oxide fuel cells generate the electricity by direct conversion of fuel energy to electrical energy unlike conventional chemical energy to thermal energy to mechanical energy path [17]. The electrons generated at the anode electrode travel through the external circuit through the cathode electrode, and the power generation is based on the electrochemical oxidation of the fuel. As depicted above, the overall reaction is two separate reactions at the anode and cathode electrodes. If it is assumed that the hydrogen is fed to the anode as fuel and the air is fed to the cathode as oxidant, reduction and oxidation reactions conclude that the driving force of the electromotive force, emf, is given by the Nernst equation (Eq. 2.10). The equation denotes oxygen concentration gradient between the electrodes where R is the gas constant, T the temperature, F the Faraday constant, P_{O_2} the partial pressure of at the anode, A, and cathode, C, electrode. Although several reactions and concentration gradients such as CO , CH_4 , can be plugged into the Nernst equation, the ideal voltage (E_o) from a single SOFC fed with H_2 under open-circuit voltage is typically around 1.1 V DC. However, the useful voltage output (V) under load conditions is affected by various losses. The voltage drop depends on the current density (current per active

electrode area, A/cm²), temperature, gas flow rate, partial pressure and cell material [17]. The ratio of cell voltage under load to the open circuit, equilibrium voltage is called the voltage efficiency and the voltage difference is called polarization or over-voltage denoted as η . Polarization cannot be entirely excluded but can be minimized by tuning the internal and external properties/parameters of the system. Previous studies have separated total polarization of the cell into four sub-polarizations: charge/activation polarization, η_A , diffusion polarization, η_D , ohmic polarization, η_Ω , and reaction polarization, η_R , (Eq. 2.11) that would allow a complementary analysis of each polarization type.

$$E_r = \frac{RT}{4F} \ln \frac{P_{O_2(c)}}{P_{O_2(a)}} \quad (\text{Eq. 2.10})$$

$$\eta = \eta_A + \eta_R + \eta_\Omega + \eta_D \quad (\text{Eq. 2.11})$$

Activation related polarization, η_A , is basically the energy barrier threshold that the reactants must overcome. These losses depend on the catalytic nature and the microstructure of the electrode and reactant activity [3]. In detail, adsorption, desorption, and electron transfer capability of the electrodes drive the activation polarization. Thus, extending the triple-phase boundary and the electrocatalytic activity of the anode determines the charge transfer process [18] Reactant polarization, η_R , has the least significant role in the total polarization. It is driven by the supplied cell reactants and removal of products. Reactant polarization is usually small at operating temperatures. Ohmic polarization, η_Ω , is caused by the electronic resistance through electrodes and ionic resistance through the electrolyte. SOFC materials selection and stack current collection components directly affect the ohmic polarization. For anodes, the internal resistance is determined by the electronic resistivity of the material and the thickness of anode. Diffusion polarization, η_D , is also referred as mass-transport related polarization [17]. Apart from the reactant (fuel and oxidant) activity, electrode porosity dominates diffusion polarization. As mentioned previously,

electrodes are manufactured porous to avoid gas starvation issues which directly affect the electrode performance. It has been reported that more than 30% percolated porosity is required to facilitate the transport of reactant and product gasses for Ni-YSZ system [18]. Figure 2.8 shows the typical current-voltage (IV) curve of a fuel cell and regions are labeled with the driven polarization type. According to the kinetics factors addressed as structure or material properties above, mitigation of voltage degradation under the current, in other words, achieving high power density, can still be attained by modifying the addressed structure or material property.

Figure 2.8. Ideal and actual fuel cell voltage/current characteristic with responsible polarization loss regions [3].

Conventional Ni/YSZ anodes provide a satisfactory catalytic activity for hydrogen oxidation and steam reforming of methane gas for syngas production. While Ni/YSZ anodes have such benefits in many aspects, the nickel has some major drawbacks that gradually affect the cell

SOFC performance. Although Ni is stable in a hydrogen environment, it catalyzes the formation of carbonaceous deposits that foul the anode under hydrocarbon exposure [19]. Moreover, sulfur impurities as low as 1 ppm in the fuel causes Ni deactivation by poisoning [20]. Long term and redox stability of conventional Ni/YSZ fuel electrodes are disturbed by the sintering, grain growth, and agglomeration of nickel phase [21, 22]. High-Temperature sintering that is needed to achieve good bonding and contact between the NiO/YSZ phase causes initial grain growth for both NiO and YSZ phases. During the reduction stage of SOFC, NiO in the ceramic electrode reduces to Ni, resulting in ~ 26% volume reduction with finer particle sizes. It has been studied that the poor wettability between Ni metal and YSZ phase accelerates agglomeration and grain growth of Ni phase which reduces the TPB area at the electrode/electrolyte interface [23].

As depicted above, one advantage of SOFCs is the fuel selection flexibility, so hydrogen or various hydrocarbons can be considered. Naturally, these fuels contain minor impurities at the ppm level. Considering the high current passing through the current collectors, high operational pressure, and the use of inexpensive, hence high impurity materials, contamination of those constituents can be fatal to electrode structure and performance [24]. The phenomenon called poisoning seriously affects cell life and stability in a few hours. Both catalytic hydrogen dissociation and TPB activity are seriously disturbed by poisoning. Shown in Figure 2.9 are possible degradation types resulting from specific contaminants on the conventional Ni/YSZ anode structure. In summary, at low concentrations of sulfur, adsorption type poisoning is driven and NiS forms on the nickel surface and TPB, which blocks the O^{2-} pathway (Figure 2.9.a). Chlorine impurity bonds with nickel and forms gaseous $NiCl_2$ (g). This type of reaction is called sublimation type poisoning and causes Ni loss out the structure (Figure 2.9.b). In deposition type poisoning, siloxane triggered SiO_2 (s), and fuel triggered carbon and sulfur deposits could be observed. Again,

these deposits grow at the TPB region and block the ionic pathway (Figure 2.9.c). Specifically, carbon deposition is called coking in the literature. At higher sulfur concentrations, Ni_3S_2 solid phase forms at the Ni surface below 600°C . This type of poisoning is called reaction type poisoning (Figure 2.9.d). This secondary phase reaction also decreases the melting point of Ni to only above 800°C by making a eutectic point. (Figure 2.9.f). With the presence of boron, grain growth of nickel is observed which adversely affects long term durability and electronic conductivity (Figure 2.9.e)

Figure 2.9. Possible impurity poisoning mechanisms of SOFC anodes [24].

Among these types of poisoning, sulfur and carbon poisoning are the most studied types. Studies are divided into two areas. One side is finding alternative anode materials such as perovskite ceramic compositions, that are resistant to sulfur poisoning and coking. The other side of research interest is to mitigate and control the poisoning of existing anode compositions by adding a protective second phase into the system. Mainly, H₂S gas reacts with nickel and forms a second phase, NiS, which deteriorates the migration of O²⁻ ions towards to the TPB. The damaging mechanism of sulfur over Ni/YSZ anode can either be by physical adsorption, sulfidation or chemisorption. These mechanisms result in different types of degradation depending on the H₂S concentration and fuel type. In addition, Ni₃S₂, another impurity phase, the formation cannot be recovered and damages the cell [25]. The formation of the sulfide phase is given below in Eq. 2.12-2.14.

Coking, or carbon poisoning, also opened various research areas including new anode compositions or modification of microstructures of existing anode systems. Carbon deposition on the Ni/YSZ system results from different reactions and temperature ranges. The type of carbon also ranges by gas type and temperature (Figure 2.10.a). It has been found that carbon deposit formation occurs when atomic carbon, C_α, is excessively produced and saturated by a metal catalyst. Hence unbonded adsorbed C_α forms a polymeric form of carbon, C_β due to lack of oxygen. Likewise, whisker/fiber carbon, C_v, and graphitic carbon, C_C, forms in the anode metal structure (Figure 2.10.c). All the carbon deposits cause rapid degradation in the fuel cell. It was reported that C_C and C_β form a barrier film over the metal catalyst surface and deactivates the metal

backbone function (Figure 2.10.b) [25, 26]. Besides, Cv causes a breakdown in catalysis (Figure 2.10.d). These poisoning mechanisms can cause a rapid voltage decrease. To achieve long term stability from SOFC's with coke free anode electrodes, microstructural and materials reconsiderations should be taken.

Figure 2.10. Determination of carbon formation region (a) C-H-O ternary phase diagram [25, 27] (b) Coking of a Ni/YSZ anode as found in TEM [25, 26] (c) Ni/YSZ anode surface after test (200 h) in H_2 by mixing 3% C_3H_8 and 3 ppm H_2S [24] (d) FESEM image of deposited carbon on the Ni/YSZ anode surface after H_2 - 3% C_3H_8 – 3 ppm H_2S for 200 h [24].

2.5.1. Nanostructured Electrodes

In SOFC's, the interest of nanoscale materials usage has been progressively increasing. Owing to the high surface area, TPB/DPB can be extended, ionic and electronic conductivity can be improved, and surface vacancy concentration of the catalysts can be enhanced. On the whole, interfacial electrochemical activities can be promoted. However, constructing the entire electrode(s) causes potential inevitable structural instabilities due to the grain growth mechanism promoted by SOFC operating temperature ranges [21]. Thus, both nano and micron-sized particles should be incorporated for electrodes. A conventional micron-sized backbone structure is used to keep the stability while nano-structured particles enhance overall fuel cell performance. Usually, the conventional sintering temperature of anode constituents is around 1300-1400 °C, and after this high-temperature sintering step obtaining micron-sized particles is inevitable.

In contrast, the decomposition temperatures of metal nitrates are between 500 to 850°C, which are much lower than the electrode sintering temperature and very close to the SOFC operation temperature. Thus, nanoparticles can be formed by introducing metal nitrate solution to a sintered electrode backbone structure.

One way to introduce nanomaterials within the electrode microstructure is called infiltration or impregnation method. The following subsections of this chapter aim to give an introduction to the infiltration method and materials for evaluating a functional SOFC anode that consists of nanoparticles.

2.5.1.1. Microstructure Engineering by Nanomaterial Infiltration

There are two main functions for depositing nanoparticles within as-sintered electrodes i) to add catalytic role ii) to enhance conduction pathways critically related to triple phase boundary

(TPB) length where ionically conductive (i.e., YSZ) and/or electrically conductive (i.e., Ni) constituents are in contact with the anode electrode.

There are few strategies to construct an anode depending on the backbone structure, in the literature, Table 1 summarizes the possible scenarios for existing anode backbone before infiltration. Depending on the anode backbone function, the optimum amount of nanoparticle material, as infiltrated material, can be engineered and introduced into the structure.

Table 1. Backbone and nanoparticles functions in each electrode class. Adapted from [28].

Porous electrode class	Backbone function	Nanoparticle function
Single component electrode composition	i) Oxygen ion conduction (YSZ, GDC) ii) Electron ion conduction (Ni-Cu)	i) Global electron supply, electrocatalyst (Ni, Cu, Co) ii) Local oxygen ion conductivity (YSZ, doped CeO ₂)
MIEC (Mixed Ionic Electronic Conductor)	Oxygen ion and electron conduction, electrocatalyst (LCrM, SrTiO ₃)	Secondary ionic or electronic pathway, electrocatalyst (doped CeO ₂)
Composite / Cermet	Global oxygen ion and electron conductivity, electrocatalyst (Ni-YSZ, Cu-YSZ)	Local oxygen and electron conductivity, electrocatalyst (Ni, Cu, Co, doped CeO ₂ , Pd, Ru, Pt)

In the literature, anode SOFC infiltration/impregnation study has had progressive attention over recent years, pioneered by Gorte et al. [29-32]. Due to the ease of infiltration application and the methodological needs, there is increasing interest as evidenced by published papers in this area over the years, as shown in Figure 2.11. Among the reviewed studies, it has been observed that the advancement of conventional YSZ and Ni/NiO backbone structures have been mostly studied (Figure 2.12). Alternatively, promising new perovskite MIEC compositions have also been chosen to facilitate desired properties such as electronic, ionic conductivity or electrocatalytic activity. Finally, Figure 2.13 assesses the literature in the infiltrated phase perspective. Initially, precious metal infiltrations were experimented starting from the early stages. However, it should be noted that Ni is the most chosen electrically conductive/catalyst phase. By experiencing the limitations/problems of micron-sized Ni particles in the anode electrode, studies have aimed to overcome those issues by downsizing the particle diameter with a homogeneous dispersion within the backbone structure. Moreover, there has been considerable attention of modified ceria, CeO_2 , based nano-catalysts infiltration. Gadolinium, Gd, strontium, Sr, zirconium, Zr, molybdenum, Mo have been used as modifiers for ceria to enhance the catalytic activity, ionic conductivity and mitigate the grain growth of the backbone. Also, few studies on tungsten-based, NaWO_3 , KWO_3 , and titanate based, LaSrTiO_3 , perovskite systems have also been infiltrated to various backbone structures.

Figure 2.11. Published anode infiltration studies in recent years [29-152]

Figure 2.12. Backbone structures of infiltrated anodes in recently published studies [29-152].

Figure 2.13. Infiltrated material compositions in recently published studies [29-152].

2.5.2. Selected Strategies of Infiltration on SOFC Anode Electrode

2.5.2.1. Electrochemical Performance Enhancement by Catalyst Infiltration

The conductive nickel phase at the anode electrode has been known to have catalytic, fuel-dissociation character. However, this property strongly depends on the particle size and the dispersion of the phase in the structure. Gorte et al. have noted that noble metals such as Pd, Pt, Au, and Ru also improved catalytic activity [30, 35, 36, 47, 48, 51, 59, 60, 63, 71, 93, 106, 112, 117, 132, 136, 139, 153, 154]. Due to the cost restrictions, the use of these precious materials can only be viable by liquid infiltration. Figure 2.14 illustrates the ideal case of isolated nanoparticle island deposition on the porous backbone structure that creates new TPB [155]. By tuning the infiltration step or the concentration of the precursor, particles can either be deposited discretely

or in a connected network. Another catalytic material doped ceria (XDC, X=Metal), attracted attention due to its flexibility of use either in the anode or cathode or even the electrolyte material [30, 32, 37, 42, 44, 45, 51, 53, 58, 59, 61, 63, 64, 69, 72, 76, 77, 80, 83, 87, 91, 96, 99, 100, 102, 103, 105, 107, 109, 113, 121, 122, 130, 134, 140, 147] . For example, gadolinium-doped ceria (GDC) acts as an ionic conductor, and also by switching the valence character of ceria from +4 to +3 repeatedly, nanoparticles can achieve hydrogen storage capability. The study by S. P. Jiang has been one of the trend-changing research for increasing the performance of conventional anodes by using the cost-effective catalyst GDC [53]. Highly concentrated $\text{Gd}(\text{NO}_3)_3$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ metal nitrates were dissolved in water, and the solution is dripped over the nickel anode surface. As a result, the particle size of infiltrated GDC particles was around 100-200 nm in the nickel anode backbone. Figure 2.15 shows the impedance curves of the cells during the operation at different temperatures [53]. It can be seen that GDC infiltration reduced impedance arcs expressively for each temperature. For instance, at 700°C, electrode resistance, R_E , decreased from 10.7 $\text{ohm}\cdot\text{cm}^2$ to 4.9 $\text{ohm}\cdot\text{cm}^2$ by one step infiltration (0.52 mg/cm^2) whereas double-step infiltration (1.7 mg/cm^2) decreased the R_E even further to 1.5 $\text{ohm}\cdot\text{cm}^2$. It should be noted that the starting points of the arcs are also shifted towards to left which was mainly due to the promotion of ionic conductivity by the GDC phase.

Figure 2.14. Scheme of the infiltrated nano-structured electrodes on pre-sintered porous electrode or electrolyte [155].

Figure 2.15. Impedance spectra for H_2 oxidation on pure Ni and Ni anode with 0.52 and 1.7 mg cm^{-2} GDC infiltration at (a) 900 °C, (b) 800 °C, and (c) 700°C [53].

2.5.2.2. Redox Stabilization

Solid oxide fuel cells are designed to operate continuously as long as the gas is fed. In case of intentional or mistaken interruptions in the fuel flow, the anode undergoes several oxidation-reduction cycles, which are called redox reactions. During these reactions, anode materials must withstand and stay stable in these reactions. However, for Ni-based anodes, significant volume changes can be observed due to the phase change between Ni to NiO. The oxidation of Ni to NiO causes a volume expansion of 69.2%, and during the reduction, the volume shrinks to 40.9 %

[156]. Due to the brittle nature of the ceramic materials, these stresses cause micro-cracks in the network which disturb the oxygen ion collection and also cause cell failure when it is not compensated by the porosity of the electrode as seen Figure 2.16. There have been some precautions held to hinder this mechanism, such as improving the strength of the material for higher redox tolerance [44, 50, 92, 110, 115, 141, 157], but one approach to overcome massive volumetric change is to infiltrate Ni precursor to the YSZ network. After low-temperature firing, nano nickel/nickel oxide particles can be formed onto the YSZ phase. This weak nickel phase does not cause stress during the redox cycles, and hence long term stability can be achieved [38]. The SEM image of such engineered cermet composites shows a continuous but thin coating over YSZ surface which EDX spectroscopy mapping identified as a homogenous distribution of the Ni phase within the cermet (Figure 2.16.b).

Figure 2.16. (a) Schematic representation of the changes occurring the conventional Ni-YSZ cermet prepared by high temperature co-sintering and the scanning electron microscopy image showing the actual microstructure of such a cermet after redox cycling (b) Schematic representation of the change occurring Ni-YSZ structure obtained by polymeric precursor infiltration, scanning electron microscopy images showing the general microstructure of such a cermet (upper) and the energy dispersive X-ray spectroscopy mapping showing the distribution of Ni phase [38].

Furthermore, sintering related cracks at the contact area of the porous YSZ backbone can deviate to micron-sized cracks on a dense electrolyte and hence resulted in a reduction in the conductivity. By infiltrating YSZ precursor to YSZ backbone, those weak contact areas can be covered by nano-YSZ particulates which reinforces the structure after heat treatment and redox

reactions. As tabulated in Figure 2.17, YSZ and nickel infiltrated cells on a porous YSZ backbone (white and blue data points) had a stable conductivity value as a function of redox cycles which supported the mechanism mentioned above. However, only the nickel infiltrated cell (35 vol %) showed continuous degradation. The studies [38-40] showed that constructing the whole anode by infiltration was an effective method to obtain redox stability.

Figure 2.17. Changes in the electrical conductivity of the samples YSZ (1150)-35 Ni, YSZ (1150)-20YSZ(1000)-35Ni and YSZ(1150)-30YSZ(1000)-35Ni upon redox cycling at 800°C [40].

2.5.2.3. Coking and Sulfur Toleration

As mentioned previously, utilization of hydrocarbon fuel such as natural and shale gas is a promising area in SOFC's. However, these fuels have a degree of undesired contaminants such as H₂S and carbon deposits which restrict their use in SOFC technology due to their detrimental nature.

To suppress carbon deposition, there are four possible strategies in the SOFC system. The first two are passing the fuel through an external reforming unit before the anode feed and/or purging a high steam-to-fuel ratio (>2 for methane) to bond all the adsorbed carbon with excess oxygen [96]. The third strategy is constructing a non-coking anode system mainly perovskite ceramic or Cu/Ceria based anodes. However, those systems have inferior catalytic or electronic properties [5, 10, 158, 159]. The infiltration of coke-resistant materials to conventional Ni/YSZ cermet is the fourth possible strategy. It has been known that some precious metals (Au, Sn, Ru, Rh, Pd, W, Pt,) transition metals (Cu, Sn, Sm,), alkaline earth metal (Ba) [32, 35, 42, 46, 47, 66, 71, 73, 84, 94-96, 98-100, 105, 116, 148, 160-166] can be infiltrated for this purpose.

The first infiltration studies were carried out for direct utilization of hydrocarbons by infiltrating precious metals by Gorte et al. [29, 153] almost two decades ago. By the introduction of a small amount of precious metal (1% Pd) into the ceria-YSZ cell, anodes can dissociate CH_4 at 923 K with increased power density.

A study by Wu et al. infiltrated Ag on Ni/YSZ system as a coke-resisting material [96]. Among other proven coke-resistant precious metals, silver is one of the cost-effective and low resistivity candidates of intermediate temperature, IT-SOFCs. Ag infiltration was performed by the dripping method applied to the Ni/YSZ surface. Three different Ag loadings were chosen by tuning the precursor concentration. Figure 2.18 showed that high silver loading influences the initial particle and the dispersion of the Ag particles as well. The microstructure of the highest Ag loaded sample (Cell C) had around 5 μm flakes with nearly full coverage of surface while other samples (Cell A and B) showed smaller particle size and discrete dispersion. Stability tests revealed that the baseline cell failed within 5 hours under CH_4 and all the infiltrated cells displayed better stability than the baseline cell (Figure 2.19). The results indicate that silver infiltration

improved carbon tolerance. Among the infiltrated cells, cell B ran steadily, meaning that critical particle size, solid loading and surface coverage played a role to passivate carbon formation. The detailed study exposed that infiltration of even small amounts of catalytic material (less than 2 wt. %) assisted to dissociate CH_4 fuel but suppressed coking of the whole anode by also promoting carbon separation into small islands [96].

Figure 2.18. SEM images of (a) blank Ni/YSZ anode and Ag infiltrated (b) Cell A: 0.89 wt. %, (c) Cell B: 1.59 wt. %, (d) Cell C: 2.48 wt. % [96]

Figure 2.19. Long-term stability of the cells with different Ag contents in dry CH₄ at 1023 K. Ag loadings of the infiltrated cells are Cell A: 0.89 wt. %, Cell B: 1.59 wt. %, Cell C: 2.48 wt. % [96].

In the literature, investigators are looking for alternatives to precious metals that have high coking tolerance and catalytic nature together. Despite the bad known coking behavior of Ni, Wang et al. studied modified nickel as an infiltrated phase for a highly coking-resistant catalytic species [94]. Ni-Al₂O₃ has a combination of good catalytic activity with high coking tolerance. Moreover, Ni-Al₂O₃ also has better mechanical performance owing to the Al₂O₃ phase. Researchers aimed to promote this catalyst system by modifying with Li, La, and Ca. Their studies on CH₄ conversion and CO selectivity of Li-La modified Ni-Al₂O₃ monitored that methane conversion was very stable within 300 hours and reached 95%. CO selectivity was 100% during that period showing an excellent performance with methane fuel (Figure 2.20).

Figure 2.20. Time dependence of methane conversion and CO selectivity under $\text{CH}_4:\text{O}_2 = 2.2:1$ conditions for the $\text{LiLaNi-Al}_2\text{O}_3$ catalyst [94].

To measure the coke tolerance of the modified catalyst systems. Temperature Programmed Oxidation (TPO) analysis was performed with purged CH_4 . As shown in Figure 2.21, the CO_2 peak area reduced when using alkali metal modification and rare earth metal oxides. Moreover, peak temperatures were also shifted to lower temperatures. As noted, CaO -promoted $\text{Ni-Al}_2\text{O}_3$ catalyst showed the best coking resistance.

This study showed the latest trend in catalyst engineering of SOFCs. Starting from the precious metals, small amounts of nano-catalysts also displayed high coking tolerance and stability.

Figure 2.21. O₂-TPO profiles of LiLaNi-Al₂O₃, LaNi-Al₂O₃, LiNi-Al₂O₃, LaCaNi-Al₂O₃, CaNiAl₂O₃ and Ni-Al₂O₃ catalysts after operation under CH₄:O₂ = 11.5:1 conditions for 100 h [94],

Experiments showed that traditional Ni/YSZ cermet anodes also could not tolerate hydrogen sulfide impurity. Studies showed that a few ppm of H₂S retards the system with a sharp decrease of voltage during initial hours and an increase in polarization resistance [34, 46, 103, 106, 154].

Hence, studies have aimed to substitute nickel with an alternative material without sacrificing conductivity and catalytic properties. Researchers are using the same precious metals (Pd, Au, Pt, Ru) and transition metal-based systems (Cu, Co) to suppress sulfur poisoning. Alternatively, owing to the high surface area and activity of the nanoparticles, catalytic particle,

or sulfur tolerant particle decoration via infiltration can be a promising method to modify the electrodes [154].

2.5.3. Wet Chemistry

Modifying the wet chemistry of the precursor solution is vital to enhance the penetration ability and hence the yield of material deposition per step. Apart from some external engineering solutions such as vacuum or pressure assistance, the surface tension of the precursor system plays an important role in the wettability of the electrode backbone. It is common knowledge that alcohol-based solvents have lower surface tension than water and hence a better wettability on solids. In that sense, non-aqueous precursor systems are more preferred [38-40, 45, 46, 57, 88, 92, 97, 167]. Meilin Liu and his coworker's controlled the wetting property of SSC ($\text{Sm}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$) precursor by tuning the solvent mixture [73, 167]. As a solvent additive, ethanol was added into the aqueous SCC solution with different ratios to modify the liquid surface tension on the LSCF cathode backbone. In Figure 2.22, the wetting angles of a precursor droplet of different water-to-ethanol volume ratios were shown on different substrates as a quantitative measure of wettability. It was observed that higher ethanol content in the precursor promoted lower contact angles regardless of the substrate material. Although using 100% ethanol as a solvent may limit the solubility hence adversely affect solution/suspension stability and drying kinetics after infiltration, optimum ratios of water-alcohol mixtures would potentially decrease the number of infiltration steps with homogenous infiltrated particles.

Figure 2.22. Wetting angles of different SSC ($\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-x}$) precursor solutions on LSCF, LSM, YSZ and GDC substrates (note: mixture 1 had a water-to-ethanol volume ratio of 1:0.3 and mixture 2 has a water-to-ethanol volume ratio of 1:0.6) [167].

2.5.3.1. Infiltrated Material Phase

Infiltration of a metal precursor solution is the most popular strategy in the literature. The precursor solution comprises dissolved metal salts (chlorides, sulfides, and mostly nitrides) into water or alcohol. After the precursor is infiltrated to the electrode, the solution dries and precipitates out the dissolved metal salt. Then in the final calcination step, the infiltrated cell is fired to 400-1000 °C to form nano infiltrated particles.

Due to the solubility limit of metal salts, molarity is usually kept low. As a result, infiltration protocol is generally carried by repetitive steps. To decrease the number of infiltrations steps, molten salts infiltration can also be done [168]. The molten-salt infiltration can be possible owing to low melting point metal nitrates. However, even near melting point, the precursors have

such a high viscosity that capillary action does not help the self-infiltration process by itself. Vacuum assistance can be utilized to provide better penetration.

One of the most straightforward approaches is dispersing pre-synthesized nanoparticles in a solvent and then infiltrating the dispersed suspension on top of the electrode [46, 54, 63, 64, 80]. High solid loading of the infiltrated phase is one benefit of this methodology, which allows fewer repetitive infiltration steps to achieve the desired deposition amount. Here, the initial particle size plays a vital role since the dispersion of high surface area particles is difficult to stabilize whereas low surface area particles – relatively larger particles – are challenging to infiltrate through the porous electrode efficiently. Moreover, pore-clogging and gas starvation issues may be other potential complications.

P.K. Lohsoontorn et al. infiltrated GDC catalyst into Ni-YSZ electrode [63]. In their experiment, GDC solid loading was kept at 20 wt % with a solvent of butanol-mixed xylene. Figure 2.23.a shows the GDC starting powder from the infiltration solution, and it is concluded that the particles are submicron-sized but highly agglomerated (Figure 2.23.b). Moreover, it was noted that the infiltration of GDC particles was not homogenous on the Ni/YSZ substrate.

Figure 2.23. SEM images of (a) GDC starting powder and (b) GDC-impregnated Ni-YSZ electrode after fired at 800°C for 2 h. [63].

S. P. Jiang et al. performed a comparison of infiltration materials [54]. NiO screen printed YSZ substrate was used as an anode and then reduced under H_2 . The final porosity of the Ni anode was calculated as 30 vol%. YSZ and GDC were selected as the ionically conductive infiltrated phases. Nano-YSZ suspension and 3 M GDC ($Gd_{0.2}Ce_{0.8}(NO_3)_x$) nitrate solution were used. The suspension or solution was deposited on the anode top surface, and the impregnated cells were fired at 850°C for 1 h to decomposition. The study showed that YSZ oxide infiltration loading was 2.7 mg/cm^2 (17 vol%) after one infiltration treatment and 4.0 mg/cm^2 (21 vol%) after repeated infiltration cycles. In case of GDC nitrate infiltration, 0.52 mg/cm^2 (3.5 vol%) was achieved after one infiltration, and repeated infiltration treatments increased the loading up to 1.7 mg/cm^2 (8.5 vol%). The solid loading yield difference between YSZ suspension infiltration and GDC solution clearly states the efficiency of these two starting routes. Due to the higher concentration of suspension, it was possible to deposit a higher amount of YSZ particles than GDC solution infiltration. Figure 2.24 shows the SEM images of the surface and fractured cross-sections of pure Ni, YSZ, and GDC infiltrated Ni anodes. As seen in Figure 2.24.c and d, a thin YSZ oxide film layer was observed on the Ni backbone. On the other hand, GDC nitrate solution infiltration was

different from YSZ suspension infiltration, as seen in Figure 2.24.e and f. It was observed that GDC coverage was not homogenous over the nickel particles.

Figure 2.24. Scanning electron microscope pictures of (a) surface and (b) fractured cross-section of pure Ni anode, (c) surface and (d) fractured cross-section of 2.7 mg/cm² Y₂O₃-stabilized ZrO₂-impregnated Ni anode, (e) surface and (f) fractured cross-section of 1.7 mg/cm² Gd-doped CeO₂-impregnated Ni anode [54].

Finally, the precursor drying parameters have a significant influence on the particle localization. Dissolved metal nitrate or particles localized unevenly and drifted through due to the phenomenon called 3-D segregation, in which ions can precipitate onto the previously calcined catalyst surface [31, 78, 80, 169-172]. The study by Zhu et al. showed that drying method of the

infiltrated cell facilitated the morphology of the gel in flower-like which facilitated the infiltration process [108].

Progressively increasing the catalyst loading with repetitive steps can improve electronic conductivity, but it requires tedious infiltration/drying/ calcination steps and could potentially reduce the original porosity of the porous scaffold, causing gas transport limitations [28] and hence increasing the polarization resistance [45]. There have been only limited efforts devoted to developing a protocol for one or two infiltration steps with high nitrate concentration in the presence of dispersant or surfactant [38, 74, 78, 156, 173].

2.5.3.2. Surfactants and Dispersants

To control the dispersion and wetting of porous structures with salt solutions, various additives have been used to facilitate infiltrated nanoparticle distribution and phase complexation that prevents individual single oxide phase impurity formation prematurely.

Triton X-100 ($C_{14}H_{22}O(C_2H_4O)_n$, Union Carbide Chemicals and Plastics Co., Inc) is a commercial surfactant that is used as a surfactant additive for precursor solutions. One proven function of Triton-X is to obtain phase stability as a complexing agent. Figure 2.25 displays that direct decomposing of LSM, metal nitrate precursors only yield to a pure perovskite phase with the use of Triton X surfactant [28]. The study by Tucker et al. demonstrated the effect of the use of Triton-X on particle size and distribution [174]. Shown in Figure 2.26, are fine infiltrated Ni particles on to the YSZ backbone. It was stated that with the use of Triton-X-100, individual particles are in the range of 40-100 nm (Figure 2.26.a). The precursor solution filled only 3 vol % of the total pore volume per step, so the protocol was repeated 12 times to build up a connected network of Ni catalyst. It is reported that, by substituting a lower chain length Triton-X surfactant (Triton-X-45), smaller micelle formation was achieved that yielded the reduction of Ni particles down to 10-50 nm [21]. Only 5 infiltration steps were needed to attain a well-connected network

(Figure 2.26.b) [174]. Although the LSM precursor is basically a cathode material, similar behavior of Triton can potentially be seen for anode compositions [80].

On the other hand, one case study of Nicholas and Barnett showed that Triton X-100 in SSC ($\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-x}$) nitrate solution did not produce an SSC phase but adding citric acid ($\text{C}_6\text{H}_8\text{O}_7$) as an ion-complexation agent, resulted in pure SSC phase as shown in Figure 2.27. [175]. Pure nitrate derived (PND) and Triton X-100 derived samples contained sub-constituent oxides, Co_3O_4 , SmCoO_3 and SrCoO_3 [175]. Furthermore, the presence of additives had little effect on the morphology or the performance of the infiltrated SSD-GDC composite cathodes.

Figure 2.25. XRD patterns of the decomposition products from LSM precursor (a) without and (b) with Triton-X 100, sintered at 800°C for 1h [28].

Figure 2.26. SEM images of porous YSZ structures infiltrated with (a) Ni once with Triton-X-100 surfactant and (b) Ni five times with proprietary (Triton X-45) surfactant [174]

Figure 2.27. XRD scans for powders produced by firing various $\text{Sm}(\text{NO}_3)_3\text{-Sr}(\text{NO}_3)_2\text{-Co}(\text{NO}_3)_2$. PND= Pure nitride derived, TXD=Triton X-100 derived, CAD=Citric acid derived [175].

The addition of glycine has also shown to be effective in promoting the uniform distribution of infiltrated yttria-stabilized bismuth (YSB) nanoparticles with reduced infiltration steps. The studies by Z. Jiang et al., on infiltrating LSM particles on a YSB ($\text{Y}_{0.5}\text{Bi}_{1.5}\text{O}_3$) backbone which were aimed of getting lower polarization resistance, R_p , than conventional LSM/YSZ system, included glycine to the metal nitrate/water solution as a complexing agent (glycine to nitrate molar ratio of 0.5) [55, 176]. After dripping the solution to the top of the porous YSB layer for only one step, the cell was heated to 800°C for 1h to form LSM nanoparticles. Phase characterization in Figure 2.28. Indicated that the presence of glycine yields single-phase LSM particle. Moreover, glycine also acted as a surfactant for the coverage of LSM particles on YSB backbone as seen in Figure 2.29.b. The authors noted that the two-step infiltration was enough to get a big upshift on the conductivity and downshift on polarization resistance of the cathode at elevated temperatures.

Figure 2.28. X-ray diffraction patterns of the pure YSB powders and the YSB after the infiltration with LSM. Both the XRD patterns of LSM nitrate precursors with and without the addition of glycine are showed [55].

Figure 2.29. Cross-sectional micrographs of (a) YSB backbone, (b) LSM-YSB composite [55].

Using of glycine in anode infiltration. L. Fan et al. added glycine with the molar ratio of metal cations-to-glycine 2:1, as a complexing agent in the GDC, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Gd}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ in a mole ratio of 0.2:0.8) solution of ethyl alcohol and deionized water (50-50 vol%) to LST ($\text{La}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$) nanofiber scaffolds [44].

Urea ($\text{CO}(\text{NH}_2)_2$) is another organic chemical that has been used to minimize the non-uniform deposition and impurity phases [28, 31]. The dissolution of urea in water gives OH^- ions to be consumed by the metal cation (M^+) in the solution. Hence, the metal cation is induced to precipitate by forming metal hydroxide $\text{M}(\text{OH})_{(\text{s})}$ before the drying step. Li et al. showed that the effect of adding urea is to enhance the distribution on the electronic connectivity of nanoparticle phases in the infiltrated Cu and CeO_2 composite anodes on porous YSZ scaffold. As shown in Figure 2.30, the addition of urea assisted the formation of a layer of finer particles homogeneously [171]. As a fact of enhanced TBP length, the power density of the urea added infiltration was 37% higher than the infiltration without urea (Figure 2.31).

Figure 2.30. SEM micrographs of Cu-CeO₂/YSZ composite anode without (a) and with (b) adding urea after operated in H₂ at 700°C for more than 10h [171].

Figure 2.31. I-V-P characteristic curves of Cu-CeO₂/YSZ composite anode impregnated with or without adding urea when operated in H₂ at 700°C [171].

Besides the single-phase infiltration, the formation of complex nano-catalyst phases such as (La, Sr)(Cr,Fe)/Ni [110] and SSC (Sm_{0.6}Sr_{0.4}CoO_{3-δ}) can also be achieved by urea precipitation

[28]. Figure 2.32 illustrates that the addition of urea attains the SSC perovskite phase while calcination of only nitrate mixture resulted in multiple secondary phases in the catalyst system. Moreover, it was found that urea can also promote preferential deposition on composite substrates. As shown Figure 2.33, reaction infiltrated SSC particles with urea tend to deposit on LSM particles instead of YSZ particles.

Figure 2.32. XRD patterns of nanoscale SSC from (a) nitrate precursor and (b) urea plus nitrate heated at 800°C for 2h. (P) Peaks corresponding to perovskite phase [28].

Figure 2.33. SEM images of an LSM-YSZ cathode with dispersed SSC nanoparticles after heating at 700°C [28].

Also, A. Buyukaksoy et al. added ethylene glycol to an aqueous $\text{Ni}(\text{NO}_3)$ solution as a polymerization agent before heating the resultant solution to 100°C until the water was removed and Ni ions were incorporated into polymer complex [38-40]. Moreover, 2-butoxyethanol was added with a 1:2 ratio of the polymeric precursor to promote the wettability of the polymer complex. Finally, in the study of particulate GDC infiltration on Ni/YSZ by P. K-Lohsoontorn et al., butvar binder and polyvinyl pyrrolidone (PVP) as a plasticizer are added to the suspension of a butanol-xylene mixture [63].

In conclusion, the main efforts of including these additives listed above are to achieve single complex phases, with isolated particulate decoration and less repetitive steps. In addition, the infiltration method has a direct influence on the final microstructure.

2.5.4. Infiltration Methods

In the first infiltration studies, researchers were seeking an easy and effective way to improve the SOFC performance without altering the process of reliable existing electrodes but by adding nano-catalyst in the structure. A technique called the dripping method has been the most

performed protocol to meet those necessities. Today, the infiltration process has received much attention and can be performed by various technologies as shown in the literature in Figure 2.34. One of the main initial goals of infiltration studies is achieving maximum dispersion/decoration within the electrode without having undesired agglomeration and performance loss over time. The second goal is to be able to monitor or predict the catalyst deposition amount by tuning just a few parameters, such as solution concentration. Although, the dripping method is the most utilized technique, there are some innovative alternative methods applied to lower the steps required to deposit material and enhance the homogeneity, such as atomic layer deposition [112, 120, 132, 136, 149], inkjet printing [134, 143, 144, 147, 177, 178], etc.

Figure 2.34. Infiltration methods applied for anode electrode in recently published studies [29-152].

2.5.4.1. Dripping Method /Tape-cast Infiltration

As seen in Figure 2.35, the infiltration protocol is mostly performed by a technique called the dripping method. In this method, precursor solution(s) or suspension(s) were dripped over the top of the anode electrode by a simple pipette. The overall process is schematically illustrated in Figure 2.35. A porous backbone structure is infused by the catalyst precursor owing to capillary action. The dripping process requires many infiltration repetitions of low-concentration metal salt

solutions to achieve sufficient solid loading to form a percolated network. To enhance the infiltration efficacy of this process, vacuum assistance can also be used. One drawback of the dripping method is the operator cannot control the process to achieve desired deposition yield and homogeneity. There is no linear correlation of deposition yield between the infiltration steps and the performance enhancement.

Figure 2.35. Infiltration of a porous scaffold. A metal nitrate is infiltrated into the scaffold. This is heated to decompose the nitrate to the oxide. The operation is then repeated several times [179].

Similar to the dripping method, Qiao et al. introduced a method called tape-casting infiltration (TCI) to control the ionically conductive electrode backbone porosity by supporting the structure with a dense electrolyte layer. In this method, thin and dense YSZ tape – 30 μm thick without pore former- was laminated with YSZ tapes containing starch pore formers – 800 μm thick. After firing of that sandwich structure, a resulting YSZ network with 60-65 % porosity was

infiltrated with nickel and ceria nitrate precursors by the dripping method under vacuum several times to get the desired infiltrated particle loading [83]. Figure 2.36 shows the porous YSZ network which will be infiltrated on the later step and dense region which will act as the electrolyte.

Figure 2.36. SEM graphs of p-YSZ/d-YSZ: (a) p-YSZ surface and (b) cross-section for p-YSZ/d-YSZ [83].

Although it is an easy application method and requires almost no equipment, the dripping method has some disadvantages. With the necessity of repetitive infiltration cycle and multiple firing steps, the dripping method is a labor-intensive process. In addition, the amount of infiltrated nano-particle is inconsistent between the cycles because of the operator handling and microstructure/porosity variance. Precursor film formation during the drying step gives inhomogeneous and localized nanoparticle precipitation, which makes the overall method irreproducible. In that sense, researchers have been studying other alternative and controlled deposition techniques for the infiltration of SOFC electrodes.

2.5.4.2. Dip Coating

Dip coating is a well-known method for the coating of planar substrates. Also, it has been used to modify or infiltrate 3-D scaffolds such as SOFC electrodes [52, 58, 60, 61, 74, 78, 80, 84, 96, 99, 103, 105, 113, 125]. A schematic representation of the dip-coating method is shown in Figure 2.37. Dip coating has few advantages over the dripping method. First, the dip-coating method is claimed to facilitate a uniform precursor coverage starting from the surface regions. Secondly, in comparison to the dripping method, dip coating is usually composed of a singular infiltration and firing step which needs less operator control and time.

Figure 2.37. Schematic representation of vacuum assisted dip coating infiltration method.

2.5.4.3. Electrodeposition

Due to the limitations of the dripping method mentioned above, the electrodeposition method first was demonstrated by Gorte et al [32, 56]. By electrodeposition, higher amounts of metal particles can potentially be deposited into the porous conductive network. To achieve

homogenous deposition within the cell, solution concentration, conductivity, and applied voltage are critical parameters.

To achieve a conductive network of the electrode, Gorte et al. demonstrated two different approaches and experimental parameters. One way was to utilize a cermet (ceramic-metal) structure of the anode [32]. A Cu salt was infiltrated into a YSZ wafer along with ceria nanoparticles, by repetitive steps, was fired at 723 K in air and then reduced in humidified (3% H₂O) H₂ at the same temperature. Hence, electrically conductive (13 vol% Cu) anode electrode was achieved. Next, the cell was immersed in Co precursor solution with H₃BO₃ and HCl and Co was deposited on to the Cu in the anode under the galvanostatic condition in one step without any need of firing. Figure 2.38 showed the ohmic resistance of cells prepared with different protocols as a function of time. It can be seen that the cell with electrodeposited Co showed the lowest ohmic resistance among other cells including, the co-impregnated Co cell. Moreover, thermal stability was also achieved by Co electroplating which demonstrated the efficacy of electroplating.

Figure 2.38. Ohmic resistance measurements at 1173 K in humidified H₂ as a function of time for (○) Co-Cu-ceria-YSZ (5 vol% electrodeposited Co, 13 vol% Cu); (◇) Cu-ceria-YSZ (18%vol Cu); (Δ) Co-Cu-ceria YSZ (co-impregnation of 5 vol% Co and 13 vol% Cu); (□) Co-ceria-YSZ (18 vol% Co); (x) Co-ceria-YSZ (30 vol% Co) [32].

The second way that Gorte et al. demonstrated was treating the porous YSZ by carbon coating [56]. A conductive carbon layer (11 vol %) was achieved by purging n-butane at 1123 K (850°C) for 10 min. An electroplating step was performed with the same protocol as above with Co and Ni chloride aqueous solutions. SEM images after the decarbonization step showed that highly deposited Ni (20 vol %) and Co (30 vol%) composites with ceria had a uniform interface within the anode electrode (Figure 2.39) [56].

Figure 2.39. SEM images of a porous YSZ matrix **(a)** before and **(b)** after incorporation of 10 vol % ceria and 20 vol % Ni or **(c)** 30 vol % Co [56].

2.5.4.4. Spin Coating

Spin coating method provides lateral uniformity and good control of the infiltrated component amounts. In the literature, the method is applied for metal-supported and porous electrolyte substrates. Buyukaksoy et al. utilized spin coating for infiltration on their studies for both anode and cathode [38-40, 180]. First, a porous YSZ backbone layer was formed by spin coating of a YSZ powder suspension on the YSZ electrolyte at 3000 rpm. After firing at 1150°C,

the porosity of the spin-coated YSZ porous backbone was around 50% after. It was required to repeat spin coating around 10-30 times to achieve the desired thickness. Then a polymeric nickel precursor was infiltrated to the porous backbone again with the spin coating technique. The cell was finally heated to 400°C for the decomposition of the polymeric precursor. To get the percolation of nickel oxide particles, it was necessary to repeat the process up to 35 times. The ratio of NiO/YSZ was around 40%. Figure 2.40 displays the structure of a porous YSZ backbone and the nickel oxide particles [40].

Figure 2.40. (a) The fracture surface where the EDS mapping data was collected (b) EDS map showing the Ni distribution in the Ni-YSZ cermet (Ni signals are in dark gray) [40].

2.5.4.5.Pasting

In this study, lanthanum promoted Ni-Al₂O₃ catalysts were prepared by the glycine method [94]. Stoichiometric amounts of nickel nitrate, lanthanum nitrate, lithium nitrate, and aluminum were dissolved in DI water with the addition glycine at a molar ratio of glycine to total metallic cations of two. The gel precursor was obtained by heating the solution on a hot plate. The gel precursor was transferred to an oven at 240°C. The obtained powder was calcined at 850°C for 5 hours as the last step. Then a slurry of the catalyst powder was painted onto the top surface of

Ni-ScSZ anode layer within a single step and sintered at 850°C in air for 1 hour. Figure 2.41 depicts the SEM image of the anode after running the fuel cell on methane for 10 hours. The pasted catalyst layer still adhered to the Ni-ScSZ layer without delamination and carbon deposition.

Figure 2.41. Cross-sectional SEM images of the catalyst-catalyst anode interface after the operation on methane fuel [94].

Figure 2.42.a shows the stability of the catalyst-pasted cell for the open circuit voltage (OCV) under methane fuel. During 150 minutes of operation, OCV was around ~1.17V and the peak power density (PPD) altered from 437 mW/cm² to 421 mW/cm², with a reduction of 3.7%. With the application of 500 mA cm⁻² current density, the voltage decreased to 0.685 V with a decrease of 1.3% after testing under the same conditions (Figure 2.42.b). The study showed that pasting LiLaNi-Al₂O₃ catalyst had high coking resistance as a promising application, although there was no diffusion study along the anode composition or coarsening study of catalysts.

Figure 2.42. Time dependence of the peak power density and open circuit voltage (a) and voltage and power density under constant polarization current density of 500 mA cm⁻² (b), of the fuel cell with the LiLaNi-Al₂O₃ catalyst layer, paste operating on pure methane fuel [94].

2.5.5. Selected Topic 1: Microstructure Altering Acid Leaching Treatments Prior to Infiltration

The study by Ye et al. mentioned the limitation of catalyst loading by the porosity of the anode matrix. However, having a critical porosity level is a requirement in order to meet mechanical strength and geometrical stability [99]. In that sense, an acid leaching process of nickel in the traditional Ni/YSZ anode is utilized by taking the advantage of insoluble character of ZrO₂ in

acidic medium. Thus, it was aimed to have a YSZ frame with a properly interconnected porosity without the influence of other properties in the nonexistence of nickel structure. Leaching was performed by immersing NiO/YSZ – current collection layer -, NiO/ScSZ - active layer – anode with ScSZ electrolyte structure to 2.2 M HNO₃ at 80°C for about 2 hours to entirely remove nickel. It was mentioned that a relatively dense active layer was not affected by the acid leaching process. Infiltration of CeO₂ and CuO₂ catalysts were then infiltrated simultaneously by a dripping method on highly porous acid leached microstructure. Figure 2.43.b-c shows the difference between microstructures before and after acid leaching. After leaching, the measured average pore size was 5 µm. EDX results of spectrum 1 and spectrum 2 of Figure 2.43.c (not shown) detected that spectrum 1 was mainly composed of infiltrated particles and zirconia, while spectrum 2 was nickel and zirconia. This indicated the efficacy of acid leaching and infiltration protocol. Though, researchers perform this route in small batches of cells, nickel leaching is not a cost-effective route to create porosity.

Figure 2.43. The cross-sectional SEM of the Cu-CeO₂-YSZ/Ni-ScSZ/PCM single cell **(a)** the interface between the Cu-CeO₂-YSZ supported anode and the Ni-ScSZ anode functional layer **(b)**, the porous YSZ matrix after acid leaching treatment **(c)** and the Cu-CeO₂-YSZ anode matrix after impregnation **(d)** [99].

2.5.6. Selected Topic 2: Microwave Firing

After each infiltration step, cells are usually fired conventionally in air atmosphere between 450 – 1000°C. Transition-metal precursors (mostly metal salts) are calcined to form oxide nanoparticles. To form metallic nanoparticles, such as nickel [85] or silver [96], the calcination

must be carried under reducing atmosphere, which is not a practical and cost-effective technique. Islam and Hill [52] demonstrated microwave irradiation as an alternative to conventional firing to shorten the time needed for subsequent calcination steps in impregnation cycle(s). In their research, the Ni/YSZ anode of an electrolyte supported cell is dipped to a beaker of Cu precursor solution, then the beaker was placed in a household microwave oven (2.45 Hz, 700 W) for 15 seconds. The measured temperature of the solution during irradiation was 365K (92°C). After washing and drying steps, the amount of Cu was 6 wt% with respect to Ni of the anode structure. In Figure 2.44, infiltrated nano particles less than 100 nm size can be seen clearly although some regions were not covered by Cu nanoparticles completely. Owing the time needed for calcination, the microwave irradiation method has shown a clear advantage over conventional firing methods both for achieving a fast calcination route and obtaining the desired metal phase. However, reproducibility of the protocol and potential cracking due to local temperature gradients between metal (nickel), metal oxide (YSZ) particles in anode cermet should be assessed in detail.

Figure 2.44. Cross-sectional SEM images of $\text{Cu}_M/\text{Ni}/\text{YSZ}$ cell: (a) anode-electrolyte interface, (b) enlarged image taken from region P. [52]

2.6. Conclusion and Comments

In this review, infiltration methods and materials were systematically assessed. According to this review, the wet infiltration/impregnation method of various nanoparticles/catalysts was shown to be a promising technique to activate or modify the porous anode and cathode electrodes. The major outcome for infiltration is decreasing the polarization resistance of the electrode as a result of increasing triple phase boundary (TPB) density owing to high surface area nano-particles. Performance improvement can be achieved by infiltrating precious metal (Pd, Ru, Pt, Au, Ag), transition metal (Ni, Cu, Co), or mixed-oxide conducting systems (ceria). The studies clearly showed that high oxygen ion conductivity and/or catalytic activity could be incorporated into electrode structures by wet impregnation/infiltration methods.

On the processing side, wet infiltration has some technical difficulties. Conventional infiltration methods mostly require repetitive steps, including multiple firing cycles, which make the whole process very labor-intensive. On each step, the liquid precursor dries previously calcined nano particles instead of the backbone which causes uncontrolled agglomeration. This potentially reduces the efficacy of the infiltration by promoting grain growth during each firing step and potential clogging risks. To avoid these issues, a single infiltration protocol with an isolated decoration of anchored nanoparticles to the pore walls could be an optimum strategy. However, due to the solubility limits of the precursor, low precursor concentrations are usually preferred for the dripping method.

Unlike successful applications for the cathode, the wet infiltration of a SOFC Ni-based anodes is typically found to be more difficult, since the most common SOFCs possess an anode-supported architecture. This means that the anode electrode is the thickest portion and the

relatively denser electrode of the fuel cell. This challenging electrode structure is the key difficulty placement of catalyst to the active area.

Another aspect is that most previous research showed an increased improvement in electrochemical performance, usually reflected in an increase in power density or decrease in polarization resistance, within a relatively short operation time. Typically the performance enhancement is only shown for the first few hours of current loading. These works showed the effect of incorporated nano-particles shown sintering and coarsening in the initial few hours of operation which negates any perceived performance enhancements. For a realistic evaluation, long-term fuel cell operation (>500 h) should be completed and characterized by these nano-infiltration studies. In that sense, possible coarsening mitigation mechanisms must be taken into account. Furthermore, infiltration experiments should be carried on off-the-shelf commercial cells for a real case reference comparison and any potential scale-up options.

2.7. References

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Chapter 3 : pDA Bio-Surfactant Assisted Nano-Catalyst Infiltration of Solid-Oxide Fuel Cell (SOFC) Electrodes

3.1. Introduction

The introduction of nano-catalysts into the porous electrode microstructure of Solid Oxide Fuel Cells (SOFC) was previously achieved through solution or suspension impregnation methods. These impregnation processes typically showed an increase in cell power density over short operation times reported by Jiang et al. [1]. According to the review, various aspects of fuel, oxidant adsorption, and diffusion can be distinctly engineered by incorporating a small volume fraction of nano-catalyst into the electrodes. This can even be accomplished after the final sintering process of the SOFC membrane-electrode assembly (MEA) is completed. One attractive aspect of this method is that the performance of the SOFCs may be increased without any extensive alterations to the anode or cathode microstructure after initial cell fabrication. Typical nano-catalyst impregnated compositions for SOFC electrodes include doped-CeO₂, Cu, Co, Pt, and Ni for the anode [2-6], and Pd, doped-CeO₂, (La,Sr)MnO₃ and (La,Sr)CoO₃ [7-10] for the cathode. Most papers in the literature describe one major processing restriction for wet infiltration/impregnation strategies; the process usually requires multiple infiltrations and drying steps in order to achieve the desired nano-catalyst loading and to insure the proper increase in performance [11]. Numerous steps are necessary since preferential drying at the surface of the porous structure results in precipitate segregation and agglomeration, eliminating the ability to further incorporate more salt solution deeper into the microstructure.

To control the dispersion and wetting of porous structures with metal salt solutions, some dispersant and surfactant additives, such as Triton X-1, glycol, urea and citric acid [9, 12] were introduced in the previous studies. The surfactants utilized for these works were specifically

associated with the composition of the substrate and/or nano-catalyst; therefore, the surfactant system needed to be re-engineered for any change in the SOFC electrode or nano-catalyst composition. One potential solution to this issue is to use a versatile substrate modifying surfactant, such as poly-dopamine (pDA). pDA is a biochemical that is commonly found in nature, for example, in the foot protein of a mussel. Owing to the multi-functional OH^- and amine groups, the molecule was shown to adsorb or react with various organic and inorganic materials [13] (Figure 3.1).

Figure 3.1. (a) A mussel sticks to the rocks by the polymerized dopamine [14]. (b) DOPA is synthesized at the mussel legs in various molarities (mfp) [15] (c) the molecular structure of DOPA and dopamine.

Recent research showed that the deposition of nanoscale, two-dimensional films of metals, oxides, and polymers onto planar substrates with various chemistries could be achieved by surface modification of those surfaces with pDA. Specifically, the OH^- groups in the polymer chain of pDA locally attract metal cations and chelate into the metal hydroxide form. The mechanism can be articulated as a deposition process that is not altered by the fast drying or cation migration towards the edges. Hence, the prime advantage of using pDA as a surfactant is the ability to grow a thin film that allows for distinct control of the nucleation and growth rate of a broad spectrum of compositions through the simple tuning of the pDA solution concentration and immersion time

[16]. In addition, being independent of the substrate and the coating material, the catechol templating has great potential in assembling nanoparticles on to the planar substrate and also potentially through the 3-D porous backbones.

The objective of this work is to develop a facile two-step dip-coating process to incorporate a controlled amount of nano-catalyst into the both porous SOFC electrodes (the anode and cathode). At first, the pDA surfactant was introduced into the porous electrode structure through an initial dip-coating procedure to control the heterogeneous nucleation mechanism (bio-coating) for this process. The second step included the dip-coating of the SOFC membrane with a catalyst precursor to deposit nano-catalyst on to the pDA layer. In this study, ceria (CeO_2) was used as the baseline catalyst composition to demonstrate the process. Cerium oxide has a cubic fluorite-type structure that has been one of the major non-noble constituents in catalytic systems due to its +4 to +3 valence switching character. Hereafter, nanostructured ceria catalysts can be used in both reducing and oxidizing environments. As shown in Figure 2.13, cerium based catalyst systems are one of the most utilized nano-catalyst systems for promoting the half-reaction kinetics on both the cathode and the anode in the literature. Off-the-shelf SOFCs were infiltrated with pDA-treated cerium nitrate protocol to demonstrate the applicability of the process to commercial cells, where the electrode microstructures did not need to be further modified in order to increase process efficiency, which is typically required for nano-infiltration/impregnation methods.

3.2. Experimental

Thermal gravimetric analysis (TGA) was performed on as-received dopamine hydrochloride (99%, Alfa-Aesar) and polymerized dopamine (pDA). For Poly-dopamine, 2 mg/ml of dopamine hydrochloride (99%, Alfa-Aesar) is polymerized in water with 0.05M TRIS (tris(hydroxymethyl) aminomethane, 99%, Alfa-Aesar) buffer at pH 8.5 for 16 hours. Then the

solution is dried in the oven overnight to precipitate the pDA. All the samples were heated to 850°C with 2°C/min rate in the air during the TGA testing.

Anode-supported button SOFCs (ASC-2.7, NexTech Materials, Ltd.) were used for this study. These cells were 27 mm in diameter and consist of a 240 µm thick NiO/yttrium-stabilized zirconia (YSZ) anode, a dense 8 µm thick YSZ electrolyte (27 mm in diameter), and a (La,Sr)MnO₃ (LSM)/LSM-GDC cathode, which was 12.5 mm in diameter and 50 µm thick.

Contact angle measurements were performed to characterize the wettability of pDA and cerium nitrate solutions in various water/ethanol ratios. NiO/YSZ pellets were prepared and sintered at 1450°C as substrates to mimic a conventional anode surface. Droplet images were taken with a Dino-lite digital microscope (AnMo Electronics Corp, Taiwan). The contact angle was measured by a drop analysis plugin in Image-J software.

The modification of the electrodes was initially completed by incorporating the pDA into the porous electrode microstructures through a well-known dip-coating (DC) process. The pDA solution was prepared by dissolving 1 mg/ml dopamine hydrochloride (99%, Alfa-Aesar) into a 0.05 M TRIS (tris(hydroxymethyl) aminomethane, 99%, Alfa-Aesar) and 1:1 vol % water-ethanol mixture at pH 8.5. The TRIS buffer stabilized the pH during the polymerization reaction [13]. Polymerization was confirmed visually by the transition of solution color from transparent to brown. Two pDA assisted dip-coating techniques were used in these experiments: 1) *ex-situ* polymerization (*ex-situ* DC pDA), in which the bio-coating solution was polymerized in a separate beaker before submersion of the SOFC membrane into the solution; and 2) *in-situ* polymerization (*in-situ* DC pDA), in which the bio-coating solution polymerization reaction was initiated after the SOFC was submerged into the solution. For the *ex-situ* polymerization process, a Nalgene® polyethersulfone 0.2 µm syringe filter (Thermo Scientific) was used to filter the polymerized bio-

coating solution to eliminate micron-sized pDA aggregates from the solution. These aggregates could potentially block pores and restrict the infiltration of the salt solution during the second step of the process.

The pDA bio-coating step was applied to both electrodes simultaneously by submerging the entire SOFC into a beaker containing the pDA solution. The beaker was placed in a vacuum chamber under 30 mm Hg vacuum for 5 min. The beaker was removed from the vacuum chamber and transferred to a rocker table for 3 h in ambient conditions. The cell was then rinsed two times with a 50 % ethanol-water mixture before immersing into the cerium solution. The cerium solution had a concentration of 0.4 M within a 1:1 vol % water-ethanol solvent and cerium (III) nitrate hexahydrate (REacton®, 99.5%, Alfa Aesar) the salt to form the solution. The SOFCs remained submerged within the cerium solution on the rocking table for a 24 h period before removal. The surfaces of both electrodes were rinsed with a 1:1 vol % water-ethanol solution, and permitted to dry in ambient conditions. After drying, all impregnated cells were fired at 750°C to obtain pure ceria nanoparticles. The impregnated cells were weighed before and after firing to measure the degree of nano-catalyst incorporation.

To compare the effectiveness of the bio-coating procedures, the cells were dipped inside the cerium solution for 24 h without pretreatment of the pDA surfactant. One SOFC sample was also impregnated using the dripping method which is the conventional method demonstrated throughout literature. The experiment included dripping 1 ml of 0.4 M cerium (III) nitrate solution from the 1:1 vol % water-ethanol mixture onto the anode side. The solution was dripped onto the top surface of the anode using a 3 ml plastic pipette, before placing the cell under 30 mm Hg vacuum. It should be noted that only the anode was impregnated with the cerium nano-catalyst for this baseline experiment. The sample was then dried in a vacuum oven at 50°C. Fuel cell testing

(current-voltage-power and impedance spectroscopy measurements) was performed at 750°C with humid H₂ fuel, using the same procedure described in a previous paper [17].

3.3. Results and Discussion

Prior to the SOFC electrode infiltration, preliminary tests were performed to determine that the pDA layer enters the system only as a sacrifice layer that does not stay in the system after the thermal treatment and does not alter the fuel cell performance itself. Figure 3.2 shows thermogravimetric analysis (TGA) dopamine hydrochloride and polymerized (poly) dopamine (pDA). From the TGA results, 20 wt% residue of dopamine hydrochloride was observed while pDA completely burns away totally around 600 °C. The left-over residue probably consists of the hydrochloride group which closely corresponds to 19.2% of the molecular weight of dopamine hydrochloride. However, the loosely bonded hydrochloride group is released to the solvent during the polymerization stage. Hence, the rest of the carbonaceous moieties burned out from the system below the operating temperature of a fuel cell.

Figure 3.2. TGA of dopamine hydrochloride and poly dopamine (pDA).

In the next stage, the electrochemical characterization was performed only on pDA coated fuel cell with no infiltrated catalyst. Figure 3.3 displays the current-voltage-power (I-V-P) curve of the baseline and the dopamine treated cells. The cells were tested at 750°C, which is above the burn-out temperature, as shown in Figure 3.3. First, open-circuit voltage (OCV) of both cells was around 1.075 V, which is close to the 1.1 V Nernst potential for the fuel-oxidant combination. This indicates the consistency of the testing set-up and conditions. Moreover, the peak power densities of both cells were very similar, around 400 mW/cm². The performance data that these cells have shown nearly identical performance meaning that the dopamine surfactant treatment altered the performance neither negatively nor positively by itself.

Figure 3.3. I-V-P curve of baseline and pDA treated anode supported cell tested with 300 sccm air and 300 sccm H₂ (3% humidified) at 750°C.

In the literature, both the dip-coating steps, the pDA surfactant and secondary coating precursor solution (nano-catalyst) solvents have usually been aqueous solutions. However, the use of water/alcohol co-solvent may enhance the wettability and penetrability through the porous electrode. Lou et al., previously reported that the addition of ethanol into the aqueous precursor solutions dramatically reduces the contact angle of the droplet onto the LSCF, LSM, YSZ, and GDC surfaces [18]. Hence, solvent modification experiments were performed on NiO/YSZ pellets. Figure 3.4 shows the contact angle change of the 2 mg/ml pDA and 0.4 M cerium nitrate droplets with various water / ethanol ratios. Droplets of 100% DI water solution showed partial wetting, where the contact angle (θ , CA) of pDA and cerium nitrate solutions were $79 \pm 7.3^\circ$ and $68.1 \pm 0.7^\circ$, respectively (Figure 3.5.a and b). The CA's dropped gradually until 50 % vol ethanol

substitution. When the solution mixture was 50 – 50 vol%, the CA of pDA droplet was $17.1 \pm 1.06^\circ$ (Figure 3.5.c.) while the CA of the cerium nitrate solution droplet was measured $28.8 \pm 4.3^\circ$ (Figure 3.5.d.). It was observed that further additions did not produce a noticeable change in the wettability. Furthermore, less water content slowed down the polymerization of the pDA. To keep the solution mixture consistency and avoiding any precipitation, both cerium nitrate and pDA solvent mixtures were kept the same (1:1 vol % water-ethanol mixture).

Figure 3.4. Contact angle drift of droplets of pDA and cerium nitrate DI water solutions as a function of ethanol substitute.

Figure 3.5. Droplet images of (a) pDA and (b) cerium nitrate of 100 vol % DI water solution and (c) pDA and (d) cerium nitrate of 1:1 vol % water-ethanol mixture on to the NiO/YSZ pellets.

The one-step conventional dripping method deposited approximately 0.4 mg (0.33 mg/cm²) CeO₂. The dip-coated cell without pDA treatment gained 0.5 mg of nano-catalyst within the electrodes. Note that the dip-coating method (using no pDA) was slightly more effective than the dripping method. The *ex-situ* polymerized pDA-assisted the dip-coating deposition by depositing ~1.1 mg of CeO₂ nano-catalyst in a single step. The *in-situ* polymerized pDA-assisted dip-coating protocol deposited 1.4 mg of nano-catalyst in a single step. These results show that the addition of the bio-coating pretreatment allowed for 3.5 times more catalyst deposition amount in a single step over the conventional dripping method.

Figure 3.6. (a-d) are SEM cross-sectional images of the *in-situ* DC pDA dip-coated cell after testing over 300 h. The SEM micrograph shows the ceria nanoparticles located within the bulk thickness and near the active layer of both the anode and cathode microstructure. The level of nano-catalyst deposition into the active anode layer was shown to be lower due to the thickness (~240 microns thick), and the density of the un-reduced anode support structures. This result highlights the limitation of infiltrating commercial anode-supported cells, where the unreduced microstructure usually possesses <30 vol% porosity, and hence restricts efficient infiltration to the active layer. The deposition within the cathode is extensive, where the single catalyst infiltration step resulted in a filled cathode porosity. The enhanced nano-CeO₂ deposition on the cathode side can be attributed to the high porosity level (35-45%) and relative thinness (~50 μm) of the cathode layer. The particle size of the infiltrated nano-catalyst was approximately 20-50 nm after 300 h testing.

Figure 3.6. Cross section SEM images of in-situ DC pDA dip coated cell, which were taken from the anode (A) middle layer, (B) active layer, and cathode (C) middle layer, (D) active layer of the anode-supported cell after testing at 750°C for 300 hours.

The SOFCs that utilized the two-step bio-coating process (where only one thermal treatment was used) were characterized using both I-V-P measurements and electrochemical impedance spectroscopy (EIS). The SOFCs were tested under constant current conditions (0.33 A/cm²) using humid H₂ fuel at 750°C for approximately 300 h. Again, the nano-ceria was incorporated into both the anode and cathode microstructure simultaneously. Figure 3.7 displays I-V-P curves for the SOFCs pre-treated with pDA (both through an *in-situ* and *ex-situ* polymerization process) and a baseline SOFC with no nano-catalyst incorporation. The I-V-P curves were taken before constant current loading at 0 h, and after 300 h of constant current loading. The data indicated an appreciable initial enhancement in power density by 20.7% and

17.9% for the *ex-situ* DC pDA and *in-situ* DC pDA samples, respectively. After approximately 300 h of fuel cell testing, the power density of the impregnated cells was 1.5% and 5.8% higher than the baseline performance, respectively. The results depict a greater gap in power density change for the *ex-situ* polymerized pDA dip-coated cells, which exhibited an 11.5 % degradation. In the *in-situ* polymerized pDA, the degradation was around 5.6 %.

Figure 3.7. I-V-P curves of baseline and impregnated SOFCs using the in-situ and ex-situ polymerized pDA surfactant before nano-ceria impregnation.

The degradation in power density was due to the sintering of the impregnated nano-catalyst over time at the operating temperature. In literature, it has been demonstrated that metallic (Ni, Pd, Pt) nanoparticles (with low thermal stability) and non-metallic (NiO, SDC, CeO₂, GDC, LSM) nanoparticles tend to coarsen over time leading to reduced surface area, activity, and triple-phase boundary area which all affect the performance of the cell [19-23]. As noted above, after testing in H₂ for 300 h, the particle size of the catalyst increased to 20 to 50 nm. In this way, an *in-situ* bio-coating process encouraged better penetration of the pDA to the electrode active zone before

polymerization. This resulted in better homogeneity throughout the porous 3-D structure and hence improved the catalyst island distribution.

EIS Nyquist plots, shown in Figure 3.8.a., display a total electrode polarization resistance (R_p) of 0.31 ohm·cm² for the *ex-situ* DC pDA cell and 0.32 ohm·cm² for the *in-situ* DC pDA cell. The R_p for the baseline cell was measured as 0.41 ohm·cm². These values correspond to a 23.4% and 21.7 % decrease in R_p for the *ex-situ* and *in-situ* DC pDA samples, respectively. However, as time proceeded to 300 h, the R_p of the cells was observed to increase. Bode plots depicted in Figure 3.8.b were generated to understand the electrochemical mechanisms and associated frequency regions. It has been established that *Region 1* is associated with the anode charge transfer reaction [10, 24]; *Region 2* is associated with the cathode polarization [10, 25]; and *Region 3* is related to gas diffusion limitations [10, 26]. As shown in Figure 3.8.b, the infiltrated cells displayed a significant decrease in *Region 1* and a slight reduction in *Regions 2 and 3*. This means that the nano-CeO₂ activated both the anode and cathode sides due to the dual infiltration. Nanoceria particles might also add additional oxygen pathway by its MIEC nature. Moreover, an increase in resistance over time in *Regions 1 and 2* was observed, suggesting that the anode and cathode showed deactivation due to the catalyst sintering/growth. The growth of the catalyst particles and the backbone structure may be responsible for the decrease in *Region 3*, which indicates a relaxation of the cathode gas path through the active area.

Figure 3.8. (a) Nyquist and (b) Bode plots of the baseline and bio-coating assisted dip-coat infiltrated cells under 0.4 A (0.325 A/cm²) at 750 °C.

3.4. Conclusion

In this study, polydopamine (pDA), a bio-inspired surfactant, was coated throughout the porosity of both SOFC electrodes (cathode and anode) to enhance and control the deposition of nano-CeO₂ catalyst throughout the microstructure. The entire infiltration process consisted of two dip-coating steps. The process included the initial submersion of the entire SOFC into a pDA solution, followed by the dip-coating of the cell into a cerium salt solution. The process was completed by a drying and high-temperature thermal treatment. The simple dip-coating protocol showed enhanced penetration and distribution of the nanocatalyst in both electrodes. The work demonstrated the process using existing commercial cell architectures (with the typical low porosity in the unreduced anode state), where most infiltration studies require the redesign of the SOFC electrode microstructure in order to facilitate liquid penetration. As indicated, ceria was

used to demonstrate the efficacy of the protocol, but the method permits the deposition of other catalyst compositions targeted for single or dual-electrode performance enhancement.

Although the use of both the pDA surfactant and the dip-coating process showed an overall enhanced deposition efficiency, the work also highlighted the need for better control of the deposition rate when the electrodes display a different level porosity (such as the anode and cathode in this work) for dual infiltration. Although dual infiltration was focused upon in this work, a single electrode can also be infiltrated with a promising catalyst(s) by masking the other electrode. In the end, the simple and efficient process resulted in a significant decrease ($0.41 \rightarrow 0.32 \text{ ohm}\cdot\text{cm}^2$) in the polarization resistances of both electrodes. Unfortunately, as in most nano-catalyst infiltration studies described in the literature (and also shown in this work), nano-catalyst sintering and grain growth decreased the enhanced performance achieved through the infiltration process, and further work is needed to stabilize the microstructure for sustained performance enhancement.

3.5. References

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Chapter 4 : pNE Bio-Surfactant Assisted Nano-Catalyst Infiltration of Solid-Oxide Fuel Cell (SOFC) Electrodes

4.1. Introduction

The wet infiltration method (also termed the impregnation method) is a practical and well-utilized technique to incorporate nanoparticles within the porous electrode microstructure of solid oxide fuel cells (SOFC). Many reports showed that the infiltration of catalytically active nanoparticles reduces the polarization resistance of the cell [1]. The decrease in electrode polarization (or the overpotential) is dependent on the catalytic nature of the metal or oxide nanoparticles, and its synergistic activity with other components within the existing electrode to enhance the oxygen reduction reaction (in the cathode) or the oxidation kinetics of the fuel (in the anode). Early studies began with incorporating precious or semi-precious metals, such as Au, Pd, Pt, Rh, etc., into both SOFC cathodes and anodes [2-5]. Those nano-particles exhibit high catalytic nature in both oxidation and reduction half-reactions. Although there are still some efforts studying precious metal infiltration, research on the use of cost-effective metal/metal oxide alternative systems has attracted increased interest recently. A review by Sholklapper et al. addresses a general perspective for the infiltrant materials and strategies [6]. Critical factors that impact the reduction of the electrode polarization using the nano-catalyst infiltration strategy include: i) catalyst loading, ii) catalyst composition and particle size, iii) surface decoration of the electrode grains with the catalyst, and iv) distribution of the catalyst throughout the volume of the porous microstructure. It should be noted that those factors are all interrelated and may or may not be achieved altogether during processing.

The nano-catalyst loading within the electrode microstructure can be tuned by performing repetitive infiltration cycles. The infiltration protocol can be completed using methods such as dripping [7], spin coating [8], electrodeposition [9], spraying [10], inkjet printing [11], and dip coating [12]. In general, a co-firing step is followed after each infiltration cycle to transform the solution precipitates (typically hydroxides and nitrates) to binary or more complex oxide compositions. The process is repeated until the desired nano-catalyst loading is achieved. The second way is to infiltrate oxide particulate suspensions or concentrated precursor solutions into the electrode microstructure. In this route, the number of infiltration cycles can be reduced dramatically, but inter-particle interactions, pore-clogging, and inhomogeneous deposition are the major potential risks in this strategy, which may result in reduced gas diffusion in the electrode architecture during the cell operation [13, 14].

The nano-catalyst deposition location through the thickness of the electrode layer after infiltration is another parameter that affects the performance of a SOFC. To be able to improve the triple- and/or double-phase boundary length, the infiltrant materials must be located in the active area, deep within the porous electrode layer near to the electrolyte interface. When the targeted electrode is the mechanical support for the SOFC, the microstructure is typically engineered with a relatively higher density, and the electrode layer is usually thick ($>500\text{ }\mu\text{m}$) to provide mechanical strength to the cell. In this case, the infiltration process becomes more challenging and inefficient. To overcome this issue, researchers often include surfactants to the precursor solution to enhance the wetting and the penetrability of the catalyst precursor solution. Also, various engineering methods, such as vacuum-assisted infiltration, can be used to remove entrapped gas within the fine porosity and help to force the solution through electrode layer porosity [15, 16]. If the salt solution precipitates the nano-catalyst preferentially at locations far from the active area

(such as a location near the surface or middle thickness of the electrode), then the electrode performance will show minimal improvement, and in some instances the performance will decrease due to gas diffusion limitations (due to porosity blockage by the nano-catalyst buildup).

The final major factor that impacts the reduction of the electrode polarization is the distribution of nano-catalyst particles over the granular microstructure of the electrode. As is common knowledge, the high surface area of the nano-particles promotes the electrocatalytic activity dramatically [17]. Since these nano-catalysts possess such a high surface area, the driving force for coarsening and sintering mechanisms are also enhanced. At elevated temperatures, the particles tend to reduce the surface area (and, therefore, associated surface energy) by driving these mechanisms. Since SOFCs are relatively high-temperature systems, nano-particle stability during operation is a major challenge. The loss of active surface area during coarsening/sintering adversely affects the long-term stability of the fuel cell [18, 19]. For this reason, the degradation rate of the infiltrated cells is as important a parameter to monitor over time as the relative performance improvement achieved with the infiltration process. To be able to maintain the stability of the cell during operation, the infiltrant particles should be decorated uniformly and discretely, with little contact with adjacent nano-catalyst particles, to limit the coarsening/sintering processes. To conclude, the goal of infiltration of SOFCs is to minimize infiltration/co-firing step(s) with the optimum concentration of the catalytically-active nano-particles within the active electrode area in a manner that enhances and stabilizes the performance.

Various additives can be added to the precursor solution such as ethanol [20] and various surfactants such as Triton-X [21] as wetting agents, glycine and citric acid as a complexation agent [22, 23], urea as a precipitation agent [24], etc. The study by Nicholas et al. noted that citric acid addition reduces the impurity content for $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-x}$ (SSC) phase in comparison to Triton-

X additions [23]. This work showed the efficacy of those additives may vary depending on the nature of catalyst precursor. According to the author's knowledge, the influence of those precursor surfactants on the control of the precipitation has not been proved.

Alternatively, internal electrode surfaces can also be treated with the surfactants, which promote deposition of the nano-catalyst. For example, the catechol chemical family, which consists of a benzene ring with a 1,2-hydroxyl (benzene diol), group configuration, has been used as a material-independent surfactant to modify substrates in order to deposit uniform metal and metal oxide thin films. This family allows for material-independent controllable coating and/or adhesion properties [25], as well as other physicochemical properties including enhanced surface wettability [26]. Poly-dopamine is one catechol surfactant used in many fields over the past decade to deposit metals, metal oxides, and polymers onto various substrate compositions [27].

Figure 4.1 is provided to assist in briefly describing how a catechol surfactant, such as pDA, assists in the direct and controlled deposition of metal oxide/hydroxide structures. The process consists of two main steps. The first step consists of the oxidative cross-linking of catechol in a basic medium at pH 8.5, and the deposition of this polymerized porous layer onto the electrode internal surface (Figure 4.1.a-b). In the second step, the coated substrate is immersed into a metal salt solution where local chelation of the metal-organic complex occurs by binding between the cerium ion and the organic layer by deprotonation (Figure 4.1.c). Previous studies assessed that the surface morphology and thickness of both the pDA layer can be engineered by the pDA solution immersion time [28, 29], pH [30], temperature [28], and pDA concentration [30, 31]. Moreover, the material coating over the pDA can be controlled by modifying the precursor solution immersion time [32, 33] and concentration [34]. Typically, the formation kinetics of catechol starts with small islands at the beginning (Figure 4.1.c). Later, the island coverage expands (Figure 4.1.d)

and a complete layer film is formed (Figure 4.1.e). For example, a study by Ryu et al. showed that a hydroxyapatite deposition begins with nuclei (island) formation in the initial immersion times onto the pDA coated substrate. Subsequently, the hydroxyapatite islands become agglomerates and then these agglomerate cover the surface after further immersion [35]. In addition, Wang et al. reported that a similar trend of silver coating on the pDA treated microspheres can be seen as a function of precursor molarity by fixing the immersion time [34].

Figure 4.1 Schematic representation of (a) untreated surface (b) pDA coated surface, (c), (d), and (e) progressive incubation of metal ion chelation with pDA layers

In the previous chapter, a poly-dopamine (pDA) assisted two-step infiltration protocol was developed for modifying the internal surfaces of three-dimensional anode and cathode electrode network to deposit catalytic cerium oxide nanoparticles [36]. In that study, a performance increase was shown at the beginning of the electrochemical test, but then a noticeable degradation over

~300 h was observed potentially due to the inter-particle interaction and coarsening at elevated temperatures. Ding et al. reported that the pDA concentration higher than 1 mg/ml inevitably promotes micron-sized aggregation [37], which is why pDA could potentially clog microporous SOFC electrode architecture and prevent homogenous coating distribution. Hence, there is a substantial need to reduce the inevitable thick micron-sized layer surfactant layer development, so that a thin, homogenous surface modification can be developed within the SOFC electrodes.

As an alternative to pDA, Lee et al. demonstrated the use of another catecholamine called poly nor-epinephrine (pNE) for the deposition of a thin layer onto a planar substrate. The pNE chemistry offered a smoother coating and a lower degree of aggregate formation due to the intermediate formation of 3,4-dihydroxybenzaldehyde – DHBA [38], which lessened agglomeration kinetics. Owing to the promising deposition properties, pNE was used to modify the substrates/particles in a few applications, including over various dense substrates [39], metal oxide particles [40], and microporous sponges [41]. Our earlier work also showed that pNE can be used as a surface modification template for porous architectures and can yield higher material depositions per coating step [42].

In the current work, poly-norepinephrine (pNE) was used as the surfactant for controlled nano-CeO₂ deposition to avoid the potential limitations of pDA stated above during the polymerization stage. The work first demonstrated metal oxide deposition improvement by pNE treatment onto the conventional SOFC anode and cathode backbone surfaces, NiO, YSZ, and LSM pellets. The protocol was applied to commercial button anode-supported fuel cells and evaluated the effect of the surfactant coating on the nanoparticle deposition rate and morphology with a change in precursor solution concentration. Moreover, the reduction of polarization resistance of the infiltrated cells as a function of pNE-assisted ceria deposition amount was characterized.

Finally, the stability of the infiltrated cell was assessed using impedance spectroscopy over 300 h of operation. The motivation of this work was to develop an efficient infiltration protocol that enables specific control of the deposition kinetics and morphology of nano-catalyst loading for commercial SOFC cells, which will retain the desired enhanced electrochemical performance achieved with the infiltration procedure over the extended high-temperature operation.

4.2. Experimental

To confirm the efficacy of the pNE coatings over the sub-constituents of the SOFC electrodes, commercial nickel oxide -NiO- (Novamet Specialty Products Corp., TN, USA), yttria-stabilized zirconia – YSZ- (TZ-8Y, Tosoh Corporation, Tokyo, Japan), and in-house fabricated lanthanum strontium manganite -LSM-, powders were pressed into pellets, fired at 1350°C, 1450°C and 1150°C, respectively. The pellets were then polished prior to the deposition protocol. A 1 mg/ml DL-norepinephrine hydrochloride ($\geq 97\%$ (TLC), Aldrich, USA) was first dissolved in a 0.05 M TRIS (tris(hydroxymethyl) aminomethane, 99%, Alfa-Aesar, USA) and 1:1 vol % water-ethanol mixture at pH 8.5. A dip-coating infiltration protocol was used to ensure uniform exposure in all the experiments. The setup was placed within a vacuum desiccator under 30 mm Hg vacuum for 5 min and then transferred to a rocker table for 12 h that permitted the surfactant to polymerize homogeneously. Meanwhile, this time-dependent oxidative polymerization step had a transition from transparent to brown color as a function of time as observed in the previous studies [38, 39].

After the polymerization of the norepinephrine (pNE) step, the pellets were rinsed with 1:1 vol % water-ethanol solution. The pNE-coated pellets were then immersed into 0.4 cerium (III) nitrate hexahydrate (REacton®, 99.5%, Alfa Aesar, USA) solution of 1:1 vol% water-ethanol solvent for 24 h. After the rinsing and drying step under ambient conditions, the pellets were finally

fired at 750°C for 1 h for nitrate decomposition, forming the ceria (CeO_2) phase. The protocol developed from this initial work was then applied in the rest of the work to actual SOFCs.

For the deposition of the nano-catalyst into actual SOFCs, commercial anode-supported button cells (cell type ASC-2.7) were purchased from Nexceris, LLC (Lewis Center, OH, USA). These cells were 27 mm in diameter and consisted of a 250 μm thick nickel oxide (NiO) /yttria-stabilized zirconia (YSZ) anode with a dense 8 μm thick YSZ electrolyte (27 mm in diameter) and lanthanum strontium manganite (LSM) / gadolinium doped ceria (GDC) cathode, which was 12.5 mm in diameter in 50 μm thick. The same dip-coating protocol was applied to the cells but the concentration of the cerium salt solution was varied in order to achieve a range of infiltrated catalyst amount. The cells were weighed after the thermal process in order to calculate the infiltrated ceria content. In this study, four infiltrated ceria loadings were investigated: ~1.3 mg ceria infiltrated cell in 0.4 M precursor solution (denoted as IC-1), ~3.5 mg ceria infiltrated cell in 0.7 M precursor solution (denoted as IC-2), ~5 mg infiltrated cell in 1 M precursor solution (denoted as IC-3), and finally, ~8.5 mg ceria infiltrated cell in 2 M precursor solution (denoted as IC-4). To be able to estimate the catalyst amount per electrode, the protocol of IC-1 was applied only to the anode electrode by masking the cathode side which resulted in a 0.8 mg weight change. From this experiment, it was deduced that ~60% of the infiltrated catalysts was impregnated into the larger area anode support electrode (~0.16 mg/cm^2) while the remaining ~40% was located into the small area cathode electrode (~0.41 mg/cm^2).

4.2.1. Testing and Characterization

The morphology of the cerium thin films deposited onto YSZ, LSM, and NiO pellet planar surfaces were characterized by atomic force microscopy (Agilent 5500 SPM, USA) in the tapping mode. The mapping area of all the samples was 2 $\mu\text{m} \times 2 \mu\text{m}$.

The current-voltage-power (I-V-P) and electrochemical impedance spectroscopy (EIS) of the impregnated SOFC button cells were completed at 750°C for ~300 h using 300 sccm humidified (3%) hydrogen fuel and 300 sccm air. During the electrochemical testing, the cells were sandwiched between alumina flanges, and the button cells were sealed using mica washers placed on both sides of the cells. For the I-V-P measurements, the connections were wired to Pt mesh using minimal Pt paste for the cathode side and Pt mesh with Ni paste for the anode side. An electronic load of (Agilent N3301A, USA) was used to apply constant current (0.325 A/cm²) to the cell during the tests. The electrode polarization measured using EIS with a frequency response analyzer (Solartron 1455A, England) and a potentiostat (Solartron 1470E, England) over a frequency range of 0.01-100 kHz under operating current load. The first data points were taken after the cathode activation within the first 48 h and then at 150 h and 300 h. The electrode microstructure of the tested ceria impregnated cells was examined by scanning electron microscopy (JEOL 7600F, Japan).

4.3. Results and Discussion

Prior to the SOFC button cell infiltration, the efficacy of the pNE treatment on the CeO₂ deposition was first demonstrated on the planar YSZ, NiO, and LSM pellets separately. The surface morphology of the untreated surfaces, and the surfaces coated using the cerium nitrate dip-coated (with and without pNE treatment) were characterized using atomic force microscopy (AFM) after the calcination step at 750°C. To deliver the particle height comparison, 1.5 µm length line profiles were drawn over areas where the particles populated in all the images. Figure 4.2.a-c show the AFM images of the finely polished NiO, YSZ, and LSM surfaces. The topography images of all polished, untreated baseline surfaces display a few pores, but overall, appear to be smooth with 0.9, 0.7, and 0.5 nm line RMS values for NiO, YSZ and LSM surfaces respectively. Figure 4.2.d-

f display the AFM images of the cerium nitrate treated surfaces that did not receive a pNE pretreatment. The purpose of completing this round of samples was to better compare the deposition morphology when the pNE treatment was later used before the cerium nitrate step. These NiO, YSZ, and LSM samples were dip-coated into the 0.4 M cerium nitrate solution for 24 h, and then the samples were removed and dried within ambient atmosphere. The images show that the deposition of the nano-CeO₂ onto the NiO, YSZ, and LSM substrates was similar showing larger particles (Figure 4.2.e) and randomly distributed islands (Figure 4.2.d and f) over the surfaces, but overall, the line scans revealed that the particles were around 15-60 nm. The islands on NiO and LSM surfaces, for example, were gathered near grain boundaries of the substrate material. The volume of nano-CeO₂ contained within these clusters distributed non-homogenously across the entire surface. In addition, the LSM surface looked noticeably deformed after the cerium nitrate treatment in Figure 4.2.f. This deformation could motive from the low chemical stability of the perovskite LSM structure under the acidic cerium nitrate medium (pH~4). However, when the surfaces were treated with the 1 mg/ml pNE treatment for 12 h prior to the cerium nitrate dip-coating, the resulting calcined particles were much finer (< ~20 nm) across the line-scan as shown in Figure 4.2.g-i. The deposited nano-ceria population was also found to be higher when the surface was treated with pNE. The RMS of the line scans across particles showed an improvement from 10.4 nm to 13.3 nm in NiO and 3.0 nm to 4.6 nm for YSZ surfaces between with and without pNE treatment indicating enhanced discrete particle population. Although, a fine and even coating of ceria particles were observed on the LSM surface with the pNE treatment (line scan (LS) RMS 8.4 nm), the trend could not be applicable as leaching of LSM surface (by cerium nitrate) disturbed the roughness vastly (LS RMS 28.1 nm). The topographic analysis of the surfaces clearly showed

the efficacy of pNE treatment on the various surfaces, on finer particle deposition, and higher decoration by anchoring the cerium cations.

Figure 4.2 AFM images, 1.5 μm line scans and line scan RMS values of (a-c) untreated and polished, and ceria coating without (d-f) and with pNE treatment (g-i) of NiO, YSZ and LSM surfaces.

After the validation of the deposition enhancement of the pNE coated surfaces, the same protocol was applied to infiltrate the cerium nitrate with various molarities into both electrodes simultaneously. After the calcination, the electrochemical impedance spectroscopy (EIS) and current-voltage (I-V) test were performed on each cell during the ~300 h operation. Figure 4.3.a presents the electrode overpotential as a function of the current density of the infiltrated cells with various infiltrated ceria amounts. The total electrode overpotential was calculated by subtracting the ohmic resistance of the cell, taken from the Nyquist plot, from the total resistance found by the I-V data at the 300th operating hour (stated as 300 h throughout the rest of the paper). Based on calculations, the baseline cell exhibited a total electrode overpotential of ~173 mV, where the dashed line is drawn at the operating current density of 0.325 A/cm². First, a substantial decrease in electrode overpotential was confirmed in the overall infiltrated cells. The electrode overpotentials of IC-1, IC-2, and IC-3 infiltrated cells at the operating current load were shown to decrease gradually, as a function of increased infiltrant concentration. The lowest electrode overpotential (~112 mV) was measured for the cell containing 5 mg ceria (IC-3 cell). With an increase of ceria loading from 5 mg to 8.5 mg, the electrode overpotential of the IC-4 cell increased back towards the value of the baseline cell. Figure 4.3.b summarizes the electrode overpotential reduction by percent of each infiltrated cell at the operating current density. The change of the IC-1, IC-2, and IC-3 cells reduced the polarization resistance by 17%, 21 %, and 35% over the baseline, respectively, while the IC-4 cell increased back towards the value of the baseline cell (~11% decrease in overpotential).

Figure 4.3 (a) Current density vs. Electrode Overpotential at 300 h **(b)** Percentage decrease in over potential vs. infiltrated CeO₂ amount at 300 h, 0.325 A/cm².

To tabulate the relative effect of the various infiltration amounts on the fuel cell performance, Figure 4.4 displays time-varying electrode polarization resistance (R_p) of the infiltrated cells calculated from the Nyquist EIS data at 48, 150 and 300 h under 0.325 A/cm² load. The R_p of the cells was calculated from the difference between high frequency and low-frequency intercepts at the x-axis (real part of the impedance) in the Nyquist EIS plots. In the plot, three separate time-dependent R_p change behaviors were observed, as labeled Zone I, Zone II and Zone III. In the Zone I, both the baseline cell and the IC-1 cell showed an initial increase in R_p as a function of operation time. The baseline cell showed a gradual R_p increase from 0.317 to 0.405 ohm·m² over the 300 h of operation. The IC-1 cell also showed a slight R_p increase from 0.359 to 0.381 ohm·cm² in 48 and 150 h, but then later, decreased to a value of 0.369 ohm·cm² at the 300 h. Although the IC-1 cell displayed 13.2 % higher R_p than the baseline cell in the 50 h, the 150 h, and 300 h R_p

values decreased by ~4.5% and ~8.9%, respectively. Based on the initial increase in R_p , it can be concluded that the IC-1 cell displayed the baseline-like behavior in Zone I.

In the Zone II, the infiltrated cells with the moderate catalyst loadings, 3.5, 5.0 mg (labeled as IC-2, IC-3), started with higher R_p values than the baseline cell at 48 h, but then all displayed a progressive decrease as a function of time. To begin with, IC-2 cell R_p decreased by 5.5% over the 250 h period. Interestingly, the IC-3 cell showed a lower decrease in polarization (~1.8 %) from 0.335 to 0.329 $\text{ohm}\cdot\text{cm}^2$ at 48 h to 150 h, respectively. Then a substantial decrease in electrode polarization was observed over the next 150 h of operation which resulted in an overall 18% reduction. By comparing the baseline, IC-1, IC-2, and IC-3 cells in Figure 4.4, it can be seen that there is a parallel trend in the reduction in the R_p with the increase in the impregnated nano- CeO_2 content up to the 5.0 mg concentration. However, when the nano- CeO_2 content increased beyond the 5.0 mg concentration, the R_p increased significantly towards values shown for the baseline cell performance as monitored for IC-4 cell (8.5 mg CeO_2 infiltrated cell) in the Zone III. The cell showed R_p values of 0.411, 0.4, and 0.393 $\text{ohm}\cdot\text{cm}^2$ at the 48, 150 and 300 h, respectively. This finding indicates that IC-4 cell in the Zone III may contain large a volume of nano-catalyst (over-impregnated), which may affect the performance negatively due to the potential decrease in the active surfaces, triple-phase boundary (TPB) length and porosity [43, 44].

Figure 4.4 Infiltrated catalyst amount vs. polarization resistance.

Interestingly, even though the IC-4 cell showed R_p levels near that of the original baseline cell, the R_p of this cell continued to decrease over the 300 h operation, similar to the infiltrated cells in the Zone III. These results indicate that the oxygen reduction reaction and/or the fuel oxidation reaction were still altered due to a time-dependent process during operation. This time-dependent process is enhanced by the incorporation of the nano-ceria inside both electrodes. This alteration could be the result of a surface reaction with the electrode composition (which is kinetically limited), or slight alterations in the catalyst microstructure over time. Unfortunately, it is difficult to distinguish in this work which of the electrodes is being most affected, since both electrodes were impregnated by the soaking process.

As stated above, the polarization resistance of the low catalyst infiltrated cell IC-1 in Zone I fluctuated (increased between 48-150 hour and then decreased at 300 h) and the infiltrated cells in the Zone II and III showed a continuous decrease over duration of operation. We would interpret this time-dependent activation is due to mainly particle coarsening and sintering of nano ceria particles. Infiltrated nano particles tend to coarsen over time at elevated temperatures. In a discrete and sparse distribution, this could result in deactivation due to the surface area and TPB loss as observed in the first stages of IC-1 cell. With the increase of nanoparticle population, the nanoparticle sintering promotes interparticle connection, which forms a continuous pathway for ionic conduction and extending TPB. Therefore, the electrochemical activation over time could achieve by interconnected particles as experienced in the infiltrated cells in the Zone II and III. There are a few other possible concurring mechanisms that may relate specifically to the presence of nano-ceria particles at the anode electrode which may cause a consistent improvement of the electrode over time. It has been known that cerium undergoes chemical-state shifting under reducing environment from Ce^{+4} to Ce^{+3} [45]. Jiang et al. proposed that the reducing environment may create active sites for H_2 oxidation at the catalyst surface within the anode electrode [46]. Therefore, even though nano-catalyst coarsening /sintering occurs over time, the increased presence of the reduced nano-ceria may overcome the effect as the activation of IC-1 cell (Zone I) was monitored at the 300 h after a major deactivation at 150 h in Figure 4.4. A second reason for the stabilization of nano-ceria particles in the anode electrode may be related to volumetric expansion which occurs during the valence change of CeO_2 , since Ce^{+3} ions are approximately 17.5 % larger in diameter than Ce^{+4} ions [47], which equates to a 60% lattice expansion [48, 49]. According to Zhang et al., the Ce^{+3} concentration in the bulk ceria can go up to 5.6 % when the particle size is around 10 nm [49]. This chemical-state shift relates to a volumetric change and

creates a lattice strain at the catalyst oxide – backbone metallic interface as Farmer et al. stated. It was reported that the localized strain created by ceria on Ag nanoparticles mitigated the particle growth [50]. In conclusion, a series of complex mechanisms could play a role in the time-dependent activation phenomena.

To better analyze the effect of pNE-assisted nano-CeO₂ infiltration on the cells (and their electrochemical processes), the EIS Bode plots for the baseline and infiltrated cells after operation for 48, 150 and 300 h are shown in Figure 4.5. According to the past studies, it was proven that the change in reactance at the high frequency (> 100 Hz, denoted as *Region I*) is associated with the anode charge-transfer reaction [51, 52]. Similar studies indicate that the middle-frequency changes (10-100 Hz, denoted as *Region II*) are associated with the cathode polarization [51, 53]. Also, it was observed that the low-frequency changes (1-10 Hz, denoted as *Region III*) are generally related to gas diffusion steps and the associated polarization [51, 54]. As presented in Figure 4.5.a, all of the infiltrated cells showed higher reactance over the baseline cell in *Region I* and *II* within the first 48 h. This observation shows that the nano-CeO₂ catalyst activation did not dominate the performance of the electrode activity within the first 48 h, as was also shown by the electrode polarization data in Figure 4.5.a. However, after 150 and 300 h of operation, the infiltrated cells displayed a lower reactance in both *Region I* (associated with the anode reactions) and *Region II* (associated with the cathode charge-transfer reactions), as displayed in Figure 4.5.b-c. Furthermore, *Region III* did not show a significant decrease between the 48 to 300 h operation time in all the cells. This could be related to possible particle coarsening / activation mechanisms stated above.

Figure 4.5 EIS bode plot of the cells in (a) 48 h (b) 150 h and (c) 300 h operation at 750 °C under 0.325 A/cm².

Figure 4.6.a-d compares the cross-sectional SEM images of the post-operated anode functional layer micrographs of the IC-1, 2, 3 and 4 cells, respectively. In Figure 4.6.a, a uniform coating with discrete particulate islands with sizes < 15 nm was observed. The island size likely corresponds to the structures shown in Figure 4.1, as the same treatment and precursor molarity (0.4 M) was applied. Also, the catalyst decoration was retained in all of the micrographs. The cross-section of the coating in Figure 4.6.b depicted that the thickness of the coating in the IC-2 anode functional layer micrograph was around 30-35 nm. The increase in the precursor molarity resulted in an increase in the infiltrated particle size. The average catalyst island of IC-3 was around 35-40 nm when 1 M precursor was used (Figure 4.6.c), whereas the size of the islands went up to > 60 nm when the precursor solution was the 2 M precursor solution (Figure 4.6.d).

Figure 4.6 Anode active region SEM images of (a) IC-1, (b) IC-2, (c) IC-3 and (d) IC-4, for 300 h of testing at 750°C and 0.325 A/cm².

Likewise, Figure 4.7.a-d represents the crosssectional SEM images of the post-operated cathode functional layer of the IC-1-4 cell. Particles in the cathode active layer in Figure 4.7.a-d maintained a thin film but were composed of smaller particle sizes in comparison to the anode functional layer decoration. In Figure 4.7.a., it can be seen that the nano-catalyst coverage resulted in a discontinuous decoration inside the pore which is probably due to the low catalyst loading by the 0.4 M precursor. As the molarity increased to 0.7 M and 1M, there was continuous particle coverage at the non-fractured surfaces, which can be observed in Figure 4.7.b-c respectively. In Figure 4.7.d. the particles were relatively larger with a higher population inside the pores. The oversaturated coverage could induce a beneficial higher contact area in terms of enhanced oxygen

ion transport and TPB, but at the same time, the case might be prone to gas mass-transport limitation.

Figure 4.7 Cathode active region SEM images of (a) IC-1, (b) IC-2, (c) IC-3 and (d) IC-4, after 300 h of testing at 750°C and 0.325 A/cm².

From all the SEM pictures, it can be deduced that the pNE protocol enabled the infiltration of the nano-catalyst into the active area, near the electrolyte region. Connor et al. reported that thin and even coatings are an indication of the positive surface interactions and good wetting [55], which confirms the use of catechol surfactants as excellent wetting agents [26] for low porosity architectures such as anode-supported electrodes. The electrochemical performance results also showed that the film formation of the nano-catalysts was beneficial for cell stability. The study by Wang et al. on silver coatings on silica microspheres using pDA mentions that the molarity of the

silver nitrate precursor influences the coating morphology continuity, thickness, and compactness [34]. In their study, the coating layer morphology shifted from a sparse and discrete island to a continuous film as the metal nitrate concentration was increased. The difference in the particle size and the decoration morphology is most likely due to the accelerated deposition/chelation kinetics in the high precursor molarity in the dipping process. Hence, the precursor molarity not only adjusted the deposition amount but also the catalyst morphology. The study by Lund et al. confirms the direct relationship of the mean grain size on the polarization resistance change and over-infiltration [56]. The finding was directly reflected in the electrochemical performance. The EIS data showed the lowest polarization resistance in the IC-3 cell (5 mg CeO₂, ~ 0.52 mg/cm² at the anode electrode and ~ 1.63 mg/cm² at the cathode electrode). Then, the IC-4 cell with 8.3 mg ceria shifted back in performance and displayed the same performance as the baseline cell.

4.4. Conclusion

A poly-norepinephrine (pNE), a bio-inspired surfactant, assisted solution infiltration method was developed for SOFC electrodes. The experiments show that the pNE treatment enhances the catalyst deposition on the electrodes sub-constituents' surfaces such as YSZ, NiO, and LSM. With the single-step infiltration of ceria, the polarization resistance of the comparison cells revealed three different trends (Zones) as a function of the amount of infiltrated ceria. In the Zone I, the baseline cell and lesser ceria infiltrated cell (IC-1) monitored a similar trend in terms of activation and deactivation during the operation period. Beyond that point, the activation improves over time, and the 5 mg ceria infiltrated cell showed the lowest R_p in the Zone II. Beyond this point the nano-catalyst activation was suppressed possibly due to the gas starvation and inhomogeneous, local nano-catalyst settlement but still activating over time (Zone III). A change in decoration and island size on the top of the film formation was observed as the precursor

molarity increased. Over ~ 300 h of testing, the infiltrated cells demonstrated initial performance boost and continuous time-dependent activation. Further measurements and performance evaluation of catechol assisted infiltration in only one-electrode may be needed to understand the driving mechanism(s) better. This systematic approach proves that not only the material chemistry but the nano-catalyst amount and decoration is also critical to maintaining stability.

4.5. References

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Chapter 5 : Kinetics of Growth Study of Catechol Surfactant and Ceria Nano particles onto the Planar Substrates

5.1. Introduction

Catechol-based molecules, such as dopamine and other benzene diaol-like derivatives that have multi-functional end-groups are a specific type of bio-monomer found in nature. Apart from the neurotransmitter functions, these end-groups are capable of strong adhesion when bio-monomers are linked and polymerized, as can be found in mussel foot protein (MFP) [1-3]. Marine mussels can naturally produce various amounts of DOPA (3,4-dihydroxyphenylalanine) as a moiety of mussel food proteins, Mefp-3, Mefp-5, and Mefp-6, in the byssus plaque to attach to solid surfaces in the marine medium [3-5]. The mechanism is virtually a spontaneous and pH-induced oxidative polymerization occurring in alkaline medium that has multiple complex intermediate species/steps [5-10]. Owing to the amine and hydroxyl groups, polydopamine (pDA) gains adhesion property where the functionalized molecules are able to adhere and polymerize over both the organic and inorganic surfaces, such as polar and non-polar polymer surfaces, and metal and metal oxide surfaces [1, 11].

The research on poly-dopamine (pDA) and related catechol thin film coatings have shown a steady increase over the past decade [6]. Many of these studies used a similar solution concentration and polymerization for deposition, which included a 24 h polymerization reaction for a 2 mg/ml aqueous catechol solution at a pH 8.5. One major drawback shown in these works for using pDA as a surfactant for a coating process is that the polymerization step is not controllable and leads to the formation of dopamine aggregates within the solution over the deposition period [12]. It was reported that non-covalent forces such as π - π bonding and Van der

Walls forces, and the insoluble nature of the melanin species, trigger the aggregation process [11, 13-15]. However, the main potential problem is that the aggregation then limits the formation of a smooth and homogenous coating with low roughness. In some works, various solutions and deposition variables such as deposition method [16], solid loading [12, 17], polymerization pH [18], time [19] and temperature [20] were tested to mitigate the agglomeration. To overcome this issue, the preparation of a fresh solution after every few hours of immersion time was also an option [12, 16]. However, in the case of a microporous interconnected 3-D network, such as found in fuel cell electrodes or membranes, pore-clogging during the coating step is an additional terminal downside of pDA aggregation. In early studies within this work, a concentration of 1 mg/ml pDA solution with 1:1 vol % water-ethanol mixture at pH 8.5 was passed every 12 h through a 0.2-micron filter to eliminate the initial aggregates [21]. However, by the nature of spontaneous aggregation, new aggregates might form inside the 3-D solid oxide fuel cell (SOFC) electrodes during the dip-coating stage, and this would restrict the catalyst precursor infiltration/penetration through an electrode structure (especially electrodes with $< \sim 25\%$ porosity). The blockage of these pores with the surfactant, and later the adsorbed nano-catalyst, would result in performance loss due to the gas diffusion limitations during operation. In the previous chapter, the problem was overcome by switching the poly-dopamine catechol to nor-epinephrine which gave a homogenous catalyst decoration throughout of the 3-D electrode architecture.

Nor-epinephrine, an alternative catecholamine that offers a material-independent coating feature, was reported by Lee et al. [22]. In their later study, they showed a low degree of aggregation as the main advantage of polymerized nor-epinephrine (pNE) over pDA, which potentially allows a higher decoration control of the secondary coating in terms of morphology and thickness [23]. Yang et al. reported that the pNE morphology on planar quartz contains fewer

protuberances and more than half of the surface roughness (measured as RMS-root mean square) compared to pDA coating under the same conditions (2 mg/ml, 24 h incubation) [24].

Once the catechol layer is deposited over the substrate, a variety of organic and inorganic secondary functional coatings can be designed [6]. One group formed metal/metal oxide layers by immersing the pNE catechol layer into a metal salt solution. The metal ion binds to the hydroxyl groups on the catechol graft through a chelation reaction [25]. After the secondary coating, the catechol coating can be thermally treated, which combusts the catechol layer and allows the functional secondary coating to calcine and bond to the substrate or template. The study of ZrO_2 /pDA multilayer films by Ou et al. reported that as the deposition proceeds, the first deposited ZrO_2 layer acted as a seed layer to boost the population of ZrO_2 particles over the initially deposited oxide layer [26]. The secondary layer morphology and thickness can be modified by varying the metal ion solution concentration [27] and/or the substrate immersion time [28]. To date, there are only a few reported works focussing on the chelation of metal ions using pNE. For example, a study by Doherty et al. assessed the ability of “a gut-signaling hormone,” norepinephrine, to chelate iron [29]. Another study by Kang et al. reported the formation of silver nanoparticles by an overnight reaction of silver nitrate immersion of the pNE coated graphene oxide surfaces [30]. A previous study showed that the use of pNE as a surface modifier for the porous, multi-phase, and 3-D SOFC electrode architecture could yield secondary coating of the cerium nitrate solution by the chelating effect [31].

Cerium oxide (also known as ceria) has a cubic fluorite-type structure that has been one of the major non-noble constituents in catalytic systems due to its +4 to +3 valence switching character. Nanostructured ceria catalysts can be used in both reducing and oxidizing environments, such as a three-way catalyst (TWCs) [32], a diesel soot combustion catalyst [33] in the automotive

industry, steam reforming catalysts (SMR)[34] , water-gas-shift (WGS) reaction catalyst [35], photo-catalyst for degradation of dyes [36], and half-reaction catalysts in the fuel cell electrodes including polymer exchange membrane fuel cells (PEMFCs) [37] and solid oxide fuel cells (SOFCs) [21].

Nanostructured materials show enhanced material properties due to their higher surface area to volume ratio. However, structural stability at elevated temperatures is a well-known challenge due to their high surface energy. Particle coarsening is the transformation of smaller particles into larger particles, driven by capillary (Oswald ripening) and/or diffusional effects [38] to reduce the overall surface energy. This evolution can be controlled by tuning the initial particle size/distribution [39, 40], grain boundary composition [41], designing sintering-resistant core-shell nanocomposite morphology [42] or sintering-resistant advance support topology with nano compartments [43]. Hence, with these efforts, the activity of nanoparticles can be stabilized over longer operating times at elevated temperatures.

In this study, pNE polymerization as a function of the time and solid loading is monitored. Then a correlation of the degree of polymerization (dp) with the adhered pNE surfactant film thickness and morphology which were deposited on yttria-stabilized zirconia, YSZ, single crystal surfaces, is constructed as a function of immersion time and solid loading. In the second part, cerium nitrate solution and palladium nitrate solutions were chosen as a secondary treatment solution for pNE coated YSZ single crystals. The chemical state of the adhered pNE layer and the secondary treatment deposits have been analyzed in detail by X-ray photoelectron spectroscopy (XPS). Finally, the surface morphology of cerium oxide formation of the fired samples as a function of pNE and cerium nitrate immersion times was assessed. The results were correlated with the ceria nucleation and growth mechanisms as a function of pNE morphology and cerium

nitrate immersion time. To analyze cerium oxide morphology, the YSZ surfaces were patterned with stripe lines as a marker by photolithography prior to the pNE coating.

5.2. Experimental

Catechol-based surfactant, DL-Norepinephrine hydrochloride ($\geq 97\%$ (TLC), Aldrich), was dissolved into a 0.05 M TRIS (tris(hydroxymethyl) aminomethane, 99%, Alfa-Aesar) and 1:1 vol % water-ethanol mixture at pH 8.5. The polymerization of the monomer was confirmed visually by the transition of the solution from transparent to a brown color. UV-Vis absorption analysis of the surfactants was carried out by means of a double beam spectrophotometer (Shimadzu 2600), at room temperature. The polymerized catechol solutions were analyzed using a diluted 1:19 vol% ratio from the stock solution for the UV-Vis spectroscopic analysis.

In the first part of the study, one-side polished 1 mm $\times$ 1 mm (100) yttria-stabilized zirconia (YSZ) single crystals (MTI Corporation, USA) were used as substrates. First, the substrates were cleaned by sonicating in acetone, ethanol and then in a water bath for 5 minutes each. The substrates were then dried at 150°C for 5 minutes. The substrates were submersed into the pNE solution for the surface coating for 1, 3, 6, 12 and 24 h. The substrates were rinsed in a 1:1 vol % water-ethanol mixture after the coating to remove loosely bonded species, then the samples were dried in air at 50 °C. The coatings were gently inscribed by a fine needle tip and areas were analyzed by atomic force microscopy (Agilent 5500 Atomic Force Microscope, AFM) using the tapping mode. As can be seen from a representative pNE AFM image in Figure 5.1.a, the needle mark created pNE piles at the edges. Also, the adhered pNE showed rough surface characteristics. The average pNE thickness was measured by combining the R_v (maximum valley depth) parameters after the pile and the R_q (RMS, root mean square) of the pNE surfaces as shown in

Figure 5.1.b. The average of three line scan measurements were taken for film thickness, using an open software, Gwyddion (Version 2.48).

Figure 5.1 (a) A representative AFM image of pNE coated YSZ surface inscribed by fine needle tip (b) A line scan profile along the needle mark and the pNE coating that shows the method of pNE layer thickness measurement. R_v denotes the maximum valley depth and the R_q (RMS) denotes root mean square parameters.

In the second part of the study, the surface-chemical state of the elements present on the bare and unfired pNE + 0.15 M cerium (III) nitrate (REacton®, 99.5%, Alfa Aesar, USA) solution treated and pNE + 0.2 M palladium (II) nitrate dihydrate (99.8 %, Alfa Aesar, USA) solution treated YSZ single crystals were characterized using monochromatized Al K α radiation (1486.6 eV) X-ray photoelectron spectroscopy (XPS, Physical Electronics PHI 5000 VersaProbe, MN, USA). The concentration of the pNE coating 2 mg/ml and substrates were coated for 24 hours for all the samples. In addition, the metal precursor immersion time was set to 3 hours. Prior to analysis, the surfaces were gently sputtered to remove contamination without changing the chemical state of elements by an Ar⁺ gun at 0.5 kV rastered over 2 $\times$ 2 mm² area for 6 sec. The adventitious C1s (284.8 eV) peak was taken as a reference for the carbonaceous surfaces.

In the third part of the study, a photolithography technique was applied to the YSZ substrates in a class 1000 cleanroom before the coating treatments. The schematic of the fabrication process is shown in Figure 5.2. First, the substrates were sonicated in acetone, isopropanol and DI water each for 5 minutes. SU-8-2 photoresist (Microchem, MA, USA) was spin-coated on the cleaned substrates using a Laurel Technologies 400 spinner (North Wales, PA, USA). The substrates were soft-baked for 1 min each at 65°C and 95°C. A 15 μ m striped pattern was transferred to the SU-8 coated substrate using a photomask (UTZ Technologies, Little Falls, NJ, USA) and cured under UV Flood Exposure (OAI, CA, USA). The substrates were then post-baked on a hot plate for 10 sec each at 65 °C and 95°C. Finally, the pattern was developed with the SU-8 developer solution (Microchem, MA, USA) for 30 sec, rinsed several times with isopropanol and dried by blowing dry N₂. The patterned substrates were immersed into the 1 mg/ml pNE solution for 3 h, 12 h and 24 h as described above. The SU-8 patterns were lifted-off by immersing the substrates into MS-111 epoxy stripping agent (Miller-Stephenson Co., Danbury, CT) for 4 min

and then rinsed with ethanol. At the final stage, the samples were moved into a 0.15 M cerium (III) nitrate hexahydrate (REacton®, 99.5%, Alfa Aesar, USA) and 1:1 vol% water-ethanol solvent for 24 h. After the precipitation step, samples were rinsed again and dried under ambient conditions. Finally, the coated substrates were fired at 750°C for 1 h for nitrate solution decomposition, forming the ceria (CeO_2) phase. The topography of the ceria layers was then analyzed using AFM.

1. Clean the Substrate

2. Apply Photoresist & Prebake

3. Align the Mask & Expose Light

4. Develop & Postbake

5. Dip into pNE Sol

6. Pattern Lift-out

7. Dip into Cerium Nitrate Sol

8. Calcine

Figure 5.2 Schematic of SU-8 patterning and pNE+ceria decoration on YSZ single crystals.

5.3. Results and Discussion

5.3.1. pNE Characterization

Figure 5.3 shows images of clear nor-epinephrine precursor and the polymerized pNE solution after 12 h of oxidation. When the pH of the freshly received nor-epinephrine solution is shifted to alkaline conditions, the time-dependent oxidative polymerization is initiated. One visual indication of catechol polymerization is the solution color which shifts from transparent to brownish color as the time proceeds. This phenomenon occurs due to catecholamine monomer grafting into larger chains [23] and can be seen in other known catechol systems such as pDA [20].

Figure 5.3 Representative images of (a) clear nor-epinephrine (b) polymerized pNE solution.

To monitor this time-dependent oxidative polymerization, UV-Vis spectroscopic analysis was performed. Figure 5.4.a, b, and c show the UV-Vis data for pNE in varying polymerization time and solid loading of 1, 3, 6, 12, and 24 h of 0.5 mg/ml, 1 mg/ml and 2 mg/ml pNE, respectively. As a general trend, a gradual upshift at 350 nm was observed both as a function of time and solid loading. The solid loading produced a negligible difference in the first hour. However, as time proceeded, the absorption variance at 350 nm became more significant and

reached 0.46, 0.69, and 0.94 at 24 h incubation of the 0.5 mg/ml, 1 mg/ml and 2 mg/ml pNE respectively. The change in absorption in the pDA was attributed to the quinone formation by Cheng et al. [19]. Kang et al. also noted that quinone undergoes pNE formation [22].

To visualize the relative degree of polymerization [dp], each absorption peak at 350 nm was proportioned with the value of 550 nm which is out of the peak area. Figure 5.4.d displays a normalized absorption peak difference [350nm- 550nm] as a function of solids loading and time. For this purpose, the Δ absorption value [350 nm – 550 nm] of 2 mg/ml pNE solution after the 24 h deposition (in the darkest brown color) was taken as 1. The figure shows that the pNE was driven close to a logarithmic behavior of catechol adhesion as a function of immersion time. It can be seen that the effect of solid loading on the rate of polymerization had more impact after 3 h of polymerization. This plot gives a preliminary mapping of the rate of the pNE oxidation.

Figure 5.4 UV-Vis spectroscopy of diluted (a) 0.5 mg/ml, (b) 1 mg/ml, (c) 2 mg/ml pNE and (d) Δ absorption values [350 nm – 550 nm] of pNE solutions as a function of time.

The pNE film thicknesses on the YSZ single crystal surfaces were analyzed by atomic force microscopy. Figure 5.5 displays the film thickness of the pNE coating layer on a YSZ single crystal as a function of solid loading (0.5, 1, and 2 mg/ml) and immersion time (1, 3, 6, 12, and 24 h). Also, the data attained from Figure 5.4.d were inserted into the plot as contour lines showing the relative degree of polymerization (dp), the Δ absorption value between 350 nm and 550 nm. It can be seen that as the pNE incubation time increases, the film thickness increases in all solid loadings. It was found that increasing the immersion time reflected minimal development when the concentration was 0.5 mg/ml. The film thickness was < 2 nm at the beginning, and the growth of the pNE was almost linear within the first 12 h where the thickness reached 8.4 nm. Then, a steeper rate to 21.7 nm film at 24 h was observed. The pNE with 1 mg/ml solid loading started with a < 2.5 nm layer in 1 h and showed slower growth within 6 h. Then the slope of growth increased between the 6 h and 24 h of immersion, reaching 39 nm in thickness. The slow growth rate of pNE 0.5 mg/ml and 1 mg/ml solid loadings can be attributed to lower concentrations which retarded the growth kinetics. Finally, the trend of pNE adhesion with 2 mg/ml solid loading was observed distinctly different. The thickness of the pNE layer started around 5 nm and grew rapidly within the initial 12 h. The slope reduced in the 24 h and the pNE layer thickness measured 48 nm. Postma et al. reported that the so-called plateauing trending of pDA could be due to the depletion of dissolved oxygen in the water or reactive catechol in the solution [44]. A similar case could be possible for the 2 mg/ml pNE concentration. The thickness data obtained in this study are also considerably closer to the study by Kang et al., where they found pNE thickness values can vary around 30-40 nm with the 18 h polymerization of 2 mg/ml solution [22]. For further investigation, Taskin et al. reported that the pNE layer reached 117.5 ± 24.63 nm thickness after 16 h polymerization of 2 mg/ml NE solution at pH 8.5 [45]. Also, Chen et al. measured the pNE

thickness as 6 nm after 24 h polymerization of 3 mg/ml pNE solution [46]. The reason for the variation could be due to the substrate chemistry, morphology or slight temperature difference during the polymerization.

The deposition kinetics of the 2 mg/ml pNE could be fitted the exponential decay trend (Eq. 5.1) as a function of time that corresponds with previous literature for pDA kinetics [12] [47].

$$d(t) = d_o + d_{max}(1 - e^{(-kt)}) \quad (\text{Eq. 5.1})$$

The d_{max} and k denote the maximal thickness and kinetic constant respectively. Hence, the exponential decay function trend is fitted to the 2 mg/ml pNE growth rate, with a satisfactory reduced chi-sqr value of 3.11. The kinetic rate constant value, k , was 0.075 h^{-1} which was fairly close to the k value of 2 mg/ml pDA growth rate at pH 8.5 (0.072 h^{-1}) [12]. Unfortunately for the concentrations below 2 mg/ml, the exponential decay function could not be fitted. As discussed above, the linearity in the pNE thickness of 0.5 mg/ml and 1 mg/ml solid loadings in the first 12 h occurred, which could probably be due to being far from the oxygen and catechol depletion times. Hence, the exponential decaying function trends were not seen.

Figure 5.5 pNE film thickness and the relative degree of polymerization contour plot as a function of immersion time.

Further surface characterization was carried out by X-ray photoelectron spectroscopy (XPS) as an indicator of chemical composition change after pNE treatment on the YSZ single crystal substrates. In order to insure the homogenous coating, a sample was coated with 2 mg/ml pNE for 48 h. Figure 5.6 compares the wide scan (a-b), C1s core-level before (c-d) and after (e-f) the soft sputtering and O1s core level region (g-h) of the untreated and pNE coated YSZ surface, respectively. The wide-range XPS analysis in Figure 5.6.a shows the untreated YSZ surface spectrum that only includes strong O KLL (974.3 eV), O 1s (530.1 eV), Zr 3s (433.9 eV), Zr 3p (346.5 and 333.1 eV), Y 3p (312.3 and 300.5 eV) and C 1s (284.5 eV) peaks. After the pNE coating, the XPS profile only shows O, N, and C peaks corresponding to a void-free homogenous coating. For further analysis, Figure 5.6.c-d compare C 1s spectra of the untreated and pNE coated surface in detail. The deconvoluted C1s spectrum of the untreated surface-displayed peaks

corresponding to C-O/C-N and C-C bonds with the low signal-to-noise ratio. The pNE coated surface, however, displayed an increased C1s intensity that was fitted with three components: C-O/C-N (at 296.2 eV), C-C (at 284.8 eV), and possibly C-Zr (at 283.3 eV), indicating pNE-substrate bonding. To confirm the carbon content, 0.5 kV Ar⁺ ion sputtering was performed for 6 s to remove any potential carbonaceous contamination without damaging the pNE layer and then the post-sputter C1s regions were taken at that spot. As can be seen, the carbon signal vanished on the untreated substrate after the post-sputtering (Figure 5.6.e). However, the C 1s region intensity of the pNE-coated substrate remained unchanged in Figure 5.6.f after the sputtering. Furthermore, the post-sputtered O1s region of the untreated substrate showed a strong peak that can be fitted with one peak at ~ 529.1 eV, indicating predominantly O=Zr bonding of substrate as shown in Figure 5.6.g. The same peak appeared in the post-sputter O1s core-level of the pNE coated sample at the shoulder of the O=C peak of the pNE layer fitted as the more contributing peak at 531.3 eV in Figure 5.6.h.

Figure 5.6 XPS survey spectra (a), (b); C 1s core level spectra before (c),(d) and after (e),(f) Ar⁺ sputtering; and O 1s core level spectra (g), (h) of untreated and pNE coated YSZ single crystal respectively.

5.3.2. Wet-deposited Ion Characterization

At the next stage, metal-ion and pNE layer interactions were assessed by XPS. As a first candidate, cerium (III) nitrate hexahydrate solution was used as a source of cerium. Uncoated and pNE coated substrates were dip-coated into cerium nitrate solution for 12 h and rinsed. The samples were directly analyzed with XPS without firing. Figure 5.7.a shows the post-sputtered (6 s) wide-range spectra of the cerium nitrate treated YSZ (red) and pNE+YSZ (black) substrates. The spectral analysis showed no traces of a cerium signal on the YSZ surface after the treatment as the wide range spectrum is identical to the untreated YSZ surface, as in Figure 5.7.a. However, a noticeable intensity upshift was observed in the Ce 3d region after the cerium salt immersion of pNE+YSZ surface. It can be noted that C1s peak was still retained after the treatment. For a detailed analysis, the C 1s spectra of this sample were fitted with three peaks similar to C1s region of pNE+ substrate plot in Figure 5.7.d. The last fitted peak at the lowest binding energy was shifted from 283.3 to 282.7 eV which is possibly assigned to C-Ce interaction after the chelation. After confirming the presence of chelated cerium on the surface, the Ce 3d core-level spectrum was analyzed in detail in Figure 5.7.c. The deconvolution of the Ce 3d core-level spectrum revealed the complex presence of peaks that originate with the Ce^{+4} and Ce^{+3} states [48, 49]. The Ce^{3+} state consists of four peaks: v_0 (881.69 eV) , v^- (886.36 eV), u_0 (900.29 eV) and u^- (905.09 eV). In addition, there are 6 peaks that correspond to Ce^{4+} state: v (883.25 eV), v^- (889.90 eV), v^{--} (899.20 eV), u (901.85 eV), u^- (908.58 eV) and u^{--} (917.71 eV). The quantification of cerium ions can be calculated by proportioning peak areas (Eq. 5.1 and 5.2).

$$[Ce^{3+}] = \frac{A_{Ce^{3+}}}{A_{Ce^{3+}} + A_{Ce^{4+}}} \quad (\text{Eq. 5.1})$$

$$[Ce^{3+}] = \frac{A_{v_0} + A_{v^-} + A_{u_0} + A_{u^-}}{(A_{v_0} + A_{v^-} + A_{u_0} + A_{u^-}) + (A_v + A_{v^-} + A_{v^{--}} + A_u + A_{u^-} + A_{u^{--}})} \quad (\text{Eq. 5.2})$$

According to the equations, the Ce^{4+} content percent in the chelated cerium complex was calculated to be 61 % (and 39 % for Ce^{3+}). To further determine the concentrations of the chelated cerium with different valence states, the O 1s core-level spectrum was fitted with three components. O-C at 533.5 eV designates the carbon in the pNE layer. The other two components at 532.1 eV and 530.2 eV were associated with cerium valence bands, Ce^{3+} and Ce^{4+} , respectively. According to the study by Zhang et al., the peak positions could most likely be attributed to the cerium with -OH groups [50]. The peak area ratio of OH- Ce^{4+} to OH- Ce^{3+} was calculated 1.54. Thus, the Ce^{4+} ratio was also confirmed with O1s region as well. Though the area calculations confirmed the presence of Ce^{4+} twice, the existence of Ce^{4+} was somewhat surprising. As commercial cerium (III) nitrate hexahydrate was used as the cerium source, the chemical state of the cerium should predominantly be Ce^{3+} . The reason for high Ce^{4+} in the precipitated Ce complex in the pNE can be explained in two ways. The first hypothesis is that the cerium had 3+ state initially as in the precursor solution, but the pNE layer shifted the valence state to 4+ during chelation. The second hypothesis is that the cerium (III) nitrate hexahydrate already contained the 4+ species, so the pNE layer did not alter the chemical state of cerium.

Figure 5.7 (a) XPS survey spectra of cerium nitrate immersed YSZ and pNE coated YSZ single crystal; (b) C 1s, (c) Ce 3d, and (d) O 1s core level spectra of cerium (III) nitrate solution immersed pNE coated YSZ single crystal.

For the validation, the Ce 3d band of the cerium nitrate hexahydrate crystal which was purchased and first opened approximately a year before analysis was compared with the Ce3d band of the chelated cerium by pNE layer in Figure 5.8.a. The plot is normalized to avoid any intensity differences. It can be seen that the peak positions and the complexity of the Ce 3d bands were almost identical and contained predominantly Ce⁴⁺. The comparison supports the second hypothesis that pNE does not change the valence state of cerium during the chelation. Figure 5.8.b

shows the Ce 3d band of cerium (III) nitrate hexahydrate crystals from the freshly opened container. In this case, the analysis of freshly opened crystals displayed predominantly 3+ as Figure 5.8.c which compares the Ce 3d difference between pure Ce^{3+} and Ce^{4+} spectra as a reference [51]. The results deduce that cerium (III) nitrate hexahydrate is not stable since Ce^{3+} crystals undergo the valence change (to Ce^{4+}) over the shelf-life.

Figure 5.8. Post-sputtered (0.5 kV, 6 s) XPS Ce3d core level spectra of **a)** chelated cerium complex and used cerium (III) nitrate hexahydrate crystals, in normalized intensity **b)** freshly opened cerium nitrate (III) hexahydrate crystals. Both are supplied from the same vendor (Alfa Aesar) and in %99.5 purity. **c)** XPS Ce-3d and O-1s core level spectra of CeO_2 (red) and Ce_2O_3 films as a reference [51].

As the second example, the interaction of pNE layer and palladium ions (a noble metal) was also observed. Figure 5.9.a provides the Pd 3d spectra of Pd nitrate-treated pNE coated YSZ single crystal surface. As noted in the graph, the Pd 3d_{5/2} peak is positioned at 335.8 eV. Brun et al. reported that the binding energies of Pd and PdO are 335.4 eV and 336.8 eV respectively [52]. Also, Khudorozhkov et al. stated that the binding energies of Pd, PdO and Pd(OH)₂ are 335.1 eV, 336.7 eV and 337.4 eV, respectively [53]. These studies confirm that the experimental data obtained from Pd + pNE layer represents the metallic Pd phase. It was also found that the C1s peak still existed while forming the Pd metallic phase (inset of Figure 5.9.a). The O1s region in Figure 5.9.b contained O=C bonds only at 531.2 eV. The other peak found at 533.1 eV was confirmed to be Pd 3p peak.

Figure 5.9 Post sputtered XPS (a) Pd 3d core level spectra (b) O1s core level spectra of Pd (II) nitrate solution immersed pNE coated YSZ single crystal.

Apparently, the results confirm that there are two different deposition mechanisms occurring between the Ce ions + pNE layer and the Pd ions + pNE layer. The schematics in Figure 5.10 summarize the difference in the mechanism that were discussed. The experiments revealed that Ce ions deposit as a form of cerium hydroxide complex precipitates inside the pNE layer as shown in Figure 5.10.a. Whereas, the Pd ions are reduced by the pNE layer and deposit as a metallic phase inside the pNE layer as shown in Figure 5.10.b. The difference precipitation mechanisms dependent on the reduction capability of the quinone form of the pNE. As it was known, catecholamine oxidation forms quinone by releasing two electrons and two protons.

According to Lee et al., this catechol to quinone transformation creates a high reducing potential (e.g., E_o of a benzene-1,2-diol = -795 mV) [54]. Since catechols have a higher E_o than Pd (E_o of Pd = + 0.915 mV [55]), the reaction spontaneously supplies electrons to the Pd ions to form metallic (reduced) nano-particle phase. Since Ce^{3+} ions have very low reducing potential (E_o = -2.336 eV), catechol to quinone transformation can not reduce the Ce ions into the metallic phase spontaneously.

The surface AFM images of these samples after immersion and rinsing indicated that the precipitated Ce hydroxide complex + pNE framework (RMS: 3 nm) was much smoother than the Pd^0 + pNE framework (RMS: 12.4 nm) as shown in Figure 5.10.c and d respectively.

Figure 5.10 Schematics of (a) Ce-complex formation and (b) reduced Pd particle formation inside the pNE layer. AFM images of (c) deposited Ce-complex + pNE framework and (d) deposited Pd particles + PNE framework.

5.3.3. Deposited Cerium Oxide Characterization

The aim of this work was to observe the morphological difference of nano-catalyst formation as a function of precursor immersion time and pNE morphology. To begin with, the bare single crystals were patterned with 20 μm wide SU-8-2 photoresist mask in a class 1000 cleanroom as a marker, as shown in Figure 5.11.a. The clean gaps between the masked layers were designed with 25 μm width (Figure 5.11.b) and 1.5 μm height (Figure 5.11.c). A lift-off process was used to de-pattern the SU-8 lines and leave only the pNE coated areas which then are exposed to the cerium nitrate solution. Finally, cerium nitrate + pNE dip-coated samples were fired at 750°C. Figure 5.11.d. shows a representative AFM image of the ceria layer after the depatterning and coating protocols were applied. It can be seen in the image that the de-patterning and firing steps left some photoresist residue behind with a height of 75 nm at the edges.

Figure 5.11 (a) Optical micrograph and (b) AFM image and the (c) AFM line scans of SU-8 2 patterns on YSZ single crystals. The pattern design is $\sim 20 \mu\text{m}$ wide, 1.5 μm height and

25 μm gap on each photoresist stripe. **(d)** A representative final AFM image of ceria formation on the clean area after the patterning and coating protocols.

To begin with, three pNE morphologies with 1 mg/ml solid loading were included in the ceria coating studies: 6 h, 12 h and 24 h adhered pNE layers on YSZ single crystals. The RMS values of the coated substrates were found to be gradually increasing from 1.8 nm in the 6 h Figure 5.12 to 12.5 nm and 16.5 nm in the 12 h and 24 h (Figure 5.12.b and c), respectively.

Figure 5.12 The AFM images of 1 mg / ml pNE coated YSZ single crystals for **(a)** 6 h, **(b)** 12 h, and **(c)** 24 h. All the AFM scans are in $25 \times 25 \mu\text{m}$ mapping area.

Initially, the 6 h pNE coated on patterned YSZ single crystals were prepared for cerium nitrate immersion and then fired at 750°C shortly after the rinsing step. Figure 5.13.a-c show the histogram plots of ceria particles imaged on the un-patterned areas that were dip-coated with 0.4 M cerium nitrate solution for 6 h, 12 h, and 24 h, respectively. The histogram analysis shows that the ceria particle distribution was right-skewed (positive-skewed) and was mostly populated < 5 nm with the low immersion times (6 h) as shown in Figure 5.13.a. When the immersion time was increased to 12 h, a slightly symmetrical particle distribution was observed with a drop in population density from 9.8 particles (prt) / μm^2 to 8.5 prt / μm^2 (Figure 5.13.b). The symmetric distribution brought a drop in the particle count at the < 5 nm range, but an increase at the > 5 nm

range but not higher than 8 nm, predominantly. As the cerium nitrate immersion time was set to 24 h, a similar right-skewed distribution was formed, but a broader range of particles was observed where the highest particle populations were between 2-4 nm. In addition, a considerable number of particles between 5-10 nm particles were observed as well (Figure 5.13.c). Here, the highest population density, 12.3 prt / μm^2 was observed within the same mapping area. Figure 5.13.d summarizes that the number of particles and the projected total particle area versus as a function of cerium nitrate immersion time. According to the plot, for a lower particle size at 6 h immersion time, the projected particle area was 0.6 % of the $10 \times 10 \mu\text{m}$ mapping area. In addition, even though the particle number dropped, the particle distribution shifted to the right which reflected a 1.1 % projected total particle area. At the last stage of the experiment (24 h immersion), the particle population reached the maximum by forming $< 4 \text{ nm}$ and $> 7 \text{ nm}$ particles. Thus, the projected particle area also reached the highest point, 1.25 % of the total area.

The results showed that the chelated cerium ion growth is a continuous process inside the pNE layer and occurs in two ways. As the first nuclei grow on the surface, these particles can grow over time to bigger particles. In addition, new nuclei also continue to form as it was observed from the histogram data.

Figure 5.13 Deposited ceria particle histogram plots of (a) 6 h, (b) 12 h, and (c) 24 h cerium nitrate dip-coated samples over the 1 mg/ml pNE coated patterned YSZ single crystals for 6 hours. (d) Particle number and projected total particle area (%) comparison of the ceria particles on the un-patterned areas. The mapping area for all the samples is $10 \times 10 \mu\text{m}$.

To observe the effect of pNE decoration on the final ceria deposition, 6 h, 12 h and 24 h (as described in Figure 5.12) 1 mg/ml pNE-coated YSZ substrates for were de-patterned and then immersed in 0.4 M cerium nitrate solution for 24 hours. As the last step, the samples were rinsed and fired 750°C. When the pNE is coated only for 6 hours, the RMS of the final ceria layer was measured at 2.15 nm (Figure 5.12.a). As the pNE coating time increased, a significant enhancement in particle growth and population occurred (Figure 5.14.b-c). As depicted in Figure 5.14.b, circular islands developed and became distinctive as the RMS of the coated area increased to 2.45 nm. When the pNE immersion time was set to 24 hours, cerium complex formation was accelerated due to the thick adhered pNE layer which resulted in highly developed ceria particles (20 to 100 nm in size) with the 8.91 RMS (Figure 5.14.c). In addition to the particulate formation, the film formation was also observed in Figure 5.14.b-c. The highlighted area in Figure 5.14.c was magnified in Figure 5.14.d to show the film formation. The line scan along the direction of the arrow showed that the film formation includes small particles that were around 2-6 nm. Hence the AFM images revealed that a very thin ceria film can be developed when the pNE layer was deposited over 6 h. However, as the pNE layer reached above a certain thickness (RMS 12.5 nm, polymerized and immersed for 12 h), ceria film + island formation developed.

Figure 5.14 The AFM images 0.4 M cerium nitrate immersed (24 h) samples over various 1 mg/ml pNE immersion times: (a) 6 h immersed (b) 12 h immersed, and (c) 24 h immersed to pNE. (d) The highlighted area of pNE 24 h (c). Mapping area for (a-c) are $35 \times 35 \mu\text{m}$ and for (d) is $10 \times 10 \mu\text{m}$. (e) The line scan height profile in the direction of the arrow in (d).

Basic thin film growth modes are classified and schematically shown in Figure 5.15. According to our experiments, it can be deduced that cerium oxide was grown by the layer + island (Stranski-Krastanov) mode. Typically, the few monolayers of the wetting layer grow on the substrate to fit the interface energy. As the layer thickens, the system tends to form islands to relieve the stress by creating dislocations, to reduce the strain energy [56, 57].

Figure 5.15 Basic thin film growth modes

5.4. Conclusion

In this study, the primary motivation was to observe the effects of controllable parameters on the morphology of the pNE surfactant layer. To correlate with SOFCs, the study was performed on pristine YSZ single crystals. First, the correlation between the degree of polymerization versus immersion time and the film thickness/aggregate size of pNE in various solid loadings was investigated. This mapping showed the flexibility of the protocol in that the pNE primary aggregate size, coating thickness, and the polymerization rate can easily be re-engineered for dense or porous microstructures. In addition, the growth kinetics of pNE at high concentration (2 mg/ml) was fitted with exponential decay function. Secondly, the chemical state of the pNE layer and the efficacy of the pNE layer on metal ion deposition (cerium) as the chelation complex were studied. The experiments showed a high cerium complex on the substrate when the pNE coating was applied. In addition, the cerium complex and the carbon pNE layer were found at the same time, indicating the formation of an organo-metallic framework. The study also revealed that the chelated cerium

complex was composed of 61 % Ce⁺⁴ and 39 % Ce⁺³. Finally, the growth of the fired ceria particles with thin pNE coatings showed that the growth of ceria particles can occur by forming new nuclei or growing over the existing nuclei. As the pNE layer thickens, islands of ceria particles formed over a few monolayer of thin film (2-6 nm). Hence, the ceria deposits grows by the layer + island mode (Stranski – Krastanov).

The work could be helpful investigating most optimum ceria or other metal-oxide layers and decoration that is aimed to mitigate the particle coarsening seen at longer firing regimes. This kinetic understanding could help to construct more stable ceria nano-catalyst decoration by engineering the infiltration protocol parameters.

5.5. References

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Chapter 6 : Investigation of Alternative Catecholamine Surfactant Assisted Nano-Ceria Infiltration Anode of Electrolyte-Supported Solid Oxide Fuel Cells (SOFCs)

6.1. Introduction

The incorporation of nanomaterials within the porous electrodes of solid oxide fuel cell (SOFC) through infiltration/impregnation is a well-used method to increase the performance and/or enhance stability. Owing to the facile and low-cost process, tailoring off-the-shelf SOFCs by infiltration becomes a favorable protocol without electrode re-engineering. To increase the effectiveness of the infiltration protocol, there are two main strategies: i) precursor modification ii) electrode backbone modification. In the first route, precursor additives such as Triton-X [1], glycine [2], citric acid [3], and urea [4] were reported to facilitate the formation of nanostructures with specific morphologies, phase stabilities, and performance criteria. The second route utilized a pretreat to the electrode scaffold, especially to the relatively thick and dense unreduced anode electrode, to open up the porosity. For example, Jiang et al. reduced NiO to Ni by purging H₂ prior to the infiltration to enhance porosity and pore network connectivity [5]. In addition, Ye et al. applied an alternative route of leaching nickel from the conventional NiO/YSZ anode matrix through the use of concentrated HNO₃ treatment [6]. These pretreatment methods enhanced the infiltration efficiency; however, the inevitable trade-offs need to be addressed, such as the loss of the nickel, mechanical weakness, and the labor cost.

Another scaffold pretreatment was performed by S.-W. Jung et al. where an additional conductive carbon layer was coated on to a porous YSZ scaffold by n-butane pyrolysis. The purpose of this conductive layer was to assist Co and Ni chloride electrodeposition to the YSZ

scaffold. After the decarbonatization step, a Ni and Co thick film on the SOFC anode was achieved [7].

Over the past decades, poly-catecholamines were used as surface modifiers (wetting agents) [8-10] for metal, metal oxide and organic coatings, as well as, adhesive agents for various coating studies [9]. These works focused on the deposition of the catechol and targeted material onto planar substrates[11, 12] and highly porous polymeric membranes [13, 14]. Poly-dopamine (pDA) was the most utilized of this chemical group over the past decade [12, 15]. When monomer dopamine (DA) oxidizes, the DA monomer will polymerize and provide a film with a range of local reaction sites due to the functional amine and 1,2-hydroxyl end-groups attached to the benzene ring (Figure 6.1). This characteristic allows the film to attach to various substrates and permits the polymerized film to adsorb various metal and metal oxide species from the surrounding solution. Over continuous exposure to a dispersion or salt solution, a significant build-up of these attracted dispersed species may result in the polymerized catechol layer. The metal chelation mechanism from a salt solution precursor onto a pDA coating was used to efficiently coat the porous electrodes of a commercial anode-supported SOFC with redox nano-catalyst, as discussed in Chapter 3 [16].

In this early work, a cerium nitrate precursor solution was chosen to infiltrate both electrodes to prove the efficacy of the protocol, after the pDA treatment. The treatment assisted in the deposition of nearly 3.5 times more ceria nano-catalyst after a single firing step. As a result, a 20% increase in power density was achieved with dual-electrode infiltration with the ceria nano-catalysts. However, the power density of the infiltrated cells dropped and resulted in only 5 % higher performance over the baseline cell in 300 h of testing. This could be attributed to the one drawback of the pDA surfactant, which is the continuous aggregation during the polymerization

step [17, 18]. Hence, the use of the pDA surfactant would potentially clog the open pores inside the electrodes, preventing effective liquid penetration and final homogenous catalyst precipitation. These issues later resulted in the nano-catalyst coarsening and deactivating during SOFC operation. To overcome this issue, the implementation of poly-norepinephrine (pNE), another alternative to pDA which has a less-aggregate formation and a smoother coating owing to the 3,4-dihydroxybenzaldehyde (DHBA) formation during polymerization was studied [19]. The new surfactant resulted in the formation of a uniform nano-catalyst thin film within the active area both at the anode and the cathode electrodes with up to 35% improved catalytic activity. Moreover, this nano-ceria morphology achieved a gradual reduction in polarization resistance over the 300 h of operation.

Apart from pDA and pNE, there are a variety of catecholamine or phenolic structured surfactants with similar chemistry. Another common point of these surfactants is their strong affinity for metal / metal oxide surfaces. Thus, there has been a growing interest in those molecules owing to their remarkable interfacial adhesion properties in colloidal chemistry. A broad review of these molecules in colloid and surface chemistry was completed by Ata et al. [20].

In this study, a combined approach is presented to introduce alternative catechol surfactants and their usage in SOFC anode pretreatment to modify internal surfaces, in order to build metal-organic-frameworks (MOFs). From the variety of catecholamine family, poly-gallic acid (pGA), poly-dihydroxyhydrocinnamic acid (pDHC) and poly-caffeic acid (pCA) were chosen due to their similar chemical structure and properties compared with poly-epinephrine (pNE) as the catechol-based surfactant for strong adsorption nature. These molecules are phenolic compounds found in nature similar to the DA and NE. In addition, the molecules have similar functional OH groups,

and also, carboxylic and/or amino groups bonded to an aromatic ring with slight variations as shown in Figure 6.1.

Figure 6.1 Molecular structures of selected monomers in catechol family.

The work initially characterizes the polymerization of these catechol surfactant by UV-Visible spectroscopy and then the surfactant coatings were analyzed by AFM. After this characterization, a two-step anode dip-coating infiltration protocol was used to impregnate the SOFCs with a similar ceria nano-catalyst. Throughout this study, the cerium nitrate precursor was only infiltrated into the anode electrode as a demonstration to compare the catalyst loading efficacy, nano-catalyst morphology, and electrochemical performance. SOFC current-voltage testing was performed at 750°C using pure H₂ fuel for these cells up to ~75 h. SEM and TEM characterization was performed at the last step to investigate the decoration properties of the ceria nanoparticles at the post-operated anode electrode structures.

6.2. Experimental

6.2.1. Catechol surfactant characterization

The characterization of catechol-based surfactants was investigated at a constant concentration, 1 mg/ml, and constant pH at 8.5. Catechol-based surfactants, dopamine hydrochloride (99%, Alfa-Aesar), DL-Norepinephrine hydrochloride ($\geq 97\%$ (TLC), Aldrich), caffeic acid (Min 98%, TCI America), 3,4-Dihydroxyhydrocinnamic acid (DHC, 98%, Aldrich) and gallic acid (3,4,5-Trihydroxybenzoic acid, 99%, Alfa-Aesar) were dissolved into a 0.05 M TRIS (tris(hydroxymethyl) aminomethane, 99%, Alfa-Aesar) and a 1:1 by volume ratio water-ethanol mixture. Samples were collected at the 1, 6 and 12 h of polymerization and were diluted 1:19 vol% ratio prior to the UV-Vis absorbance (300-900 nm) spectroscopy using a double beam spectrophotometer (Shimadzu 2600).

For adhered catechol topography analysis, one side polished 1 mm $\times$ 1 mm sized, (100) yttria-stabilized zirconia (YSZ) single crystals (MTI Corporation, USA) were used as a substrate. The crystals were first cleaned by soaking in an acetone bath for 5 min then rinsed with 1:1 vol % water-ethanol solution. Then the clean substrates were submerged for coating into catechol surfactant solutions for 12 h. After coating, the substrate is immersed into the clean 1:1 vol % water-ethanol solution to remove loosely bonded moieties from the samples. The samples were dried in the oven at 75°C. The surface microstructure was imaged using an atomic force microscopy (Agilent 5500 Atomic Force Microscope, AFM) in over random 50 x 50 μm^2 areas. The AFM image was processed using open source software, Gwyddion (Version 2.48).

6.2.2. Anode Electrode Infiltration

Commercial electrolyte-supported button SOFC's (NexctCell-HP-2.5, Nexceris, LLC, OH, USA) were used for this study. These cells consisted of a 12.5 mm diameter anode with $\sim 15 \mu\text{m}$

thick nickel oxide (NiO) /yttria-stabilized zirconia (YSZ), a ~10 μm , (Ni, Co) Samaria-doped ceria (SDC) composite and a ~5 μm SDC barrier layer anode structure. The electrolyte was 25 mm diameter (~150 μm thick) of dense scandium stabilized zirconia (ScSZ). Finally, the cathode consisted of a 12.5 mm diameter (~ 30 μm thick) lanthanum strontium manganese (LSM)-gadolinium-doped ceria (GDC) / LSM electrode.

In this study, the anode electrode was only infiltrated by exposing the infiltration solutions only to the anode layer using a hollow cylinder which was sealed around the outer edge of the anode layer. Hollow cylinders (50 mm tall, 25 mm in diameter) were printed using chemically-resistant CPE+ filament. The cells were placed under the hollow cylinders facing anode-side up, and the outer rim was sealed with a hot adhesive (Crystalbond 509, Aremco Products, Inc., NY, USA) to protect the cathode electrode from the precursor solutions. In the first step, 1 mg/ml catechol-surfactants were first dissolved in a 0.05 M TRIS (tris(hydroxymethyl) aminomethane, 99%, Alfa-Aesar, USA) and 1:1 vol % water-ethanol mixture at pH 8.5. The surfactant precursors were then filled into the infiltration cup. To remove the air bubbles, the set-up was placed in a vacuum desiccator under 15 mm Hg vacuum for 5 min, and then transferred to a rocker table for 12 h, which allowed the surfactant to polymerize homogeneously within the internal surfaces of the anode electrode. After the *in-situ* catechol polymerization, the solutions were emptied, and the anode area was rinsed with 1:1 vol % water-ethanol solution. In the second step, the cup was immediately filled with 0.15 M, the cerium (III) nitrate hexahydrate (REacton®, 99.5%, Alfa Aesar, USA) solution of 1:1 vol% water-ethanol mixture. The vacuum and immersion parameters were repeated in the second step. After the cerium nitrate immersion, the cells were rinsed again and dried under ambient conditions. The epoxy around the outer rim was cleaned carefully with acetone dipped cotton sticks. Finally, the infiltrated cells were removed from the infiltration cup

and fired at 750°C for 1 h. This method is called cup-infiltration throughout this chapter. The infiltrated catalyst amounts were measured by weight difference before and the after the infiltration protocol.

All the cells were operated at 750°C for ~75 h using 300 sccm humidified (3%) hydrogen fuel and 300 sccm air. During the electrochemical testing, the cells were sandwiched between alumina flanges, and mica gaskets were placed on both electrode sides as the sealant. For current collection and voltage readings, the connections were wired to Pt mesh with Pt paste for the cathode side and Pt mesh with Ni paste for the anode side. An electronic load of (Agilent N3301A, USA) was used to apply constant current (0.35 A/cm^2) to the cell during the tests. The performance of the cells was evaluated by electrochemical impedance spectroscopy (EIS) using a frequency response analyzer (Solartron 1455A, England) and a potentiostat (Solartron 1470E, England) with the frequency range of 100 kHz - 0.01 Hz under operating current load. The electrode microstructure of tested ceria impregnated cells was examined by scanning electron microscopy (JEOL 7600F, Japan). The samples were denoted as: p“surfactant” as. inf. to imply polymerized surfactant assisted infiltration, such as pNE as. inf for polymerized norepinephrine assisted infiltration.

6.3. Results and Discussion

Prior to the SOFC anode-electrode infiltration, a comparative study of polymerization and adhesion characterization of the selected alternative catecholamine surfactants were performed. Time-varied UV-Vis spectroscopic analysis was completed in the 1, 12 and 24 h after initiating the pH-induced oxidative polymerization. Figure 6.2.a-d show the UV-Vis spectral data in the 300 nm to 800 nm range for pNE, PGA, pDHC and pCA, respectively. At the beginning of the

polymerization step, all of the solutions were transparent (images not shown). The progression of the oxidative polymerization of each solution was visually confirmed by indicative color transitions. The solution color after the 12 h polymerization was brown for the polymerized norepinephrine (pNE), yellow-green for polymerized gallic acid (pGA), orange for polymerized 3,4-Dihydroxyhydrocinnamic acid (pDHC), and red for polymerized caffeic acid, (pCA), as shown within the inset pictures in Figure 6.2.a-d. The spectroscopic data show the absorption bands for each solution, where certain wavelengths appeared with a time-dependent rise. For pNE and pGA, the rise in the absorption peak was observed at 350 nm (Figure 6.2.a, b). This band was also found during the polymerization of pDA, where it is often correlated with the quinone formation and the development of higher molecular weight species throughout the polymerization [21]. Tóth et al. also reported that the irreversible GA oxidation to quinone-hydroquinone species produces a color change under ambient conditions [22]. The pGA spectra also revealed minor absorbance bands at the visible range, 495 nm and 700 nm, which are indicators of the orange-green pGA solution color. During the pDHC solution analysis, the observed visible band was at 415 nm, which links to the high blue light absorption for yellow solutions (Figure 6.2.c). Also, the shoulder at 350 nm got narrowed with higher intensity as the polymerization time proceeded. Unlike the other surfactants, the UV-Vis of pDHC during polymerization did not show any noticeable peak. Small increments of upshift were observed at 450 nm during the polymerization step, which is responsible for blue/indigo light absorption of red colored solutions. Behboodi-Sadabad et al. also reported the same trend in their time-dependent kinetic study for caffeic acid [21]. They assumed that the absorbance curve is convoluted and the absorbance value at 380 nm is an indicator of oxidation (polymerization) similar to other catechol surfactants. In Figure 6.2 all the surfactants experienced a rising trend of absorbance intensity at lower wavelengths but only the time-

dependent reduction of the band at 312 nm in pCA could be measured under the testing spectrum (300-800 nm) in Figure 6.2.d. According to Tóth et al., this trend could potentially happen due to the deprotonation of the carboxyl groups which indicates the consumption of carboxylic groups through polymerization [22].

Figure 6.2 UV-Vis spectra of 1 mg/ml (a) pNE, (b) pGA, (c) pDHC, (d) pCA polymerized for 1, 6 and 12 h.

The self-adhered coatings of these catechol solutions were tested by the dip-coating method in 1 mg/ml solid loading for 12 h at pH 8.5. The morphology of the adhered layer onto the ultra-flat YSZ single crystal surfaces was characterized by AFM in the tapping mode, using a 40 μm line scans on a 50 $\times$ 50 μm^2 mapping area. The surface profiles of pNE, pGA, pDHC and pCA are shown in Figure 6.3, respectively. Firstly, the reference sample, pNE, morphology included a homogenous blend of medium-sized (~ 40 nm) and predominantly fine particles (< 20 nm) as shown in Figure 6.3.a. In addition, the measured RMS of the pNE surface was 8.1 nm. The adhered pGA

surface shown in Figure 6.3.b consisted of large and anisotropic aggregates (60-80 nm) with smaller particles underneath. Hence, the RMS of the pGA surface increased to 19.9 nm. Similarly, the pDHC treated surface also included some aggregates, but showed a lower population of islands in comparison to the pGA treated surface, as shown in Figure 6.3.c. Sparse and discrete aggregate morphology aided in the reduction of the RMS to 17.4 nm.

The pCA morphology, shown in Figure 6.3.d, contained the mostly homogenously distributed equiaxed, spherical particles which were less than 10 nm in size. The RMS was measured to 4.9 nm, the lowest among the other candidates, including the reference surfactant, pNE. The aggregate free, smooth coating of the caffeic acid showed the most promising coating morphology under these experimental conditions (1 mg/ml solution at pH 8.5 and 12 h immersion).

Figure 6.3 AFM images of 1 mg/ml (a) pNE (b) pGA, (c) pDHC and (d) pCA polymerized for 12 h. Mapping area is $50 \times 50 \mu\text{m}^2$, line scan length is $40 \mu\text{m}$.

After the catechol polymerization and the adhesion validation, polymerization procedures were applied to the anode electrode with a so-called cup infiltration method. The cup prevented any leakages during the anode infiltration and protected the cathode electrode. After the infiltration and calcination step was completed, the entire cell weight was measured and compared against the initial weight. This gave an estimate of the total ceria infiltration within the anode electrode. The infiltrated ceria amounts were approximately 0.2 mg ($\sim 0.16 \text{ mg/cm}^2$) for all cells, except for the pDHC assisted infiltration which showed $\sim 0.3 \text{ mg}$ ($\sim 0.25 \text{ mg/cm}^2$) deposition. As a reference, a

non-surfactant infiltration protocol, denoted as only Ce N., was performed, and the infiltrated ceria amount for this sample was 0.06 mg ($\sim 0.05 \text{ mg/cm}^2$).

Figure 6.4 (a) Nyquist (b) Ohmic resistance (c) Polarization resistance and (d) Bode plots of baseline and only cerium nitrate and pNE, pCA, pDHC, pGA assisted cerium nitrate infiltrated cells operated at 750°C, 0.35 A/cm² for 75 h.

The time-dependent EIS Nyquist plots of the baseline and the infiltrated cells are shown in Figure 6.4.a. Surprisingly, the ohmic resistances at the 0 h varied up to 28.5 % from cell to cell in the same batch. At first glance, this makes the spectra more complicated for the analysis of the influence of ceria infiltration. For further analysis, the impedance spectra were extracted and the ohmic resistance and the non-ohmic resistance changes are plotted in Figure 6.4.b and Figure 6.4.c, respectively. The beginning point (first leg) of the impedance near abscissa was taken as the ohmic resistance in Figure 6.4.b. As stated above, the cell to cell variance in the ohmic resistance can be seen at the 0th hour. The ohmic resistance of the baseline cell was measured as 0.59 ohm·cm², where the rest of the infiltrated cells showed values that were 15.4 % (pNE assisted infiltrated cell) to 28.5 % (pGA assisted infiltrated cell) lower R_o than the baseline cell. The reduction of R_o may be related to additional ceria phase at the SDC barrier layer which potentially increased the density of ionic conducting phases. At the end of the run, the ohmic resistances of all the cells were higher than that of the beginning of the test for all samples. The increase in ohmic resistance was 8.5 % for the baseline cell and ranged from 2.6-6% increase in ohmic resistance for the infiltrated cells. In Figure 6.4.c, the non-ohmic parts (also referred as polarization resistance, R_p) were represented by taking the net resistance between the two legs of the impedance curve where they intercept to the abscissa. First, it can be observed that the baseline cell had the highest R_p of 0.38 ohm·cm² at the beginning of the test, and it is followed by the infiltrated cell without the surfactant step. The R_p non-surfactant assisted infiltrated sample was ~23.6 % below the baseline cell (-23.6 %). Further initial enhancements were seen in the surfactant-treated infiltrated cells where the R_p are 0.227 (-40.3%) , 0.206 (-45.6%) , 0.173 (-54.2%) and 0.172 (-54.6%) ohm·cm² for pNE, pGA, pDHC and pCA assisted infiltrated cells, respectively. At the end of the operation (~75 h), it was shown that the non-ohmic part of the baseline cell dropped about 13.2% to 0.33 ohm·cm². On the

other hand, all the infiltrated cells were deactivated over time. The R_p at 75 h of the non-surfactant infiltrated cell was 9.6% higher than the baseline cell which indicates particle-particle interactions and coarsening related deactivation. The R_p 's of surfactant-assisted protocols at 75 h were also found to be higher than the initial R_p 's, but they at least remained below the baseline cell. In addition, a correlation of initial performance versus percent deactivation can be deduced from the plot. The slope of the line is found to be steeper as the initial enhancement was better. For example, pNE assisted infiltrated cell (green line) had the lowest enhancement at the beginning and also showed the lowest deactivation rate, 17.2 % increase in R_p between 0 to 75 h. The trend was similar with the pGA assisted infiltrated cell with 27.8 % and finally, the pDHC and pCA assisted infiltrated cells ~ 39%. To better analyze the electrochemical effect of surfactant assisted ceria infiltrated anodes, the EIS Bode plots for the baseline and infiltrated cells for 0 h and 75 h are shown in Figure 6.4.d. Previous studies showed that the change in reactance at the high frequency ($> 10^2$ Hz, denoted as *Region I*) is associated with the anode charge-transfer reaction [23, 24]. Correspondingly, the middle-frequency changes (10 - 10^2 Hz, denoted as *Region II*) denote the change in cathodic polarization [23, 25]. In addition, it was observed that the low-frequency changes (1 - 10 Hz, denoted as *Region III*) are generally related to anodic gas diffusion polarization [23, 26]. *Region IV* is not considered in the analysis and negligible due to the lower inductance. As can be found Figure 6.4.d, all the infiltrated cells displayed lower reactance in *Region I* which indicates overall activation of ceria at the anode electrode. The slight upshifts in pDHC, pCA and only Ce assisted infiltrated cells were relatively noticeable than the other cell. These cells showed also showed higher R_p change over time as shown in Figure 6.4.c. except for pCA as. inf. cell. Along with the pNE as. inf. cell (the lowest recorded time dependent R_p degradation), pCA as. inf. cell did not show any shift in reactance in the *Region I* between 0 h and 75 h. At the low

frequency range (*Region III*), the ceria infiltrated cell without surfactant (only Ce N.) positioned at a remarkably high arc and the baseline cell with a time dependent upshift which can be evidence of inhomogeneous deposition and agglomeration of ceria nano-particles. Even though the infiltrated ceria amount resulted in only one-third of the surfactant assisted ceria infiltrated cells, the high reactance at the *Region III* showed that gas diffusion issues due to poor infiltration. The general trend for the surfactant-assisted ceria infiltrated cells, on the other hand, the initial (0 h) and the final arcs (75 h) were lower than the baseline cell, although the final arcs were always higher than the 0 h which can also be a sign of coarsening.

To be able to compare the actual time-dependent electrode performance, the electrode overpotential versus time is plotted in Figure 6.5. The electrode overpotential calculation was formulated in Eq. 6.1. The total overpotential (η_{total}) was assumed to be the combination of the ohmic (η_{ohmic}) and electrode overpotential ($\eta_{electrode}$). Thus, the electrode overpotential was calculated by subtracting the ohmic overpotential from the total overpotential. The total overpotential (η_{total}) is the difference between open circuit voltage (OCV) and operating cell voltage (V_{cell}) under operating current (0.43 A or 0.35 A/cm²) (Eq. 6.2). The ohmic overpotential (η_{ohmic}) is obtained by the ohmic resistance multiplied by the operating current (Eq. 6.3).

$$\eta_{electrode} = \eta_{total} - \eta_{ohmic} \quad (\text{Eq. 6.1})$$

$$\eta_{total} = OCV - V_{cell} \quad (\text{Eq. 6.2})$$

$$\eta_{ohmic} = R_o * I \quad (\text{Eq. 6.3})$$

Figure 6.5 Time-dependent electrode overpotential change plot of baseline, only cerium nitrate, and pNE, pCA, pDHC, pGA assisted cerium nitrate infiltrated cells operated at 750°C, 0.35 A/cm² for 75 h.

As shown in Figure 6.4.b, the ohmic resistance of the cells was only measured at the beginning (0 h) and at the end of the test (~75 h). The rate of the time-dependent changes of the ohmic part was relatively 3 to 5-fold lower than the non-ohmic part. Hence, the difference in the ohmic resistance was assumed to be linear and the change was obtained by linear interpolation. Since the ohmic overpotential was excluded from the total overpotential, and the cathode electrode was untouched, any change in the electrode overpotential must be due to the anode electrode contribution (and as such, due to the effect of the anode infiltration). In the plot, the electrode overpotential of the baseline cell initially was 130 mV. Then after a gradual decrease over the first 24 h of operation, the cell showed a stable performance where the overpotential change between the 24 h to the end of the run was -0.082 mV/hr. This gradual drop can be attributed to the typical burn-in period of the cell with LSM cathodes. Hence, a vertical reference line at 24 h was set to

separate the burn-in and post burn-in stages. In Figure 6.4.b, the ceria infiltrated cell without the application of the surfactant showed a lower initial R_p but higher R_p than the baseline at ~ 75 h. In Figure 6.5, it is clearly depicted that the deactivation took place in the first hours of the run in the burn-in stage. In addition, the deactivation continued at the post burn-in stage at the rate of 0.168 mV/hr. Concerning the infiltrated cells, it can be observed that the initial overpotential reduction ranking (from lowest to highest reduction) followed as pGA, pNE, pDHC and pCA assisted infiltrated cells respectively. At the pre burn-in stage, all the cells exhibited an increase in electrode overpotential. The pGA and pCA assisted infiltrated cells showed a sharp increase in the first 3 h in this stage, whereas the pNE and pDHC assisted cell had a moderate increase in electrode overpotential. After the burn-in stage, the trend continued as the deactivation rates during the post burn-in stage were measured as 0.093, 0.177, 0.180 and 0.183 mV/hr in pGA, pNE, pCA and pDHC respectively.

The electrochemical test for the pCA and pDHC assisted infiltration showed the most promise over 75 h of operation. However, the pCA assisted infiltration protocol showed lower initial electrode overpotential compared to pDHC with having less catalyst deposition. Since the infiltrated cell stability is as important as the performance boost, the pCA assisted protocol was chosen for further testing. Hence the pCA protocol was modified by raising the cerium nitrate immersion time from 12 h to 24 h. The infiltration resulted in the doubling of the infiltrated ceria amount to 0.4 mg (0.32 mg/cm^2) (denoted as pCA 2).

Figure 6.6 shows the electrode overpotential comparison of pCA-2 with the pCA and the baseline cell. The long immersion time resulted in almost a two-fold increase in the initial electrode overpotential over that of the IC-1 sample. However, the cell was stable in both burn-in and post burn-in stage. During the burn-in stage, the overpotential rose to only 5 mV. The post burn-in

stage resulted in an additional 2 mV change with a change rate of 0.042 mV/hr which was four-fold less than the original pCA assisted protocol. Despite the pCA assisted infiltrated cell having a 4.5 mV lower overpotential at ~75 h, the low deactivation rate of pCA-2 seemed further promising for longer operation.

Figure 6.6 Time dependent electrode overpotential change plot of baseline, pCA and pCA 2 assisted infiltrated cells operated at 750°C, 0.35 A/cm² for 75 h.

The Bode plot shown in Figure 6.7 corresponds to the deactivation behavior identified in the overpotential analysis. The initial pCA 2 reactance values at the high-frequency zone (*Region I*) and low-frequency zone (*Region III*) were higher than the pCA assisted infiltrated cell, which could indicate the drawback of more catalyst loading causing deactivation and gas starvation. On the other hand, a slight drop of pCA 2 in *Region I* indicates a slight degree of activation due to achieving a more interconnected catalyst network after particle coarsening.

Figure 6.7 Bode plot of baseline, pCA and pCA -2 assisted infiltrated cells operated at 750°C, 0.35 A/cm² for 75 h.

To analyze the particle size, location, and population of post-operated pCA and pCA 2 as. inf. cell and the baseline cell anode regions were analyzed by Scanning Transmission Electron Microscope (STEM) in annular dark-field (HAADF) imaging and energy-dispersive X-ray Spectroscopy (EDS) modes. Figure 6.8 depicts the barrier layer region images of baseline cell, pCA and pCA 2 as. inf. cells in HAADF and EDS modes (Sm and Ce mapping). As shown in Figure 6.8.a, a barrier layer pore of baseline cell observed particle-free and in the SDC phase. On the contrast, Figure 6.8,a and b revealed infiltrated particle population difference between pCA and pCA 2 as. inf. cell. According to the EDS elemental mapping, the nanoparticles found inside the pores did not show any Sm signals which confirms that composition of the particles was pure ceria, hence the infiltrated nanoparticles. This high catalyst load at the barrier layer in both pCA

and pCA 2 could contribute to explain the reason of low ohmic resistance of the all infiltrated cells compared the baseline cell. Interconnected ceria nano-particles may have created additional ionic pathway that reduced the ohmic resistance of the cell. Since pCA 2 assisted infiltrated cell deposited two-folds more catalyst, it can be observed that the nano-particle population in the pores of pCA 2 as. inf. cell (Figure 6.8.b) was more than in pCA as. inf. cell (Figure 6.8.c). The decrease in R_o from $0.487 \text{ ohm}\cdot\text{cm}^2$ (pCA) to $0.472 \text{ ohm}\cdot\text{cm}^2$ (pCA 2) also supported the trend. These ohmic resistance values of the pCA and pCA 2 as. inf. cells were 17.4% and 18.2 % lower than the baseline cells, respectively. Interestingly, the pCA 2 as. inf. cell's R_o degraded 4.5 % over 75 h operation while pCA as. inf. cell's ohmic resistance increase was only 2.6%. Under the same operating conditions, the ohmic resistance increase of the baseline cells was recorded 8.5 %.

Figure 6.8 HAADF and EDS mapping of (a) Baseline (b) pCA as. inf. cell, (c) pCA 2 as. inf. cell.

The EDS mapping of pCA 2 as. inf. cell also revealed cerium signals at the pore edges of the nickel phase in the anode active area as depicted in Figure 6.9.a-b. The observation provides thin film formation of over the nickel phase which attributed to the catalytic activity of the anode.

Figure 6.9 (a) HAADF mode and (b) EDS mode images of the cerium film phase over the nickel backbone at the active area of pCA 2. inf. cell.

The semi-quantitative confirmation of higher ceria content inside the Ni / YSZ current collection regions was also performed in long dwell time (5000 ms). Figure 6.10 shows the Ce L-alpha line comparison of baseline, pCA and pCA 2 cells. The results showed that ceria content was also found to be the highest pCA 2 than the pCA and the baseline cell at the current collection region which is $\sim 10\ \mu\text{m}$ down to the electrode surface. The TEM studies at the barrier layer, active layer, and the current collection layer suggest that ceria nanoparticles exist in every region of the anode. Moreover, semi-quantitative results confirm the higher ceria content in PCA 2 assisted infiltrated cells which showed: 1) higher particle population at the barrier region, 3) higher Ce L alpha line at the current collection region.

Figure 6.10 Cross-section of Ce L-alpha shell signal comparison of baseline, pCA and pCA 2 as. inf. cells.

6.4. Conclusion

In this study, selected catecholamine group surfactants, polymerized gallic acid (pGA), polymerized 3,4-Dihydroxhydrocinnamic acid (pDHC), polymerized caffeic acid, (pCA), were introduced to enhance and control the nano-catalyst infiltration throughout the anode of a SOFC. These materials were used in order to compare with previous work, where similar catechol surfactants were studied (pNE and pDA). The monomer forms share similar functional OH groups, carboxylic and/or amino groups bonded to an aromatic ring with slight variations. As for pDA, the most utilized catechol surfactant discussed in the literature, these surfactants can also be functionalized by oxidative polymerization within an alkaline solution. This was verified by UV-Vis spectra analysis in this work. The adhered particle morphology also revealed the adhered particulate sizes can vary between 80 nm (pGA and pDHC) and 15 nm (pCA). Nevertheless, the nanocatalyst infiltration experiments showed that these polymerized surfactants could promote up

to 4 times more catalyst deposition compared to non-surfactant infiltration with enhanced infiltrated particle morphology. The two-step pCA+cerium nitrate infiltration enhanced infiltration protocol resulted in up to 37 % reduction in electrode overpotential. The TEM studies for pCA and pCA 2 as. inf. cells showed the nanoparticulate existence at the barrier layer. Hence, nano-ceria infiltration may also be responsible for the decrease in the ohmic resistance by creating additional ionic pathways at the barrier layer region. Also, the ceria thin film formation bonded to the Ni phase was observed at the active area. The crosssectional line scans depicted the semiquantitative comparison of pCA 2, pCA and the baseline cells, showing that pCA 2 as. inf. cell had higher ceria content at the current collection zone (~ 10 μm near the surface).

6.5. References

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Chapter 7 : Conclusion

7.1. Thesis Summary

This dissertation contains a systematic investigation of the use of catecholamine surfactants in Solid Oxide Fuel Cell (SOFC) electrode systems as chelators and wetting agents to control and improve the incorporating nano-catalysts. The review of the SOFC infiltration methods and materials in Chapter 2 revealed that there is a lack of research to pre-modify the internal porous surfaces to control the wetting precursor solutions throughout the porous SOFC electrode. There are very limited studies in the literature on the precipitation efforts of various oxide catalysts using these agents. This would potentially permit the controlled deposition and growth of these catalytic particles as well as the population.

The use of a mussel-inspired catechol, poly-dopamine, has been used for decades in coating planar and highly porous membranes. The monomers in the catechol solutions can be polymerized (or grafted) naturally and adhere to the internal electrode surfaces, owing to the multi hydroxyl bonds. When the treated electrodes are exposed to a catalyst precursor, the metal ions can be chelated by the grafted (polymerized) layer, forming a precipitated nano-catalyst population inside the carbonaceous framework, as well as, enhancing the wetting properties. In this set of studies, cerium nitrate precursor infiltration was used as an example to show the efficacy of the technology, but other metal precursors (and multiple compositions) can be utilized with the protocols demonstrated in this work.

The study first established the initial experiments on the most utilized catechol monomer, dopamine (DA) in the literature in the Chapter 3. As discussed in the Chapter 2, the process of depositing secondary material systems onto substrates requires an initial soaking of a substrate

within a monomer solution. This solution needs to be polymerized, mostly by natural oxidation, by shifting the pH to the basic condition (pH 8.5). The polymerization step is crucial to the deposition of the secondary material systems on to the substrate. Two methods of the polymerization route termed in-situ, and ex-situ polymerization were tested for dopamine as described in the second chapter. In-situ polymerization is defined by a dip-coating process where the SOFC was dipped into the DA solution, allowing the monomer infiltration inside the porous structure before the oxidative polymerization is started. In the ex-situ polymerization, the DA solution polymerization was first initiated in a beaker and the SOFC electrode was then immersed into the polymerized DA (pDA) solution. This allows the poly-dopamine to infiltrate into the porous structure. This work showed that both routes successfully deposited a proper surfactant layer required for the efficient deposition of the later nano-catalyst layer. Both methods resulted in almost a three-fold increase in the deposition amount over non-surfactant infiltration. The electrochemical cell performance data showed that ex-situ polymerization route brings higher degradation rates during the operation potentially due to clogging of pores by a known phenomenon of unstoppable pDA aggregation. The continuous pDA aggregation is driven by the oxidative polymerization that causes pDA polymers to keep growing and form micron-sized aggregates instead of adhering to the substrate walls. Hence these aggregates might clog the SOFC pores and/or limit further penetration of the polymer layer which also limits the catalyst precursor deposition. The in-situ polymerized pDA assisted ceria infiltration, and showed a better method to promote discrete particle formation homogenously. The best performing, in-situ pDA assisted infiltrated cell showed 5.8% higher power density than the baseline cell after 300 h operation.

As seen in the initial work, a key issue is the clogging or blocking of the surface and/or near-surface electrode pores when the pDA becomes agglomerated during the initial step. This

known phenomenon becomes problematic with commercial SOFC's which have < 35% porosity in the range of < 5 μm pore size. The polydopamine showed initial promising results, but a catechol candidate that shows better size stability and allows agglomerate-free thin coatings was needed. Therefore, the next stage of the work focused upon alternative catechols that could provide the same wetting and coating characteristics.

As a substitute, polymerized norepinephrine (pNE) assisted infiltration was introduced in Chapter 3. The substitution from the pDA resulted in a better penetration through the electrodes active area and achieved a uniform coating with particle + island ceria formation. This decoration type led to no degradation within 300 h of electrochemical testing where the polarization resistance was improving (activating). Also, the work demonstrated a systematic study on finding the optimum amount which could be achieved by simply changing the catalyst precursor molarity. For a commercial anode-supported NiO/YSZ/LSM button cells, 5 mg ceria infiltration (0.61 mg/cm^2 loading at the anode side, 1.63 mg/cm^2 loading at the cathode electrode) showed the highest decrease in the polarization resistance, which means the highest activation in both electrodes.

The accomplishments of the Chapter 3 and 4 are:

- 1) Decreasing the number of infiltration step by developing catechol surfactant assisted infiltration protocol.
- 2) Controlling the liquid segregation and promote the material deposition.
- 3) Pinning the nanoparticles at the active area hence boosting the performance (up to 35%)
- 4) Featuring continuously activated cells without degradation and discussing the possible mechanism(s).

- 5) Performing electrochemical and material characterization to correlate performance versus microstructural changes, such as observing optimum infiltration amount and over infiltration.

In Chapter 5, the correlation of pNE polymerization kinetics versus solid loading and adhered film thickness on planar substrates was explored. UV-Vis spectra of the pNE solutions assisted to revealed absorbance upshift at 350 nm wavelength which denotes the quinone formation. Hence, this information was an indicator of, degree of surfactant polymerization. The atomic force microscopy (AFM) analysis on the pNE layer proved that both solid loading and polymerization time are important parameters on adhered catechol thickness. At early stages (3 h), pNE adhesion was in < 10 nm size islands. The population and the coverage of these islands expanded as a function of time. Finally, at the higher immersion times (24 h), a film coating of ~48 nm in thickness was achieved. In addition, the chemical states of the pNE film and chelated cerium nitrate deposit were investigated by XPS. The study revealed that both cerium complex and the carbon (pNE) were found at the same time, indicating an organo-metallic framework was formed. Finally, the study on the analysis of the ceria particles with different cerium nitrate precursor immersion times on pNE coated YSZ substrates showed that the ceria growth was driven by two mechanisms: 1) forming nuclei 2) growing over the existing islands. As the pNE layer thickens, the islands of ceria particles formed over a 2-5 nm thin film. The growth mode of ceria particles fit the layer + island mode (Stranski – Krastanov).

The accomplishments of Chapter 5 are:

- 1) Observing the growth of pNE layer up to <50 nm in thickness with given parameters (0.5-1- 2 mg/ml solid loading and 1-24 h immersion time).

- 2) Fitting the pNE film thickness rate with exponential decay function at high solid loading (2 mg/ml).
- 3) Performing XPS for pNE and pNE + metal ion soft framework with gentle sputtering conditions.
- 4) Identifying different precipitation mechanisms of a lanthanide group metal ion (cerium) and a noble metal group metal ion (palladium) was observed by XPS.
- 5) Investigation of the growth of ceria nanoparticles was investigated with nanometer accuracy. The growth trend was associated with the possible film growth models and was likely matched with the Stranski-Krastanov (Layer + Island model).

In Chapter 6, the study concluded with the application of the method with alternative catechol systems with similar phenolic structures with small variations in their end-groups or configuration. Some potential alternative catechol surfactants such as poly-caffeic acid, poly-hydroxyhydrocinnamic acid and poly-gallic acid were adapted to the SOFC infiltration. The UV-visible spectrum showed that all the alternative surfactants can be subjected to oxidative polymerization. In addition, the characterization of the adhered catechol morphology revealed that pCA showed the smallest features, predominantly in the 10 nm size range. Thus, the pCA assisted infiltration protocol showed the best initial performing cell over the 75 h of electrochemical testing.

The accomplishments of Chapter 6 are:

- 1) A new infiltration protocol is developed to infiltrate only anode electrode (with the same efficacy of dip-coating method)

- 2) Compared the aggregate size of pCA, pGA and pDHCA on planar substrates by taking pNE as a reference. pCA adhered with the fines coating among the other surfactants analyzed by AFM (4.9 nm RMS).
- 3) All the alternative surfactant treatments resulted 4X more catalyst deposition as compared the non-treated electrode dip-coat infiltration.
- 4) Alt. Surfactant treatment also reduced the Rp of the cells 19.7 (pNE) to 27.8 % (pCA) after 75 h operation.
- 5) PCA protocol was improved with 2X higher immersion time which resulted 2X more catalyst amount with better stability ($\Delta 25.3$ mV within 75h (pCA) versus $\Delta 7$ mV within 75 h (pCA-2)).
- 6) TEM characterization identified nanoparticles at the anode barrier layer and Ce skin layer at the anode active area.

7.2. Future Works

Future works can focus the investigation of other catecholamine oxidation and/or polymerization mechanisms such as UV-light assisted or water oxidant catalyst (WOC) assisted oxidation. The WOC assisted oxidation not only reduces the oxidation time but also may control the aggregate size depending on how much oxidant is introduced to the system. The technology should be adapted for a rapid polymerization with the addition of a water oxidant catalyst (WOC) agent. The reaction of WOC can be formalized as in (Eq. 7.1);

where O_x is the oxidant, H_2O is water, Red is the reduced form of O_x , and n is the number of equivalents necessary to consume $4 e^-$ from water (Mills et al., *J. Mater. Chem.*, 2016). Therefore, non-aqueous solvent systems can be used to improve wetting properties.

Also, further studies on building layer by layer (LbL) approach (catechol + catalyst + catechol + catalyst) structure that allows the decoration/deposition of multi-functional catalyst systems inside internal pore might be performed. The composite catalyst infiltrated electrodes may run efficiently under various conditions/purposes such as SOEC / SOFC cycling. 3-D printing method can also be used for targeting this LbL approach to specific locations of the fuel cells

Apart from future studies, the current results from the kinetic investigation of catechol surfactant polymerization, growth and chelation properties, as well as, the successful adaptations of the SOFC infiltration protocols, should be ready to be driven towards to commercialization of this protocol. Preliminary experiments have already been performed with an industrial collaborator, Nexceris LLC. The modified pNE assisted dip-coat infiltration protocol was applied to a planar fuel cell with 77.5 cm^2 active anode area. The reported performance enhancement is 4.6 % at 650°C , 4.9% at 700°C and 9.4 % at 650°C in comparison to the baseline cell after ~100 hours of operation. The collaboration showed that the technology is flexible to be scaled up and already shows enhanced performance on large-area cells with a 48 h of a process without compromising the existing manufacturing line. As the outcomes of this dissertation, three patent applications regarding the SOFC electrode infiltration methods have been submitted. The WVU Technology Transfer Office should bridge the potential partners and the inventors on licensing these technologies.