

OPERANDO OPTICAL STUDIES OF NEXT GENERATION ANODE MATERIALS IN
HIGH TEMPERATURE SOLID OXIDE FUEL CELLS

by

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DEDICATION

To my family, with love ♥

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GLOSSARY

A.....	Ampere
AC	Alternating Current
BZY.....	Yttrium-doped Barium Zirconate
CGO	Gadolinium-doped Ceria (or GDC)
cm ⁻¹	Wavenumber of Raman Shift
DC	Direct Current
E	Nernst Potential
E _{2g}	Doubly Degenerate Vibrational Mode
EIS.....	Electrochemical Impedance Spectroscopy
F _{2g}	Triply Degenerate Vibrational Mode
FEM	Field Emission Microscopy
I	Current
LO	Longitudinal Optic Mode
LSM	Lanthanum Strontium Manganite
MIEC.....	Mixed Ion Electron Conductor
η	Overpotential
OCV	Open Circuit Voltage
P	Power
P_{H_2}	Partial Pressure of H ₂
P_{H_2O}	Partial Pressure H ₂ O
P_{O_2}	Partial Pressure of O ₂
PEMFC.....	Proton Exchange Membrane Fuel Cell
R.....	Resistance
R _B	Bulk Resistance
R _P	Polarization Resistance
RC	Resistor Capacitor Circuit
RQ.....	Resistor Constant Phase Element Circuit
SCP.....	Spectrochronopotentiometry
ScSZ	Scandia stabilized zirconia
SOFC.....	Solid Oxide Fuel Cell
SOEC.....	Solid Oxide Electrolysis Cell
STN	Niobium-doped Strontium Titanate
TO	Transversal Optical Mode
TPB	Triple Phase Boundary
V.....	Volt or Potential
ν	Frequency
XPS	X-ray Photoelectron Spectroscopy
Z	Impedance
YSZ	Yttrium-Stabilized Zirconia

ABSTRACT

Solid oxide fuel cells (SOFCs) are high temperature energy conversion devices capable of efficient and sustainable energy production. Because of the need to electrochemically reduce molecular oxygen and the relatively high activation energy required for oxide ions to diffuse through the dense, solid-state electrolyte, SOFCs typically operate at temperatures ≥ 500 °C. High operating temperatures endow SOFCs with many advantages, including fuel flexibility and high conversion efficiencies, distinguishing them from other types of fuel cells. However, high temperatures also present challenges related to the stability of the electrode materials, accelerating cell degradation and limiting the development and integration of SOFCs into large scale power production strategies. These mechanisms are the result of fundamental changes in material properties that remain poorly described and difficult to predict. Studies presented in this work utilized *operando* Raman spectroscopy and electrochemical measurements to directly correlate material changes with changes in cell performance under various operating conditions. Research focused on developing and characterizing new electro-catalytic materials having improved conversion efficiencies and mechanical resilience to thermal and chemical stress. Because current state of the art SOFC Ni-YSZ cermet anodes are sensitive to oxidation, the first two studies investigated the effects of adding small amounts of Al_2TiO_5 to Ni-YSZ anodes and the impact of resulting secondary (2°) phases that formed on SOFC tolerance to electrochemical and environmental reduction and oxidation (redox) cycling. Results show that Al_2TiO_5 helps improve tolerance to both types of redox cycling by maintaining electrode-electrolyte connectivity and minimizing catalyst coarsening. The third study illustrates how this same dopant improved anode carbon tolerance when operating with hydrocarbon fuels. Because excessive carbon accumulation on SOFC anodes can lead to rapid cell failure, ways to improve carbon tolerance was further explored in the last two studies. These studies investigate the effect of decoupling the electro-catalytic and the electronically conductive phases of the anode under pure methane and biogas-surrogate environments. Collectively, the studies described in this dissertation provide insight into the materials-specific mechanisms responsible for limiting degradation of doped and functionally decoupled anodes to help guide the design of new SOFC electrode materials.

CHAPTER ONE

INTRODUCTION

Research Motivation

Current energy infrastructures are changing as a result of international agreements and implemented policies promising to reduce dependence on nonrenewable energy resources and regulate emissions of greenhouse gas pollutants. To facilitate these goals, many countries are committed to transforming their transport and energy networks into low-carbon systems that reduce greenhouse gas emission while maintaining high energy security and competitive global energy positions.^{1,2} While renewable energy resources like solar and wind power have seen significant integration into existing power producing infrastructures, these resources suffer from seasonal and weather intermittency as well as inadequate storage media, motivating the investment into other resources and the creation of a broader energy portfolio.

To bridge the gap between intermittent renewables and conventional nonrenewable energy sources, fuel cells stand out as a promising technology. Fuel cells are electrochemical devices capable of moving power distribution from large scale, centralized grids to more efficient and securely distributed supply systems. A fuel cell, much like a battery, can convert chemical energy directly into electrical energy thereby avoiding the need for thermal cycling or moving mechanical assemblies apart from gas handling systems. Additionally, the emission of regulated pollutants are substantially lowered compared to conventional power systems.³ Fuel cells are generally distinguished by their

electrolyte materials, type of ionic conduction, and operating temperatures. Examples of these, and their corresponding efficiencies compared to conventional power generation methods, are highlighted in Table 1.1. Low temperature fuel cells, such as the proton exchange membrane fuel cells (PEMFC) have been successfully developed for commercial applications, but PEMFCs require expensive precious metal catalysts (commonly platinum), high purity fuels, and are susceptible to poisoning by hard-to-remove fuel contaminants such as CO. These constraints render PEMFCs less suitable for applications where fuel streams may have varying compositions and where large scale deployment drives up costs.

Work presented in this dissertation examines the properties and durability of a different type of fuel cell, namely the high temperature solid oxide fuel cell (SOFC). High temperature cells are less susceptible to fuel contaminant poisoning and do not require precious metal catalysts. While solid oxide cells can be used as fuel cells, SOFCs, they can also work reversibly as solid oxide electrolysis cells (SOECs) for hydrogen or carbon monoxide production. SOECs can utilize surplus energy from intermittent renewable devices such as solar panels or wind farms and produce hydrogen to be used in the same device with an opposite bias (as a SOFC) when the intermittent renewable is no longer producing power. In principle, this scheme creates a self-contained energy conversion system with net zero emissions. As a fuel cell, SOFC fuel flexibility is a tremendous advantage given that these devices can generate electricity from a wide variety of sources, including CH₄, syngas, biogas, and higher molecular weight hydrocarbons. SOFCs therefore have the unique ability to serve as a bridging technology that can accommodate

both traditional, fossil-fuel based energy sources as well as emerging, renewably generated fuels.

Table 1.1. Operating conditions for various types of fuel cells compared to conventional technologies.³ (*CHP combined heat and power)

Device	Typical Capacity Range	Operating Efficiency (%)	Operating Temperature (°C)
<i>Conventional</i> Internal Combustion Engine Gas Powered Turbine	50 kW – 5 MW 1 MW – 100 MW	25 – 40 30 – 40	n/a n/a
<i>Fuel Cells</i> Proton Exchange Membrane Molten Carbonate (Alkaline Solid Oxide Solid Oxide *CHP	1 kW – 100 kW 5 kW – 3MW 1 kW – 100 kW 5 kW – 2 MW 5 kW – 2 MW	40-60 50 60 45 – 65 Up to 90	< 120 600 -700 < 100 500 – 1000 500 – 1000

Despite their advantages over PEMFCs, SOFCs have not seen extensive commercial development because of challenges related to their resilience and durability. High operating temperatures required for adequate cell performance (typically ≥ 700 °C) lead to material transformation and degradation that occurs much more quickly than in lower temperature electrochemical devices. Temperature induced degradation mechanisms can include mechanical and thermal stresses as well as chemical decomposition and phase transformations. This chapter introduces the operating principles of SOFCs and details strategies for overcoming several of the challenges limiting mass production and large scale implementation.

Solid Oxide Fuel Cells

SOFCs are made up of two porous, catalytic electrodes separated by an ionically conducting electrolyte. As the name suggests, the SOFC electrolyte is an oxide conducting ceramic. The electrolyte must be electronically insulating while allowing for ionic conduction through the ceramic material. Additionally, the SOFC electrolyte needs to be chemically stable under both reducing and oxidizing conditions experienced in the anode and cathode environments respectively. Due to these requirements, cubic phase zirconia (ZrO_2) stabilized with yttria (Y_2O_3) is typically used as the current state of the art (SoA) electrolyte material (YSZ). The replacement of Zr^{4+} ions with lower valence Y^{3+} ions creates the necessary oxide vacancies allowing for ionic conductivity. Maximum ionic conductivity of this material mixture is achieved with 8% yttria by mole fraction⁴ (8YSZ) giving a conductivity value of 0.1 S/cm at 1000 °C.⁵ Y_2O_3 doping of ZrO_2 ($\geq 8\text{-}9\text{ mol}\%$) stabilizes the cubic structure of zirconia, achieving chemical and mechanical stability and preventing the formation of the non-ion conducting monoclinic phase of ZrO_2 otherwise present at temperatures below 1170 °C.⁶ Because the activation energy for oxide diffusion in YSZ is ~ 100 kJ/mol, high operational temperatures, often between 500 – 1000 °C, are required in order to produce sufficient oxide flux and generated current.^{7,8} Depending on the electrolyte requirements, SOFCs can be fabricated having several different architectures including electrode (anode or cathode) supported or electrolyte supported cells as shown in Figure 1.1. Electrolyte supported cells use thicker electrolytes ($\sim 300 - 800\text{ }\mu\text{m}$) and thinner electrodes ($\sim 20\text{ }\mu\text{m}$) while electrode supported cells use thinner

electrolytes ($\sim 10\ \mu\text{m}$) and a thicker supporting electrode ($\sim 800\ \mu\text{m}$). The use of thinner electrolytes in electrode supported cells lowers ohmic losses through the cell leading to lower operating temperatures. Despite these benefits, thin electrolytes show greater susceptibility for cell fracture and cracking. Furthermore, electrode supported cells require more steps to fabricate, raising their costs and limiting their opportunity for commercial development. While electrolyte supported SOFCs are not as efficient (due to higher electrolyte impedance), they are mechanically sturdy and simpler to construct. Experiments described in this thesis use electrolyte supported cells.

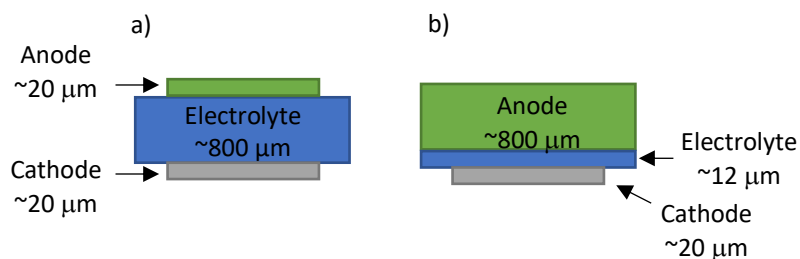


Figure 1.1. Schematic diagrams of (a) electrolyte supported and (b) electrode supported SOFC architectures.

Activation energies associated with oxygen reduction at the cathode of an SOFC also require high operating temperatures. Requirements for SOFC cathode design include high electrical conductivity, high catalytic activity for oxygen reduction, and compatibility with the electrolyte components. Oxide conducting materials, such as lanthanum manganites, are used for these purposes as base metals are often unstable in highly oxidizing environments.^{4,9} An example of SoA materials for cathode design is the $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) perovskite where replacement of La^{3+} ions with Sr^{2+} ions forms electron holes on the manganese sites, increasing conductivity to maintain charge

neutrality. In order to accommodate mechanical-thermal differences between the cathode and electrolyte, composites of LSM (or other perovskite materials) and the electrolyte material are used. These mixtures will also lower the activation energies associated with the oxygen reduction reaction and increase ionic conductivities.^{10,11}

Similar requirements with respect to conductivities and stability are required for the fuel electrode (anode) of an SOFC. Furthermore, these electrodes require high catalytic activity for fuel oxidation and high electronic conductivity for electron transport from the sites of electrochemical oxidation and the electrode current collector. Typical SOFC anodes consist of a porous cermet, combining an electrocatalytic metal with an electrolyte material.³ Most often this cermet is comprised of metallic Ni and the ion conducting YSZ, referred to as Ni-YSZ. Ni is affordable, has high electronic conductivity, stability under reducing conditions, and high catalytic activity compared to other anode cermets¹², thereby meeting the requirements of a SOFC fuel electrode. Under *operando* temperatures and reducing conditions, NiO is reduced to Ni creating the triple phase boundary (TPB) with YSZ and the gas phase fuel where electrochemical oxidation takes place. In order to provide sufficient electrical conductivity, Ni is normally present in quantities greater than 30 vol.%.¹³

When operating with hydrogen, SOFCs supply DC electricity to an external load via chemical reactions occurring on the electrodes (Figure 1.2).

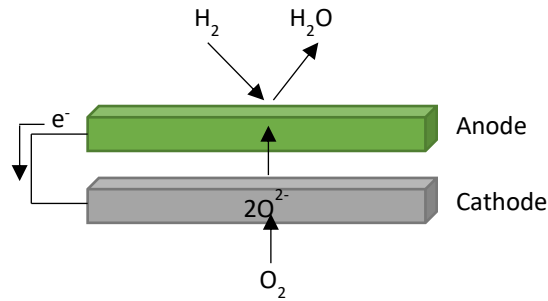
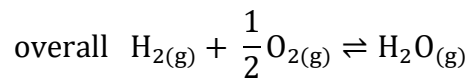
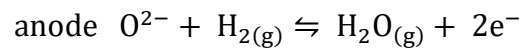
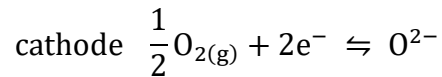


Figure 1.2. Schematic of a SOFC operating with H_2 to produce H_2O and electricity.

Molecular oxygen is electrochemically reduced at the cathode to produce oxide ions that are then transported through the electrolyte to the anode. At the anode, H_2 oxidation produces water and electrons. The electrons are transported through the external circuit back to the cathode. This process is summarized by the reactions shown below:



When the SOFC is in thermodynamic equilibrium, or when no current is flowing through the cell, the theoretical potential across the cell can be described by the Nernst equation shown below.

$$E_{\text{N}} = \frac{\Delta G^\circ}{nF} - \frac{RT}{nF} \ln \frac{P_{\text{H}_2\text{O}}}{P_{\text{O}_2} P_{\text{H}_2}}$$

In this equation, E_N describes the theoretical Nernst potential (also called the open circuit voltage or OCV) and assumes standard operation conditions with no side reactions or gas leakage. R is the ideal gas constant (8.314 J/K·mol), T is the temperature of the system, F is Faraday's constant ($\sim 96\,500$ C/mol), and n is the number of electrons. When a load is applied to the cell, the cell potential will be lowered due to polarization losses. The new cell potential can then be described by the following expression¹⁴:

$$E = E_N - \eta_{\Omega} - \eta_{conc} - \eta_{act}$$

where η_{Ω} is the ohmic loss associated with the resistance to ion conduction through the electrolyte, η_{conc} is the concentration or diffusion losses that occur when electrode reactions are hindered by mass transport effects such as slow supply of reactants or removal of products, and η_{act} is the charge transfer polarization, or overpotential, necessary to overcome the energy barrier associated with the electrochemical reactions.

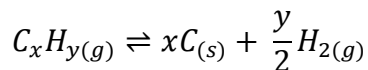
While polarization losses described above will limit cell performance, the major performance limitations of SOFCs are degradation mechanisms associated with the chemical reactions occurring on the electrodes. For Ni-YSZ anodes, these include metal particle coarsening, metal particle oxidation, electrode poisoning, and carbon deposition. Work described in this dissertation focuses on SOFC degradation caused by particle coarsening, catalyst oxidation, and carbon deposition. These studies did not consider poisoning by common gas impurities such as sulfur or chlorine.

High operating temperatures can lead to rapid, thermally driven Ni particle coarsening (or metal particle sintering). As a result of the high surface free energy intrinsic to small particles, this process can occur via particle coalescence where particles migrate

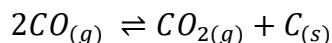
towards each other or via Ostwald ripening where atomic scale masses are transferred from smaller particles to larger particles.^{15–17} Particle coarsening will decrease the number of active triple phase boundaries as Ni particles merge and results in irreversible mechanical deterioration of the anode.

Ni-YSZ anodes may also degrade as a consequence of anode oxidation. Ni-YSZ anodes are susceptible to oxidation if the cell is starved of fuel or subjected to strong polarizations, referred to as electrochemical oxidation, or as a result of gas leakage between the anode and the cathode, referred to as environmental oxidation. Because the NiO unit cell is approximately 40% larger than Ni, repeated reduction and oxidation (redox) cycling leads to structural degradation and cell failure via fractures and/or anode delamination.^{8,18,19} Re-oxidation of Ni will also decrease catalytic activity and electronic conductivity.^{19,20} Extending the useful lifetime of SOFCs, therefore, requires minimizing the amount of redox cycling experienced by the anodes.

Carbon formation on the anode surface is another challenge related to Ni-YSZ anodes. Ni's high efficiency for C-H bond activation render Ni-YSZ anodes particularly susceptible to carbon accumulation. Carbon accumulation on SOFC anodes during operation with hydrocarbon fuels can cause cell degradation and failure via several mechanisms. These can include blockage of catalytic sites, hindering mass transport, and irreversible metal dusting of the Ni.^{21–23} Carbon formation on SOFC cell anodes is controlled by both temperature and fuel composition.²⁴ At temperatures above 700 °C, carbon is deposited mainly through hydrocarbon cracking when using hydrocarbon fuels such as methane, as described by the reaction²⁵:



or by Boudouard chemistry in the case of CO fuel compositions such as syngas:²⁶



Preventing degradation from the processes described above has proven difficult due to the uncertainties associated with validated mechanistic descriptions describing material evolution in functioning SOFCs. Multiple strategies have been developed to enhance the SOFC performance and durability. One advance has been the development of Ni-free anodes, requiring complete replacement of the Ni with alternative materials such as copper, ceria, or perovskites. While removing the Ni will avert problems associated with Ni itself, this approach is associated with increasing costs and questions about material compatibility. Additionally, performance characteristics of these alternatives anodes are often poor in comparison to Ni-containing anodes due to decreased catalytic capability and co-sintering.^{13,27–29} An alternative to replacing Ni is to physically protect Ni from conditions that drive coarsening and redox stress. Endowing Ni-based anodes with improved resilience can be accomplished through co-addition of a more tolerant catalyst or diffusion barrier on the external surface of the electrode. Both approaches have proved helpful in increasing carbon tolerance as well as tolerance toward coarsening and redox stresses.^{30,31} The properties of Ni itself can also be modified by smaller, more subtle materials changes such as leveraging metal alloy stability or infiltration strategies. Bulk alloys such as Ni-Cu and surface alloys of Ni-Sn have both shown promising carbon tolerance.^{32,33} Infiltration of the Ni-YSZ microstructure with secondary (2^o) materials such

as metals or metal oxides have also been reported to solve multiple problems associated with a pure Ni catalyst.^{16,34–37} As an example, ceria nanoparticles have been found to help with sulfur tolerance, carbon tolerance, and increased ionic conductivity.³⁸

Chapters 2-4 in this thesis explore the beneficial effects of infiltrating Ni-YSZ anodes with small amounts of aluminum titanate (Al_2TiO_5 or ALT) prepared from a mixture of aluminum oxide and titanium oxide. This infiltrate has previously been shown to decrease Ni particle coarsening, increase mechanical strength, and enhance long term performance.^{16,34,39} Specifically, Chapters 2-4 investigate the mechanisms responsible for observed redox resilience (both electrochemical and environmental) and carbon tolerance. One last method to optimize SOFC performance involves decoupling the current conducting path from the electrocatalytic path. Chapters 5-6 explore the effects of infiltrating catalytic transition metals into an electronically conducting $\text{Sr}_{0.94}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_3$ (STN) backbone on SOFC electrochemical performance and carbon tolerance. Taken together, all chapters address mechanisms responsible for enhancing SOFC anode performance and provide guidance for creating high temperature, functional electrodes with improved durability and stability to endow SOFCs the longevity and efficiency necessary for commercial development and distribution.

Experimental Methods

Due to high temperatures and strong oxidizing and reducing environments, SOFCs are difficult to study using materials specific *operando* techniques having relevant spatial and temporal resolution. Therefore, most SOFCs experiments are performed using

electrochemical methods alone, or comparing ex-situ data from cells prior to and post-operation. While these methods provide useful information on performance and final state of the fuel cell, they cannot provide the direct understanding of materials behavior and mechanisms that occur *operando* on a molecular specific level. Arguably the only way to obtain this type of information is by the use of optical spectroscopy techniques. Because of the blackbody radiation prominent at typical SOFC operating temperatures, most spectroscopy techniques are incapable of providing sufficiently strong signal on top of a large background. Vibrational Raman spectroscopy, however, can be performed with shorter wavelength light so that signals are less likely to be overwhelmed by blackbody interference. Carefully comparing material changes observed using real-time Raman spectroscopy with changes in SOFC performance, monitored by electrochemical methods, provides direct correlation between SOFC anode composition and electrochemical activity.

Raman Spectroscopy

Raman spectroscopy is a form of vibrational spectroscopy used to characterize and identify molecules through the process of inelastic scattering. Oscillating electromagnetic radiation induces a polarization in molecules and materials that result in photon scattering.^{40,41} Raman spectroscopy is usually referred to as a two-photon process since the incident photon results in the creation of a second photon of a different energy. The incident and scattered photons can be characterized by their frequencies ν_i and ν_s respectively. The energy difference between the incident and scattered photons corresponds to a vibrational mode within the scattering medium or material. Experiments are typically performed by

irradiating a sample with laser light in the visible, ultraviolet, or near infrared region of the electromagnetic spectrum. Scattering can occur in one of three processes illustrated in Figure 1.3, below.

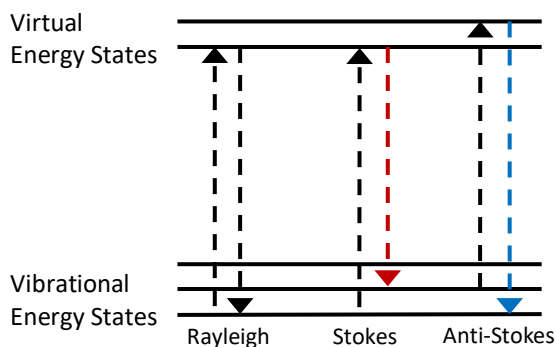


Figure 1.3 Schematic representation of Rayleigh, Stokes, and Anti-Stokes Scattering for Raman Spectroscopy.

The majority of photons undergo elastic or Rayleigh scattering where the energy of the photon is preserved, while it is estimated that only 1 in 10^{10} incident photons undergo successful Raman scattering.⁴⁰ Stokes Raman scattering refers to the process when $\nu_s < \nu_i$ and some quantum of energy is transferred from the incident photon to the material resulting in an increased vibrational state. Anti-Stokes Raman scattering occurs when the molecule is initially in an excited vibrational state and $\nu_s > \nu_i$. Here, energy is transferred from the material to the scattered photon resulting in vibrational relaxation. Because the intensity of anti-Stokes scattering is low compared to that of Stokes scattering⁴⁰ due to the temperature dependent Boltzmann distribution, Raman spectroscopy normally records frequency changes caused by Stokes scattering. In crystals, most observed vibrations are known as lattice phonons. Frequency shifts between Raman scattered light and incident

light, known as Raman shifts, are plotted on an intensity spectrum where vibrational modes are shown as peaks. The x-axis is conventionally expressed in wavenumbers, while the y-axis is expressed as intensity as seen in Figure 1.4 below. Figure 1.4 shows spectra of an oxidized Ni-YSZ anode at room temperature and SOFC operational temperature. The red shift in band frequency observed between the two spectra occurs as a consequence of lattice expansion upon heat-up. The room temperature spectrum shows a strong low-frequency vibration band at 610 cm^{-1} corresponding to 8YSZ and a band at 1098 cm^{-1} corresponding to the 2 phonon mode of NiO.^{42,43} As the sample is heated to operating temperatures these features shift $\sim 25\text{ cm}^{-1}$ and 35 cm^{-1} respectively. The intensity of a Raman mode will depend on the molecules Raman cross section (dependent on the polarizability of the mode) and the properties of the incident light. Intensity can be described by the proportionality shown below:⁴⁴

$$I \propto P_i \alpha^2 \nu_i^4$$

where P_i represents the power of the incident laser light, α is the polarizability, and ν_i is the incident frequency.

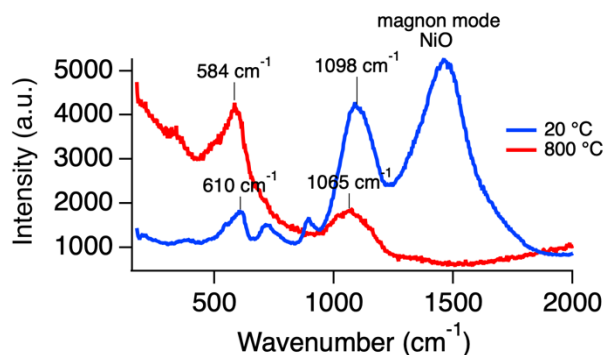


Figure 1.4. Raman spectra showing shifts in NiO and YSZ vibrational modes at room temperature and 800 °C. The magnon mode of NiO at 1490 cm^{-1} is only visible at temperatures below NiO's Néel temperature, 525 K.

Since every material has a distinct phonon structure, Raman spectroscopy can be used to provide a fingerprint region in which molecules can be recognized and identified. Changes in temperature, pressure, and atmospheric environments can all lead to distinct Raman spectra, useful for characterizing the SOFC materials. In this thesis, Raman spectroscopy is used to observe secondary phase formation and quantify compositional changes in SOFC anodes associated with changes in temperature, atmosphere and electrochemical performance.

Electrochemical Measurements

Cell condition and performance can be monitored *in operando* by the use of electrochemical measurements. Data acquired from voltammetry and impedance measurements can be used to determine and predict the mechanisms responsible for enhanced or diminished performance in a system as well as to identify individual contributions to performance from processes associated with the electrolyte, the anode, or

the cathode. In combination with Raman spectroscopy which directly monitors surface species, this provides a broad overview of the particular processes occurring in the cell.

Linear Sweep Voltammetry. Linear Sweep Voltammetry (LSV) is used to monitor how cell performance evolves over time with changes in operating conditions and provides a direct measurement of the cell's electrocatalytic activity.⁴⁵ LSV measures the forward current (I) produced by the cell as a function of linearly varying potential (V). Plots of voltage versus current as well as power versus current (calculated from $P = I \cdot V$) are shown in Figure 1.5 below. The slope of the current versus voltage plot corresponds to the total resistance of the cell and is inversely related to the maximum power that the cell can produce. LSV measurements performed in this work start at open circuit voltage where no current passes through the potentiostat, and the voltage reading reflects the potential difference of the half cells relative to an external reference in the potentiostat. Experiments end at either short circuit voltage (0 V), corresponding to the maximum cell current, or at 80% of maximum cell current to avoid damaging the samples by drawing excessive current loads. Scan rates were always fixed at 0.1 V/s leading to full LSV collection in the timeframe of seconds.

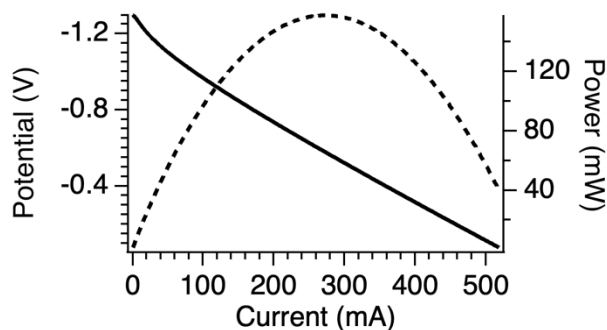


Figure 1.5. LSV plot of a SOFC operating with H_2 , acquired at 800 °C showing the V - I line (solid) and P - I curve (dashed).

Electrochemical Impedance Spectroscopy. Kinetic and mechanistic information about a cell can be inferred from electrochemical impedance spectroscopy (EIS).⁴⁶ In an EIS experiment an alternating potential is applied to the cathode, and the resulting AC current is measured out of the anode over a wide frequency range, typically 100 kHz to 0.10 Hz. Acquiring measurements over a frequency range allows the probing of different electrochemical processes and to separate various contributions from the total response. The current measured out of the cell will be phase shifted due to a capacitive response and be measured as an imaginary impedance (Z_{imag}). This quantity is typically assigned to reactions at the electrode-electrolyte interface. The amplitude change measured out of the cell is an ohmic response related to the real resistance (Z_{real}) and attributed to ohmic resistances of both the electrolyte and the electrodes. The information attained from an EIS experiment can be plotted in a Nyquist plot where equivalent circuits may be used to model the data (Figure 1.6) in order to evaluate the overall condition of the cell. SOFCs are often modelled using RC circuits where the resistors account for the solution resistance

and bulk or charge transfer resistance found in the cell, and the capacitors (sometimes replaced by constant phase elements) account for the electrochemical double layers.^{47,48} Figure 1.6 shows a sample SOFC EIS spectrum where each data point is collected at a specified frequency. The bulk resistance (R_B) is the resistance related to the diffusion of oxides through the electrolyte. The polarization resistance (R_P) shown can further be divided into processes including anodic and cathodic charge transfer and fuel activation processes at higher and mid frequencies, and mass transport processes at lower frequencies. EIS modeling in this work was performed using ZSimpWin software or a Python based software RAVDAV developed by C. Graves at the Danish Technical University⁴⁹.

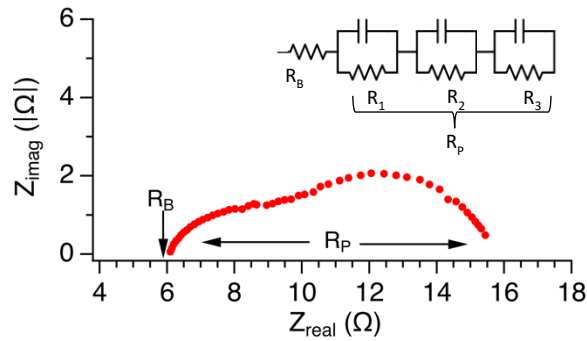


Figure 1.6. EIS spectrum of SOFC and 800 °C operating with H_2 at OCV. Figure shows the resistance values of R_B and R_P as well as an example equivalent circuit for modeling.

Field Emission Scanning Electron Microscopy

Information regarding the microstructure and topography of cells can be acquired using Field Emission Scanning Electron Microscopy (FE-SEM). Images are formed from a focused electron beam that scans over the surface area of a sample with a large depth of field resulting in images with three dimensional appearance.⁵⁰ FE-SEM measurements

were particularly useful for *ex-situ* analysis in the following work in order to compare the microstructure of cells post degradation to that of pristine samples. These measurements compliment Raman and electrochemical data to provide additional, visual information to elucidate mechanisms responsible for cell degradation.

X-ray Photoelectron Spectroscopy

Elemental surface composition of a material can be measured using X-ray photoelectron spectroscopy (XPS). When X-ray photons are absorbed by an atom, electrons are ejected from the atom's core orbitals. A hemispherical electrostatic focusing assembly analyzes the ejected electrons based on their kinetic energies. These electrons carry with them information about both the chemical and oxidation state of the element. A typical XPS spectrum shows a plot of ejected electron intensity versus binding energy. The electron's binding energy is simply the difference in energies between the energy of the incident X-ray photon and the kinetic energy of the ejected electron. Electrons coming from different core orbitals will have binding energy differences on the order of hundreds of eV, whereas electrons coming from the same core orbital but from an element having different oxidation states will have binding energies that typically differ by tens of eV. More subtle shifts in binding energy result from elements bound to different neighbors.⁵⁰ In this dissertation, XPS measurements were used to evaluate the chemical composition of Ytria-doped Barium Zirconate (BZY) in different fuel environments (Chapter 7).

Experimental Assembly

Experiments performed in this work couple Raman spectroscopy and electrochemical measurements using the experimental assembly shown in Figure 1.7. The assembly, colloquially referred to as “Rocket”, allows SOFC experiments to be run under *operando* conditions where temperature (≤ 900 °C), gas compositions, and polarization can be controlled. A detailed description of the workings of the assembly can be found in published work by Pomfret *et al.*⁵¹ In short, current collectors with gold wire are attached to the electrodes of an SOFC. The cell is then secured to an alumina tube of equal diameter using alumina paste to create a hermetic seal. Smaller diameter alumina tubes are attached to the outside as the fuel inlet and outlet. The complete assembly is then positioned inside of a quartz tube in order to allow optical access to the top surface of the cell. The bottom of the quartz tube is sealed with a silicone stopper with holes for electrical and fuel connections. The assembly is then positioned inside of an insulated tube furnace and brought to operating temperature.

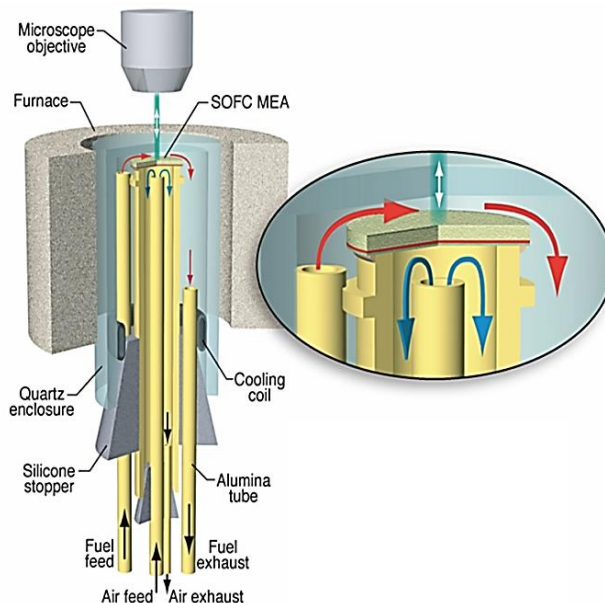


Figure 1.7. Schematic of high temperature assembly used for operando studies of SOFC materials and assemblies.

Electrochemical measurements are collected using a Princeton Applied Research VersaStat MC potentiostat. Raman measurements are collected using a Renishaw inVia Raman microscopy system coupled with a 488 nm laser excitation source (Lexel 85-SHG Ar-ion Laser). A long pass edge filter with a 150 cm^{-1} cutoff and a Pelletier cooled CCD detector is used to collect the Stokes scattered light. The system has a temporal resolution of ≥ 2 seconds and spatial resolution of $\sim 2\text{ }\mu\text{m}$ for a long working distance 10x microscope objective (as determined by $1.22\lambda/\text{NA}$, where λ is the laser wavelength, and NA is the numerical aperture of the microscope objective). Depth resolution is determined by $\lambda/4\pi nk$, where k is the materials refractive index and n is the extinction coefficient. Using values for NiO-YSZ materials, the estimated penetration depth of the Raman excitation source is $\sim 6\text{-}8\text{ }\mu\text{m}$. The specified resolutions allow for kinetic tracking

of material change that accompany changes in SOFC polarization, fuel identity, and temperature. Typical Raman measurements were acquired using 10-30 second exposure times in the range of 150 – 3200 cm^{-1} . Kinetic measurements were typically collected using static scans with a shorter frequency range of 200 to 1800 cm^{-1} and repeating 10-30 second exposure times. Adequate Raman signal levels for a 10 second exposure of an *in-house* made NiO based anode are typically thousands of counts at room temperature. Exact intensity will depend on sintering temperature and the NiO material used. At operating temperatures of 800 °C Raman signal of the characteristic NiO 2P mode at $\sim 1100 \text{ cm}^{-1}$ is normally reduced to about 1/3 of the room temperature intensity (Figure 1.4). Signal intensity above ≥ 500 counts for the NiO 2P band is normally considered adequate at operating temperatures.

Synopsis and Scope of Thesis

Work presented in this dissertation uses *operando* Raman spectroscopy coupled with electrochemical and *ex-situ* techniques to investigate the reaction mechanisms and behavior of SOFC anodes doped with secondary phases or infiltrated with a combination of metal electrocatalysts. Using the experimental set-up described above, the combination of optical and electrochemical techniques can directly identify how compositional changes in SOFC anode materials affect cell performance and durability as fuel composition, temperature and polarization are varied. This work has demonstrated the benefits of strategically altering materials common to existing SOFC technologies in order to mitigate degradation mechanisms and fabricate more durable and efficient SOFC electrodes.

Fundamental information acquired from this work does not only benefit SOFC development but also high temperature catalysis and energy systems in general.

Chapters 2-3 of this dissertation describe experiments exploring the benefits of ALT addition to Ni-YSZ anodes for improving resilience to environmental and electrochemical redox cycling. Chapter 4 demonstrates how this same dopant can suppress carbon formation on the anode compared to anode samples without ALT when operating with CH₄ fuel. An investigation into the mechanisms responsible for the observed carbon suppression are also investigated. Chapters 5-6 investigate the effects of separating the electronic and catalytic phases of the SOFC anode. Work described in Chapters 5 and 6 was carried out in collaboration with colleagues from the Danish Technical University using novel infiltrated anodes. Cell anodes were fabricated using an electronically conducting STN backbone infiltrated with Gd_{0.20}Ce_{0.80}O_{1.95} (CGO) for ionic conductivity and Ni or Co for electrocatalytic activity. Similar to results of ALT-doped anodes, these material combinations demonstrate promise with regards to decreasing carbon formation on the cell anodes under both CH₄ and syngas conditions. Finally, Chapter 7 explores future directions in SOFC related research and showcases preliminary studies on high temperature proton conducting materials for the use in high temperature proton conducting fuel cells (PCFCs). Chapters 2-5 have already been submitted for publication or have already appeared in press, therefore some redundancy is present, especially in the introduction and experimental sections of these chapters. Chapter 6 has been prepared for submission to a relevant journal.

CHAPTER TWO

OPERANDO STUDIES OF REDOX RESILIENCE IN ALT ENHANCED NIO-YSZ SOFC ANODES

Contribution of Authors and Co-Authors

Manuscript in Chapter 2

Author: Märtha M. Welander

Contributions: Collected and analyzed all data, generated figures and wrote manuscript in preparation for publication.

Co-Author: Marley S. Zachariasen

Contributions: Prepared samples for high temperature studies. Edited and commented on manuscript.

Co-Author: Clay D. Hunt

Contributions: Aided in preparation of samples for high temperature studies. Wrote MATLAB algorithm for voltage data fits.

Co-Author: Stephen W. Sofie

Contributions: Contributed important insight into performing experiments and interpreting results. Edited and assisted in the preparation of the manuscript.

Co-Author: Robert A. Walker

Contributions: Contributed important insight into performing experiments and interpreting results. Edited and assisted in the preparation of the manuscript.

Manuscript Information

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Walker

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OPERANDO STUDIES OF REDOX RESILIENCE IN ALT ENHANCED NIO-YSZ
SOFC ANODES

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Abstract

This work explores the effects of aluminum titanate (ALT) as a dopant in standard NiO-YSZ SOFC anodes on cell resilience under reduction and oxidation (redox) cycling. Cells operated galvanostatically (50 % $I_{\max}$) at 800 °C for the duration of a single redox cycle with hydrogen exposure lasting for 20 minutes prior to electrochemical oxidation. Observable reduction and oxidation of the Ni anode was monitored using *operando* vibrational Raman spectroscopy and electrochemical potential measurements, while electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV) measurements were performed to determine cell condition and performance following each redox cycle. Repeated electrochemical redox cycling led to irreversible cell degradation for both ALT doped and standard anodes, but ALT conferred significantly more resilience to the doped anodes. Increased stability of Ni catalyst microstructure resulting from ALT addition was shown to slow degradation rates and increase average cell tolerance to redox cycles by a factor of two.

Introduction

Solid oxide fuel cells (SOFCs) provide attractive energy solutions by creating electricity electrochemically from a wide variety of fuel sources. Unlike conventional gas and coal fired power plants that operate with ~30% efficiency, SOFCs can function with efficiencies approaching 90% in combined heating and power applications.^{8,52–55} Furthermore, because SOFCs produce power electrochemically rather than through combustion, they are not a source of NO_x, SO_x, or other regulated pollutants.^{7,56} Despite their many benefits, however, the high operating temperatures and electrochemical polarization required for SOFC performance can lead to irreversible material degradation that limits the development and integration of these devices into large scale power production strategies. One significant limitation to SOFC operation is the sensitivity of nickel yttria stabilized zirconia (Ni-YSZ) cermet anodes to re-oxidation under both typical and adverse operating conditions. Reduction and oxidation (redox) cycling in SOFCs can result from gas phase leakage between the cathode and anode or from the presence of an oxidizing agent in the incident fuel. This type of anode oxidation is referred to as environmental oxidation. Alternatively, oxidation of the anode can be electrochemical as a result of concentration polarization or high fuel utilization.

Repetitive redox cycling is detrimental to cell durability as nickel oxidation leads to a ~40% volume increase relative to elemental Ni, and redox cycling is associated with redistribution of the nickel metal phase.^{8,18,57–62} Solutions proposed for improving stability to redox cycling include replacing the Ni-YSZ cermet altogether by the use of other

materials such as noble metals, carbides, or conductive oxides.^{27,63–68} However, these materials typically cannot match Ni's electrocatalytic activity.^{27,69} A second promising approach involves adding small amounts of oxide dopants that suppress anode oxidation kinetics and enhance Ni catalytic activity compared to standard un-doped Ni-YSZ anodes.^{70–73}

Recent reports have shown that small amounts of different metal oxide dopants that include aluminum and titanium reduces Ni coarsening and improves mechanical strength in Ni-YSZ cermets.^{71,74–79} Specifically, aluminum titanium oxide (Al_2TiO_5 or ALT) added to Ni-YSZ cermet electrodes has been shown to improve SOFC performance, longevity, and strength.^{16,34,39} Fabricating anodes from ALT enhanced Ni-YSZ cermets creates secondary phases including a nickel aluminate spinel (NiAl_2O_4) and a zirconium titanate ($\text{Zr}_5\text{Ti}_7\text{O}_{24}$). Following anode reduction (to generate electrocatalytic Ni), the NiAl_2O_4 reduces to form elemental Ni and Al_2O_3 . The $\text{Zr}_5\text{Ti}_7\text{O}_{24}$ remains stable at SOFC operational temperatures (700-800°C) under reducing conditions.^{16,34,39} Of the secondary phases that form, NiAl_2O_4 is believed to suppress Ni coarsening, while the $\text{Zr}_5\text{Ti}_7\text{O}_{24}$ may have mixed ion electron conducting properties. While both effects – preserving a percolated Ni network and expanding an electrode's three phase boundaries –enhance SOFC performance³⁴, their effects on electrode resilience to electrochemical redox cycling is unknown.

The studies described below use electrochemical methods and *operando* Raman spectroscopy to quantify and compare the effects of repeated electrochemical redox cycling on ALT-enhanced and ALT-free Ni-YSZ anodes. Benchmark voltammetry and EIS

measurements are used to evaluate the resilience of ALT enhanced cells relative to those cells operating without ALT. In this context resilience is defined as the capacity of each system to experience oxidative stress and then recover its original function and structure. Results show that ALT improves SOFC resilience by approximately a factor of two.

Experimental

Electrolyte supported cells were made using commercially available 8YSZ electrolytes with 0.35 – 0.3 mm thickness from Fuel Cell Materials. Anodes of 50 μm were applied through aerosol spraying of an aqueous mixture of 8YSZ (34 wt. % ; Tosh Corp. TZ-8YS), NiO (66 wt. % ; JT Baker), and cornstarch used as a pore forming agent. The anode-electrolyte bi-layers were allowed to dry overnight before being sintered at 1250 $^{\circ}\text{C}$ for two hours with a heating and cooling rate of 10 $^{\circ}\text{C}$ per minute. ALT was added to doped anodes by infiltration with a solution of aluminum nitrate and titanium lactate dissolved in de-ionized water to produce Al_2TiO_5 . After pipetting the solution onto the anode, organics were removed by heating the infiltrated cell at 400 $^{\circ}\text{C}$ for two minutes. Enough ALT was added to have 4 wt. % of dopant (relative to the total anode mass). Doped and undoped cells, were then sintered to 1400 $^{\circ}\text{C}$ with heating and cooling rates of 5 $^{\circ}\text{C}$ per minute to enable accurate comparisons between the two electrode types. Previous reports have shown that this processing leads to the formation of NiAl_2O_4 and $\text{Zr}_5\text{Ti}_7\text{O}_{24}$.³⁴ After anode processing porous LSM-YSZ (LSM - FuelCellMaterials) cathodes were tape cast on the center of the electrolyte in a 12.5 mm diameter opposite the anode using Kapton-tape to create electrodes having a thickness of ~ 0.6 mm. The cathodes were sintered at 1150 $^{\circ}\text{C}$

for 1 hour with a heating and cooling rate of 1 °C per minute. Gold current collecting wire (Alfa Aesar) was attached to the anode using silver mesh (Alfa Aesar) and gold paste (Heraeus) and to the cathodes using platinum mesh (Alfa Aesar) and platinum paste (Heraeus). The cathode side of the cell was then attached to an alumina tube (Sentro Tech) of 25 mm diameter using ceramic paste and placed inside a quartz tube. The quartz tube was sealed at the bottom with a rubber stopper and placed inside a tube furnace. Raman spectra were acquired with a Renishaw InVia spectrometer using output from a 30mW, 488 nm Ar-ion laser and integrating spectra with 10 second exposures. The backscattered light was directed through an edge filter with 150 cm⁻¹ cutoff to allow Stokes scattered radiation to be measured by the charge coupled device detector (CCD). Further details about the experimental assembly can be found in previous publications.^{43,51,80,81}

A Princeton Applied Research VersaStat MC was used to collect Linear Sweep Voltammetry (LSV) and Electrochemical Impedance Spectroscopy (EIS) to determine cell performance and the condition of different components, respectively. LSV measurements were collected using a sweep rate of 0.1 V per second. LSV was not carried out to the maximum current in order to avoid damaging the cells. EIS data was measured at OCV over a frequency range of 100 000 Hz to 0.10 Hz with an AC voltage amplitude of 0.01 V. Cell potentials were measured in reference to the reduction of O₂ on the cathode resulting in OCV with negative values.

Cells were heated to 800 ± 5 °C at a ramp rate of 1 °C per minute under argon on the anode and air on the cathode. Once at stable temperature, gas flows were increased to 100 sccm argon and 85 sccm air over the anode and cathode, respectively. The anode was

reduced using 20 sccm of H_2 for one hour prior to performing benchmark electrochemical measurements. Once cell performance was established, cells underwent repeated redox cycling to determine cell resilience to electrochemically-induced oxidative stress. Each cycle consisted of a cell being polarized at 50% I_{max} for 20 minutes under 20 sccm H_2 . During this period, cell performance was evaluated by monitoring the operating potential. After this period, H_2 was turned off but the cell remained polarized. In the absence of fuel, the cell potential rose steeply before reaching a plateau around 0.6 V. As the potential began to plateau, *operando* Raman spectra showed evidence of NiO formation, suggesting that the cell was cannibalizing its anode in order to maintain the required current. Following two kinetic scans showing NiO, the cell was re-reduced and benchmark LSV and EIS were collected. A schematic diagram illustrating this sequence is shown in Figure 2.1. Cycling was continued until the cell could no longer produce 50% of its original maximum current. In cases where cells survived more than 20 redox cycles under polarization of 50% I_{max} , subsequent cycles were performed at 65% I_{max} .

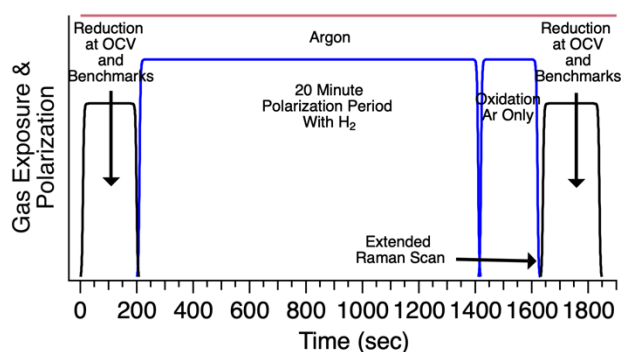


Figure 2.1. Schematic diagram showing the sequence of gas exposure for a single redox cycle. H_2 was present in an Ar carrier gas.

Results and Discussion

Experiments described in this work sought to determine how secondary phases modify cell behavior and resilience to electrochemically induced oxidative stress. Specifically, these studies examined the consequences of adding small amounts of ALT to functional SOFC Ni YSZ cermet anodes. Previous reports had shown that ALT improved the durability of model cermet anodes, but in those original studies, Ni loadings were kept intentionally low (20% by mass) meaning that small changes in microstructure induced by particle coarsening had a disproportionately large effect on performance.³⁴ Additional studies of Ni YSZ cermets reported that adding small amounts of ALT (~1-10% by mass) to Ni-YSZ cermets strengthened these anode materials by up to 30% as evidenced by modulus of rupture measurements.³⁹ These findings, however, did not address the effects of ALT and resulting secondary phases on functional Ni YSZ anodes having fully percolated Ni and YSZ networks. Data presented below show that ALT-doped Ni-YSZ cermet anodes are approximately twice as resilient to electrochemically-induced oxidative stress relative to undoped Ni-YSZ anodes.

Figure 2.2 shows representative cross sectional FEM images of undoped (2.2a) and doped (2.2b) anodes following redox cycles with indicated microstructural features present throughout the anodes. Several observations stand out. First, doped cells show a superior continuity between the anode and the electrolyte whereas significant gaps are present at the boundary between the anode and electrolyte of the pure cells. These images corroborate a growth in bulk resistance EIS data observed in pure anodes as discussed below.

Additionally, enhanced sintering is more apparent in doped cells where a more uniform thickness is seen throughout the length of the cross section. These results are consistent with previous findings that reported significant redistribution of Ni away from the electrolyte-anode interface under extreme polarization conditions.^{82,83} From the FEM images, we infer that ALT suppresses Ni migration/redistribution similar to findings reported recently by Driscoll and coworkers.³⁴

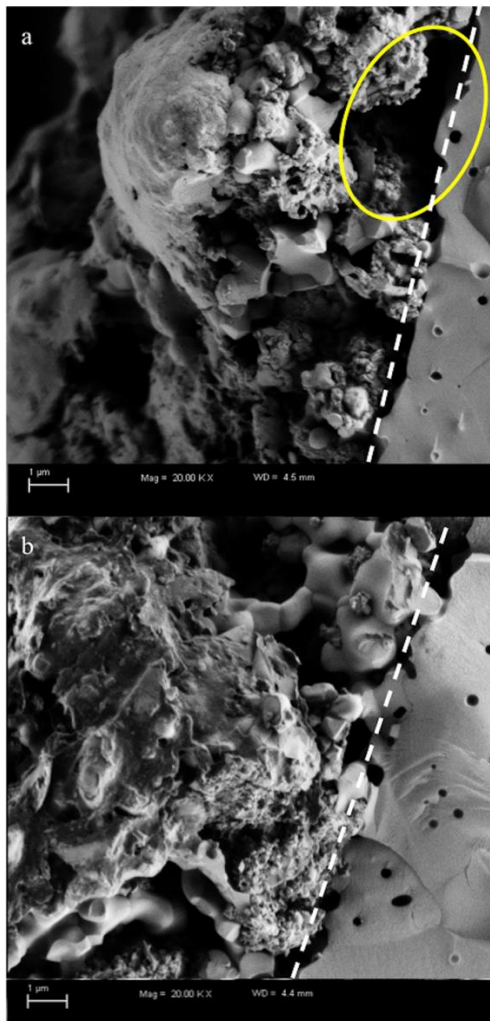


Figure 2.2. Cross sectional FEM images of undoped (a) and doped (b) anodes with electrolytes on the right hand side and Ni-YSZ anodes on the left taken at 20kx magnification with a working distance of ~ 4.5 mm and scale bars of $1\ \mu\text{m}$. Yellow circle highlights the loss of connectivity between the electrolyte and the electrode in undoped samples.

Identifying materials in the doped and undoped anodes was accomplished using vibrational Raman spectroscopy. Figure 2.3 shows representative Raman spectra acquired at room temperature prior to a redox cycling experiment. Each spectrum represents a 10 second acquisition and shows strong low frequency vibrational bands at $615\ \text{cm}^{-1}$

associated with cubic YSZ and bands at 1090 cm^{-1} and 1450 cm^{-1} corresponding to NiO.^{42,81,84} The spectrum from the doped anode shows an additional sharp feature at 766 cm^{-1} that is assigned to NiAl_2O_4 , the secondary phase that is thought to drive Ni particle anchoring.³³

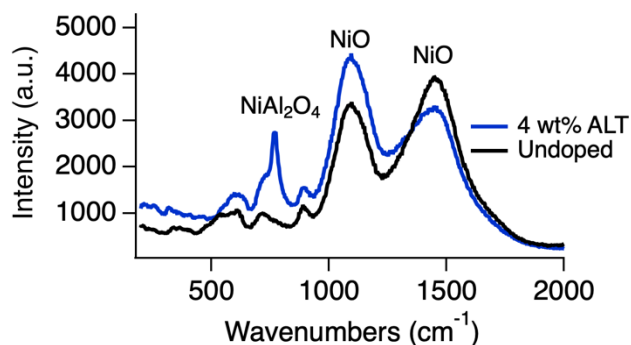


Figure 2.3. Representative Raman spectra of NiO-YSZ anodes with and without ALT enhancement. The vibrational band at 766 cm^{-1} corresponds to the formation of NiAl_2O_4 in doped anodes.

At operational temperatures following anode activation, benchmark LSV and EIS data show clear differences in performance between the doped and undoped anodes. Representative data prior to redox cycling are shown in Figure 2.4. ALT doped cells consistently outperform pure cells with maximum currents of ~ 120 mA compared to ~ 80 mA for pure cells (Figure 2.4a), an important outcome that is complementary to prior studies, but emphasizes the enhancement provided by ALT in considering the anodes have an equal volume of electro-catalytic nickel. Impedance spectra under OCV conditions show an initial average bulk resistance (R_b) of $\sim 5 \Omega$ for doped cells and $\sim 6.5 \Omega$ for pure cells (Figure 2.4b). This result is consistent with expectations given the thickness of the cathodes and values recorded in previous publications of similarly prepared electrodes.^{59,85}

Similar to Rb, polarization resistances (R_p) for doped cells were also consistently lower than those of pure cells with average values around $14\ \Omega$ (doped) compared to $20\ \Omega$ (undoped), suggesting increased catalytic activity at the triple phase boundaries.⁸⁰

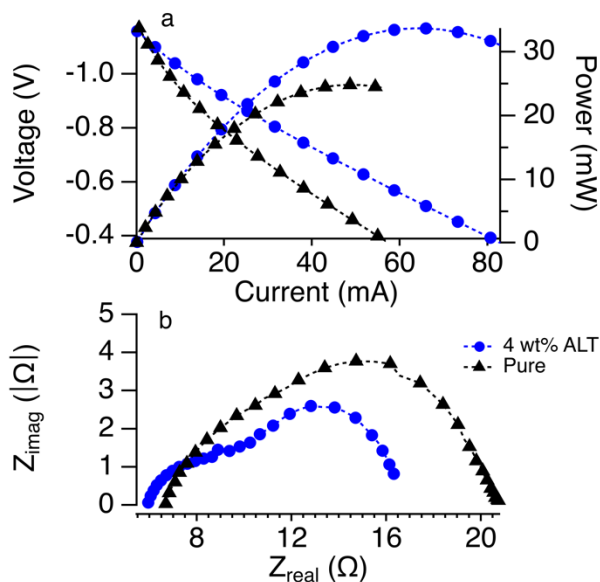


Figure 2.4. Benchmark LSV (a) and EIS (b) traces of doped and undoped anodes taken after reduction for 1 hour at $800\ ^\circ\text{C}$ under OCV conditions. Lines in LSV show the voltage (V) as a function of current (mA) and curves correspond to power.

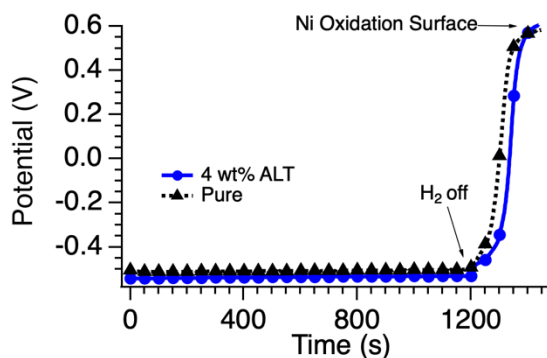


Figure 2.5. Potential measurements of doped and undoped cells during a full redox cycle. Cells are polarized at $50\% I_{max}$ with hydrogen exposure terminating after 20 minutes leading to anode oxidation and increased voltage measurements.

The potential change during a full redox cycle is seen in Figure 2.5. Hydrogen was turned off after 20 minutes of stable operation (at 50% I_{max}) while the cell remained polarized. This condition led to a rapid rise in cell potential as the Ni itself was oxidized in order for the cell to continue providing current. Shortly after the rise in cell potential, Ni oxidation was observed directly on the surface as evidenced by the vibrational NiO feature at $\sim 1050 \text{ cm}^{-1}$ and a corresponding plateau in the cell potential as seen in Figure 2.6. Cell potential decreased in magnitude with each subsequent cycle for both types of cells, but the change was much more pronounced for undoped anodes. Figure 2.7 shows the potential versus time trace of cells during the 1st and 14th redox cycle under galvanostatic conditions. A difference in potential of 0.18 V between the 1st and 14th cycles was seen for doped cells while a difference in 0.35 V was seen for pure cells after the same number of cycles.

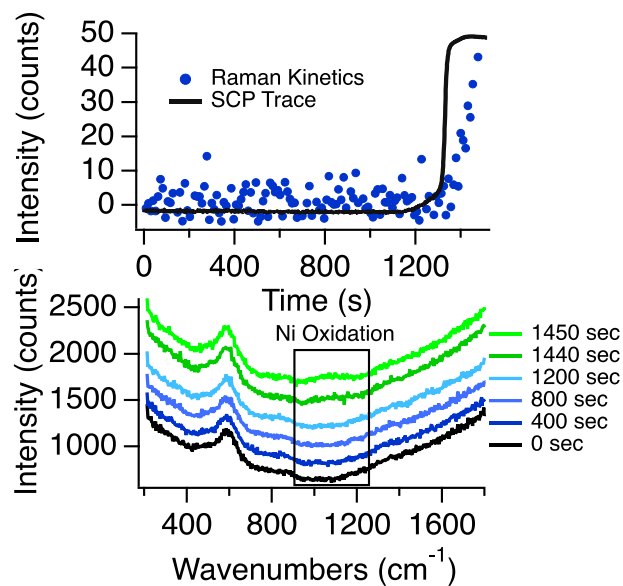


Figure 2.6. Bottom: Sequential Raman kinetic spectra using 10 second exposures showing the oxidation of Ni on the anode surface. Top: Raman kinetics of NiO growth (blue dots) taken every 10 seconds overlaid with a voltage curve showing a plateau in potential corresponding to the appearance of NiO in the Raman data.

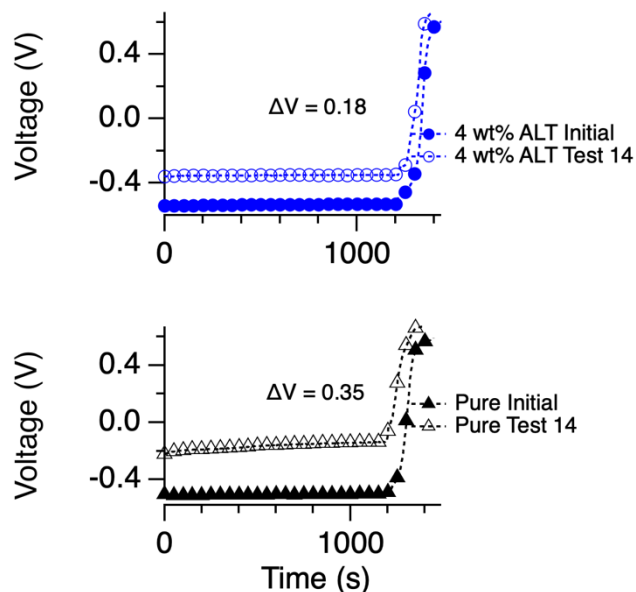


Figure 2.7. Representative voltage traces of doped and undoped cells during the initial and 14th redox cycle. The difference in potential is much more pronounced for undoped cells indicating quicker cell failure and lower resilience to redox cycling.

Following repeated redox cycling, irreversible cell degradation was observed for both types of cells, although the degradation rates and resilience of the cells differed substantially. Degradation was evident in both LSV and EIS measurements. Figure 2.8 shows LSV traces for doped and undoped cells at the start of an experiment and after repeated redox cycling when $I_{\max}$ has dropped to 50% of its original value. Figure 2.9 summarizes the redox results observed for both type of cells as a function of trial number. Benchmark LSV and EIS measurements were taken following each subsequent redox cycle to determine the change in cell performance over time. Undoped cells typically failed after ~ 15 cycles as evidenced in a gradual rise in the bulk resistance (R_b , Figure 2.9a) and a steep drop in $I_{\max}$ (Figure 2.9c). Interestingly, the polarization resistance (R_p , Figure 2.9b) stayed

relatively constant after rising slightly for the first 6 trials. Cells with ALT doped anodes lasted on average about twice as long as cells with un-doped anodes indicating strong stabilizing effects of the secondary phases formed by reactions of ALT with Ni and YSZ. Furthermore, failure in cells containing ALT doped anodes followed more monotonic degradation rather than the precipitous loss of performance observed in cells having pure anodes. Given the material changes that occur within the NiO-YSZ cermet as a result of redox cycling, we propose that ALT addition creates a more stable and supportive catalyst network that limits structural stresses induced in the electrolyte due to agglomeration and nickel oxidation in standard (undoped) anodes.^{60,86,87} While the results reported here are pertinent for anodes in electrolyte supported button cells, we expect that such structural enhancements will also benefit SOFCs constructed with a anode supported architecture where electrolyte cracking is the ultimate irreversible cell failure mechanism that results from redox cycling.^{8,60,88–90} Stabilizing the nickel microstructure with secondary phases will prevent reduction of the triple phase boundaries caused by redistribution of the nickel during cell reduction and oxidation.

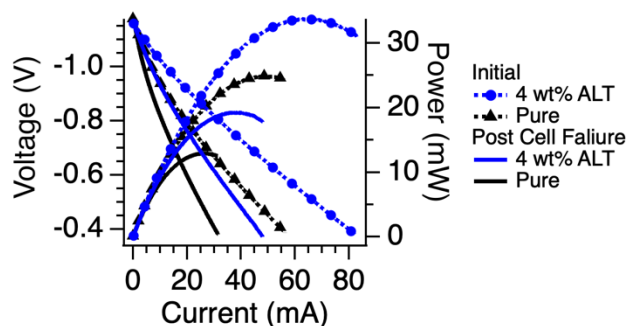


Figure 2.8. Initial and final LSV traces of doped and undoped anodes. Cell failure was defined by a 50% drop in $I_{\max}$ relative to initial benchmark measurements.

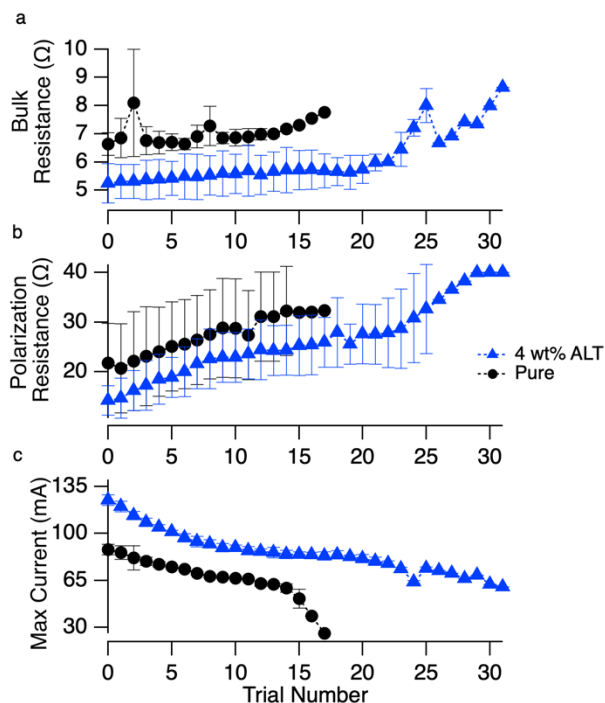


Figure 2.9. Electrochemical properties of doped and undoped cells during full cell lifetimes including bulk resistance (a), polarization resistance (b), and maximum currents (c).

Trends in the bulk and polarization resistances were similar for both doped and undoped cells but overall lower resistances were observed for doped cells. Average R_p values showed slight, continuous increases with each cycle while R_b values remained relatively constant during the initial redox cycles. A marked increase in R_b values were seen towards the end of the cell lifetimes indicating a loss in the connectivity between the electrolyte and the anode as well as damage to the anode microstructure, presumably from the volume changes that occur upon repeated redox cycling. Figure 2.9 shows that the increase in R_b for doped cells was minimal prior to test 20 during which polarization currents of 50% I_{max} were maintained. Increasing polarization currents (60% I_{max}) was believed to be the

main contributor to loss in connectivity between the electrolyte-electrode interface in subsequent cycles.

To determine differences between the resilience of cells to redox cycling to that of standard operation, cells were run under hydrogen for 12 continuous hours with intermittent benchmark LSV and EIS measurements. Figures 2.10 and 2.11 show voltage change and degradation rates for doped and undoped samples during these periods. The measured voltage is not matched between doped and undoped cells as cells were run under galvanostatic conditions to accommodate cell to cell variability including variance in current collector sizes. Fuel cell voltage over time was fit to a MATLAB algorithm and degradation rates of each cell was normalized with respect to the measured current. Cells with ALT doped anodes typically showed degradation rates of less than 0.3% per hour after 12 hours, while undoped cells degraded at rates of more than 0.6% per hour. These degradation rates further support previous results showing that doping standard NiO-YSZ anodes with ALT improves general performance³⁴ but also that ALT doping will increase cell resilience to the harmful effects of redox cycling. Correlation between spectroscopic and electrochemical data show that the chemical mechanism(s) responsible for the observed differences in cell durability during redox cycling between un-doped and ALT doped anodes is directly related to the formation of the secondary phases. Measuring the maximum current over time shows that pure cells degraded faster than doped cells as expected given ALT's ability to slow nickel coarsening.¹⁶

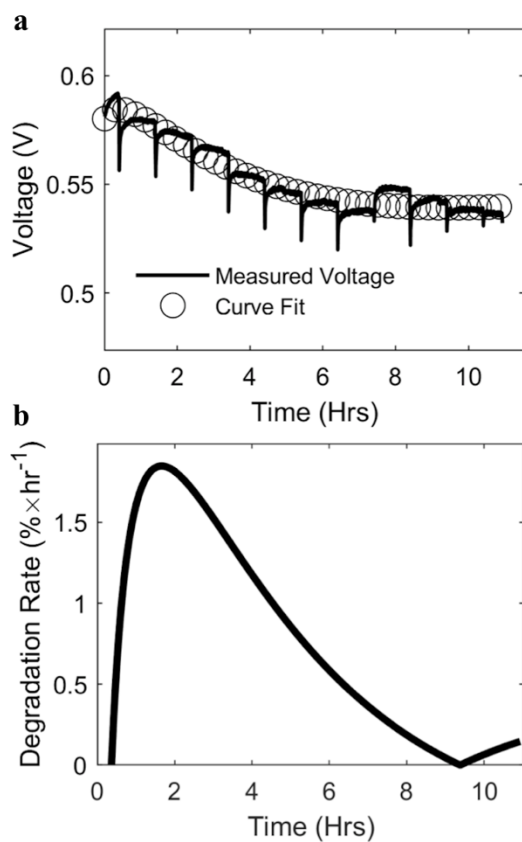


Figure 2.10. Voltage versus time data for ALT-doped cell operating at 50% $I_{\max}$ (a) and degradation rate (b) calculated using method described in the text. Downward spikes in the voltage data correspond to brief halts to operation in order to record EIS data.

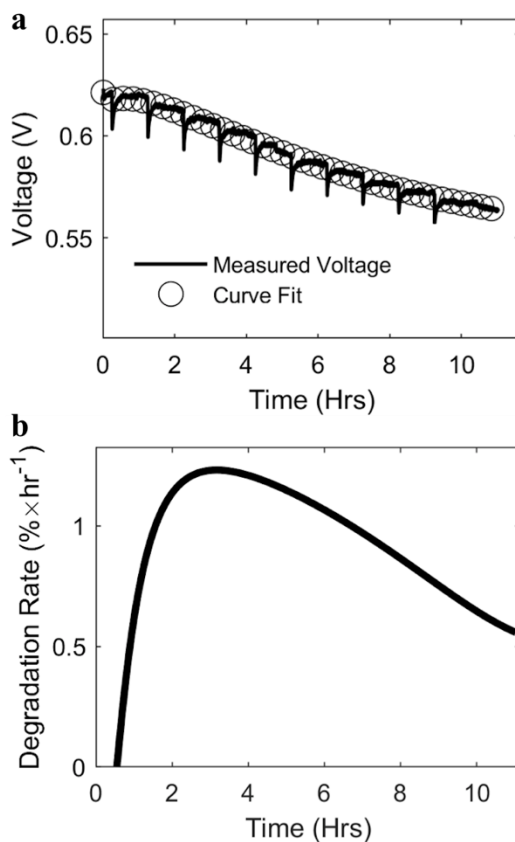


Figure 2.11. Voltage versus time data for undoped cell operating at 50% $I_{\max}$ (a) and degradation rate (b) calculated using method described in text. Downward spikes in the voltage data correspond to brief halts to operation in order to record EIS data.

Conclusion

Raman spectroscopy coupled with electrochemistry has been used to study the effects of ALT doping on NiO-YSZ anodes when the anode is subject to repeated electrochemical redox cycling. In-situ Raman spectroscopy showed the growth and disappearance of NiO throughout cycling, while electrochemical methods assessed cell performance prior to and after each subsequent cycle. While irreversible degradation

occurred in both doped and un-doped cells, doped cells showed much greater resilience, surviving on average twice as long as standard (undoped) anodes. Additionally, doped anodes were able to survive numerous trials using higher polarization prior to cell failure. The improved cell durability during electrochemical redox cycling is directly attributed to the formation of secondary phases upon ALT doping. In summary, the results of this paper provide further insight into the beneficial effects of secondary phase materials on standard SOFC anodes.

CHAPTER THREE

ENHANCING Ni-YSZ ANODE RESILIENCE TO ENVIRONMENTAL REDOX
STRESS WITH ALUMINUM TITANATE SECONDARY PHASESContribution of Authors and Co-Authors

Manuscript in Chapter 3

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Contributions: Collected and analyzed all data, generated figures and wrote manuscript in preparation for publication.

Co-Author: Marley S. Zachariasen

Contributions: Prepared samples for high temperature studies. Edited and commented on manuscript.

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Contributions: Contributed important insight into performing experiments and interpreting results. Edited and assisted in the preparation of the manuscript.

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Contributions: Contributed important insight into performing experiments and interpreting results. Edited and assisted in the preparation of the manuscript.

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ENHANCING Ni-YSZ ANODE RESILIENCE TO ENVIRONMENTAL REDOX
STRESS WITH ALUMINUM TITANATE SECONDARY PHASES

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Abstract

Voltammetry, impedance spectroscopy and *operando* vibrational Raman spectroscopy were used to examine the resilience of traditional and modified Ni-based SOFC anodes to environmental reduction/oxidation (redox) cycling. Traditional anodes were fabricated from Ni-yttrium stabilized zirconia (YSZ) cermet while modified anodes consisted of the Ni-YSZ cermet containing 4 wt % Al₂TiO₅ (ALT). Anodes were part of full membrane electrode assemblies that included a YSZ electrolyte support and a LSM cathode. Experiments were performed at 800°C. To examine anode resilience to redox cycling, cells operated with hydrogen under galvanostatic conditions for 20 minutes prior to oxidation at OCV using either H₂O or O₂. While H₂O only partially oxidized anodes, O₂ exposure fully oxidized anodes and rapidly accelerated degradation in undoped cells. Undoped cells typically suffered a 50% loss in conversion efficiency after approximately 15-20 redox cycles with O₂. Under equivalent conditions, cells with ALT doped anodes degraded on average only 13 ± 3 %. EIS modeling and ex-situ FE-SEM measurements

provide further insight into the mechanisms responsible for enhanced resilience shown by Ni-YSZ cermet anodes doped with ALT.

Introduction

Solid state electrochemical cells are energy conversion technologies capable of either producing or using electricity to help balance a growing production and consumption mismatch in current renewable power sources.^{91,92} When run as a solid oxide fuel cell (SOFC), these devices can meet power requirements up to 300 kW and energy conversion efficiencies as high as 90% without the release of pollutants such as NO_x, and SO_x and with reduced greenhouse gas emissions.^{8,52–55,93} The critical components of an SOFC are the electrodes as these directly determine the device's performance and durability. Because an SOFC is cycled between room temperature and operating temperatures above 700 °C, the electrode thermal expansion must be relatively close to that of the electrolyte to prevent mechanical stress and/or electrode delamination. Most SOFC anodes are typically a porous ceramic-metallic (cermet) composite³ that, when coupled to a conventional electrolyte material such as yttria stabilized zirconia (YSZ), provide sufficient electrocatalytic activity. Because of its low cost, high catalytic activity, electronic conductivity, and stability under reducing conditions, Nickel is the most commonly used electrocatalyst in SOFC cermet anodes.¹²

While Ni-based anodes endow SOFCs with many benefits, one significant limitation to Ni-YSZ cermets is the material's sensitivity to oxidation. Given that the molar volume of NiO is ~1.66 times larger than the molar volume of Ni, reduction/oxidation

(redox) cycling can lead to severe mechanical degradation including cracking, cell fracture and loss of connectivity between the anode and the YSZ electrolyte.^{8,18,19,58,62,94-96} In addition to any mechanical damage suffered by the SOFC, redox cycling will also adversely impact the anode microstructure through decreased triple phase boundaries and lower overall electrochemical conversion capacity.⁹⁷⁻⁹⁹ Anode oxidation can result from fuel starvation under strong polarizing conditions, referred to as electrochemical oxidation, or as a result of either gas leakage between the anode and the cathode or the presence of an oxidizing agent in the fuel, referred to as atmospheric or environmental oxidation. These two sources of redox stress will impact Ni-YSZ cermet anodes in different ways: electrochemical oxidation from fuel starvation will first affect the electrode-electrolyte interface resulting in delamination and loss of electrocatalytic material.^{100,101} Environmental redox cycling is expected to cause a more uniform degradation throughout the anode with the majority of damage visible on the surface of the electrode. These differences are shown schematically in Figure 3.1. The question addressed in work presented below is whether or not ALT confers the same resilience to Ni-YSZ cermet anodes subject to environmental redox stress as it does to equivalent anodes that have been electrochemically redox cycled.

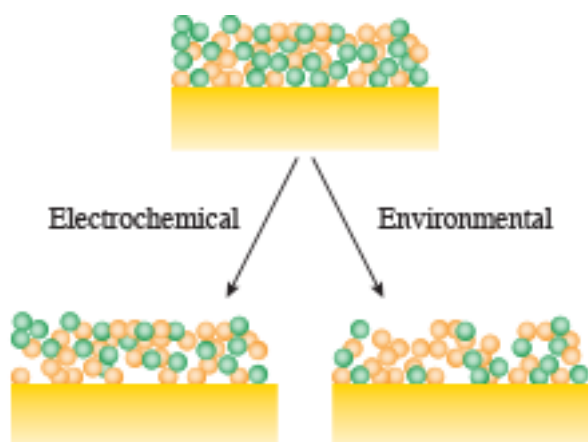


Figure 3.1. Schematic illustration of redox degradation mechanisms. Electrochemical oxidation results in loss of electrode-electrolyte connectivity, while environmental redox cycling results in loss of Ni percolation and pore formation on the anode surface.

The process of anode delamination as a result of electrochemical redox cycling has been reported in previous studies where oxidation is shown to decrease the connectivity of the nickel phase and causes delamination of the anode away from the electrolyte as nickel at the interface is oxidized and subsequently reduced.^{100–102} Loss of Ni-Ni contact and increased pore formation at the electrolyte-electrode interface is also reported in cells operated in electrolysis mode at high current densities.¹⁰³ Additionally, in the case of anode supported cells, the critical extent of oxidation before device failure is reported to be much lower for cells oxidized electrochemically compared to cells oxidized environmentally.¹⁰⁴ Reports focusing on environmental oxidation highlight an increase in anode porosity as a major reason for cell degradation rather than loss of electrode-electrolyte contact.^{60,96} These studies show that successive environmental oxidation leads to an increasingly porous anode structure where pores appear coarser and more coherent with successive oxidation cycles. As both environmental and electrochemical oxidation proves problematic for a

device's long term durability, finding ways to stabilize anode microstructure and maintain Ni percolation and electrode-electrolyte connectivity is vital for successful SOFC operation.

Strategies intended to improve SOFC tolerance to redox cycling have focused on strengthening anodes with secondary materials.^{27,63,65,68} One successful example of this is infiltrating free-standing Ni-YSZ cermet with small amounts of oxide dopants.^{16,39} Previous studies have shown that the addition of aluminum and titanium based oxides can improve the thermal expansion match between the Ni-based anodes and a YSZ electrolyte^{105,106} as well as prevent Ni particle coarsening at high temperatures leading to enhanced SOFC strength^{39,107} and improved performance and longevity.^{16,34,74} An example of a promising aluminum and titanium based oxide is aluminum titanate (Al_2TiO_5 or ALT). When added to Ni-YSZ anodes, ALT reacts with NiO and YSZ during processing to form secondary phases that includes a nickel aluminate spinel (NiAl_2O_4) and a zirconium titanate ($\text{Zr}_5\text{Ti}_7\text{O}_{24}$). In addition to providing standard Ni-YSZ anodes with improved mechanical strength and electrochemical performance,^{39,107} these secondary phases have also been shown to enhance anode resilience to repeated electrochemical redox cycling by a factor of two compared to conventional, undoped cermet anodes.¹⁰⁰ Experiments described below expand upon the previous findings by examining how ALT doping improves the anode resilience to *environmental* redox cycling from direct exposure to H_2O and O_2 . Previous studies using Sn and Ba doped Ni-YSZ cermet anodes showed that environmental oxidation by steam was self regulating with a measured OCV of $\sim -0.73\text{V}$ due to the $\text{Ni-H}_2\text{O} / \text{NiO-H}_2$ equilibrium. The impact of these dopants on anode resilience to

environmental redox cycling, however, was not addressed specifically.^{80,85} In the studies described below, *operando* Raman spectroscopy is used to monitor surface chemistry and the extent of anode oxidation while electrochemical methods including voltammetry and impedance spectroscopy provide both a quantitative measure of anode performance and mechanistic insight into how aggressive environmental redox conditions affect the material composition and performance of doped and undoped cells.

Experimental

Complete SOFC assemblies were constructed using commercially available, 0.3 mm thick, 8YSZ electrolytes (Fuel Cell Materials). Aerosol spraying was used to apply anodes composed of a mixture of 8YSZ (34 wt. %, Tosh Corp.), NiO (66 wt. %, JT Baker), and cornstarch for pore formation. Anodes were dried overnight and then sintered at 1250 °C for two hours with a heating and cooling rate of 10 °C per minute. ALT was added to doped anodes by infiltration with a solution of aluminum nitrate and titanium lactate dissolved in deionized water of stoichiometric proportion to produce Al_2TiO_5 . ALT was added to anodes to produce a 4 wt. % loading by pipetting the solution onto anodes and removing organics by heating the infiltrated cells at 400 °C for two minutes. To form the requisite secondary phases in ALT doped anodes³⁴, all cells (doped and undoped) were then sintered at 1400 °C with a 1 hour dwell time at the high temperature. Heating and cooling rates were 5 °C per minute. Cathode paste (Fuel Cell Materials, 50%/50% LSM/YSZ) was used to paint cathodes on the center of the electrolytes opposite the anodes in a 12.5 mm diameter using a Kapton-tape mold to create a thickness of ~0.6 mm. The

cathodes were sintered at 1150 °C for one hour with a heating and cooling rate of 1 °C per minute. Current collectors were composed of gold wire (Alfa Aesar) attached with silver mesh (Alfa Aesar) and gold paste (Heraeus) on the anode and platinum mesh (Alfa Aesar) and platinum paste (Heraeus) on the cathode. The cathode side of each cell was attached to a 2.5 mm diameter alumina tube (Sentro Tech) using ceramic paste to provide a gas tight seal. After drying, the assembly was covered with a quartz tube sealed with a rubber stopper on the bottom and placed inside of a tube furnace. Further details about the experimental set up can be found in previous publications.^{43,51} Raman spectra were acquired with a Renishaw InVia spectrometer and a 30 mW, 488 nm Ar-ion laser with 10 second exposures. The backscattered light was directed through an edge filter with 150 cm⁻¹ cut off to allow Stokes scattered radiation to be measured by the charge coupled device detector.

A Princeton Applied Research VersaStat MC was used to collect electrochemical measurements including Linear Sweep Voltammetry (LSV) and Electrochemical Impedance Spectroscopy (EIS) (Figure 3.2). LSV measurements were collected using a sweep rate of 0.1 V per second. LSV was carried out to 80% of the maximum current to avoid damage to the cell. EIS data were measured over a frequency range of 100 000 Hz to 0.1 Hz with an AC voltage amplitude of 0.01 V. Cell potentials were measured in reference to the reduction of O₂ on the cathode resulting in OCV with negative values.

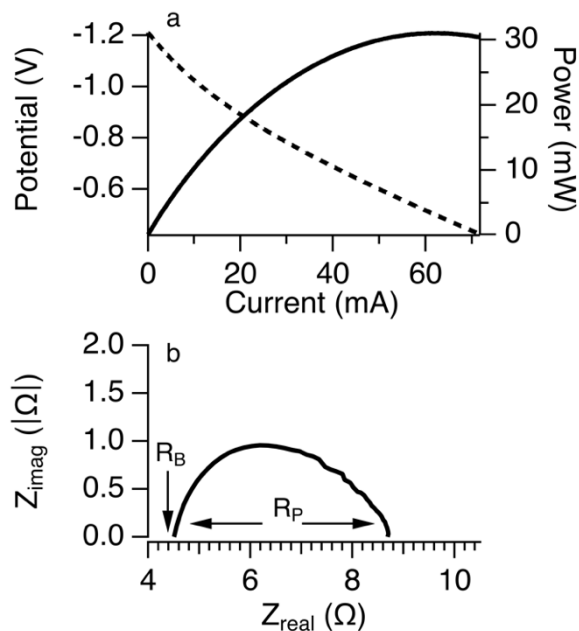


Figure 3.2. LSV (a) and EIS (b) for a representative ALT doped fuel cell operating at 800 °C after reduction. LSV dashed line correspond to the potential (V) as a function of current (mA), and the solid line corresponds to power (mW). R_b and R_p signify bulk (or series) and polarization resistances, respectively.

Cells were heated to $800\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ at a ramp rate of $1\text{ }^{\circ}\text{C}$ per minute under low flow argon on the anode and low flow air on the cathode. Once at stable temperature, gas flows were increased to 100 sccm argon and 85 sccm air. The anode was reduced using 20 sccm of H_2 for 1 hour while Raman kinetics and OCV were monitored. Benchmark LSV and EIS measurements were then acquired to determine initial cell performance and cell condition respectively. Cells were subjected to repeated environmental redox cycling to determine resilience and durability. Redox cycling consisted of first operating the device for 20 minutes at 50% of the initially measured maximum current (I_{max}) with 20 sccm of H_2 supplied as the fuel. The hydrogen fuel and applied polarization were then turned off to allow the inlet gas line to clear. The cells were then exposed to either H_2O (3%) in Ar or

20 sccm of O_2 in Ar for 5 minutes while NiO signals were monitored using Raman kinetics. Finally, cells were re-reduced with H_2 and benchmark LSV and EIS measurements were collected at OCV. Redox results described in the manuscript are based off of the average of four ALT doped cells and four undoped cells. However, initial conditions for both doped and undoped samples have been consistent over dozens of cells. A schematic diagram illustrating this sequence of steps in the redox cycling experiment is shown in Figure 3.3. EIS data were plotted in a Nyquist plot and modeled using ZSimpWin 3.60 software.

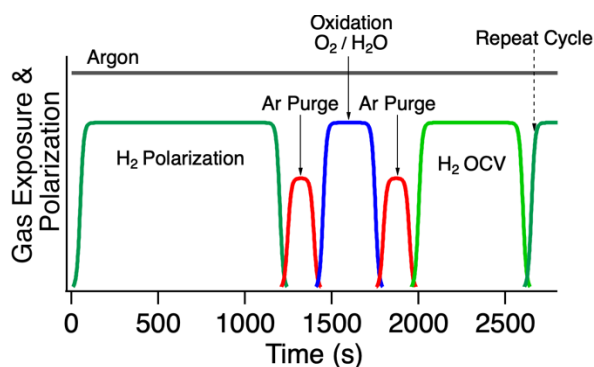


Figure 3.3. Schematic figure showing gas exposure and polarization sequence for each redox cycle. All fuels were present in an Ar carrier gas.

Results and Discussion

Previous studies have shown improved cell resilience to electrochemical redox cycling in ALT doped NiO-YSZ anodes where the increased stability of the Ni catalyst microstructure resulting from ALT addition slows degradation rates and significantly increases anode durability.¹⁰⁰ In that study, membrane electrode assemblies operating galvanostatically produced current in the absence of an incident fuel, forcing the device to

oxidize Ni at the electrode-electrolyte interface. Repetitive electrochemical redox cycling led to material depletion and loss of connectivity across this boundary. Within 15 cycles the current produced by devices with undoped anodes dropped by >50%. Adding ALT (4% by mass) to the anode improved resilience to electrochemical redox cycling, extending by a factor of 2 the number of cycles an anode could withstand before cell performance dropped $\geq 50\%$.

Experiments described in this work examine the effects of this same dopant on an anode's *atmospheric* redox tolerance using environmental redox cycling methods to test the Ni-YSZ electrode's resilience to repeated oxidation and reduction. Figure 3.4 shows voltage traces acquired as a function of time during experiments performed using both H₂O and O₂ as oxidizing agents.

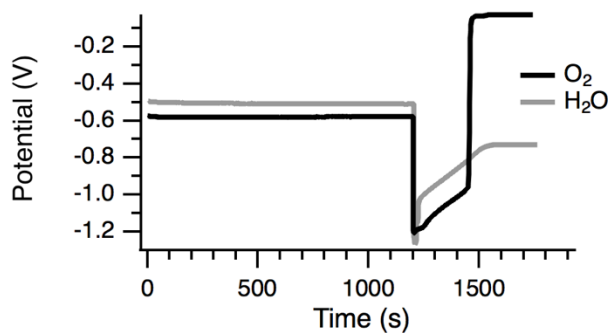
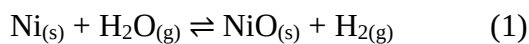


Figure 3.4. Representative potential traces of cells during redox cycling with O₂ and H₂O oxidizing fuels. Hydrogen was turned off after 20 minutes followed by a system purge and oxidation.

In these redox cycling experiments, SOFCs were operated with hydrogen and polarized to 50% $I_{\max}$ for 20 minutes before the fuel flow was turned off and the cell returned to OCV. The atmosphere above the anode was then switched to either H₂O (3%)

in Ar or O₂ (5%) in Ar. Immediately upon cessation of cell polarization, the potential returned to a dry H₂ OCV (-1.23V) before starting to rise as the atmosphere was changed to an oxidizing environment. For cells exposed to H₂O, the OCV stabilized at approximately -0.73 V coinciding with the Ni/NiO standard reduction potential. This result has been reported previously and illustrates the reversible nature of Ni oxidation by H₂O and NiO reduction by the newly generated H₂ (Equation 1).^{80,85,108}



For O₂ oxidation the OCV briefly leveled off at -0.73 V before quickly climbing to ~ 0 V with the small residual OCV reflecting differences in pO₂ above the cathode and anode.⁷⁰ *Operando* Raman spectra corroborate these electrochemical results showing that O₂ is a much more aggressive oxidant compared to H₂O. Appearance of a vibrational band at 1060 cm⁻¹ following the switch from H₂ to H₂O or O₂ confirms the formation of NiO^{42,81,84} (Figure 3.5a). In the case of H₂O exposure the NiO signal intensity never rose above 150 counts while in the case of O₂ exposure, NiO signal intensity routinely exceeded 250 counts. Interestingly, NiO formation in the ALT-doped anodes appeared slightly suppressed (~10%) compared to the standard Ni-YSZ anodes implying that the resilience observed with the doped cells may be related to the doped materials being less susceptible to environmental oxidation (Figure 3.5b).

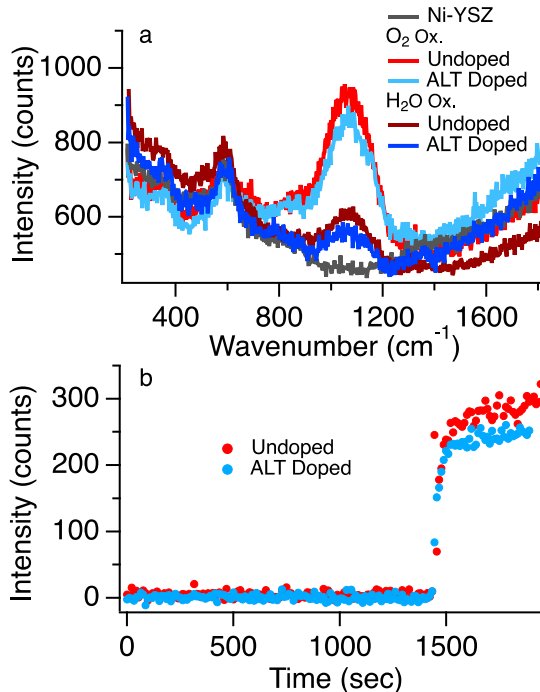


Figure 3.5. Raman spectra of undoped and doped anodes showing the difference in NiO intensity after exposure to O_2 and H_2O (a) compared to reduced Ni-YSZ spectrum. Kinetic plots shown in (b) highlight the slightly reduced NiO signal seen in anodes doped with ALT.

Degradation rates, as calculated from voltammetry measurements following each redox cycle, further indicate the benefits of ALT doping as well as the more aggressive nature of O_2 as an oxidizing agent. Figure 3.6 summarizes the average maximum currents, of four doped and four undoped cells, derived from LSV measurements acquired at the end of each redox cycle. The errors given pertain to the final measured drop in current for each type of cell after the allotted experimental time. ALT doped cells were consistently higher performing, providing initial currents of over 100 mA compared to ~ 80 mA for undoped cells. This result is consistent with observations reported previously and may be related to improved percolation and reduced size of the Ni phase in the doped system.^{16,34,100} While

irreversible cell degradation was observed for both doped and undoped samples, H₂O oxidation did not result in cell failure, as defined by a drop in 50% of $I_{\max}$, for either type of cell. However, undoped cells subjected to H₂O-induced redox cycling degraded more than doped cells. With O₂ oxidation undoped samples repeatedly failed in ~20 redox cycles, while the degradation rate of doped cells was similar to rates observed in the H₂O-induced redox cycling studies.

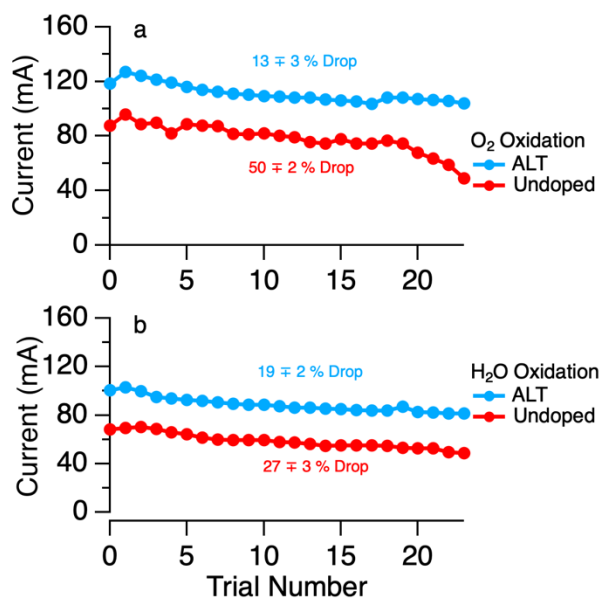


Figure 3.6. Maximum currents measured after each redox cycle using O₂ oxidation (a) and H₂O oxidation (b) for both ALT doped and undoped cells.

Figure 3.7 shows representative *post-mortem* electron micrographs of anode surfaces after being exposed to redox cycling with H₂O and O₂. Doped and undoped samples exposed to H₂O show little difference in surface structure and retain relatively uniform microstructure. After O₂ exposure, however, dramatic differences are observed between the doped and undoped cells (Figure 3.7c and 3.7d). While the doped cell surface

looks much like those of cells after H₂O exposure, the undoped anode surface shows considerable material loss and evidence of large gaps in the anode microstructure. Significant particle clustering is apparent in the undoped anodes as a result of the volume changes and stresses associated with aggressive redox cycling with O₂. Additionally, little difference is observed in cross sectional FE-SEM images where both types of cells show well maintained connectivity between the electrode and the electrolyte. This observation supports the hypothesis that environmental redox cycling, occurring top down through the electrode, causes severe damage throughout the anode microstructure at rather than specifically at the electrode-electrolyte interface as has been reported for systems subjected to electrochemical redox cycling. These observations also support the hypothesis that secondary phases formed by ALT endow Ni-YSZ SOFC cermet anodes with significantly enhanced tolerance to environmental redox cycling by preserving electrode microstructure. Additional FE-SEM images are included in Supplemental information, showing wider field views over the anode microstructure (Figure S1) as well as images of anodes subjected to *electrochemical* redox cycling (Figure S2).

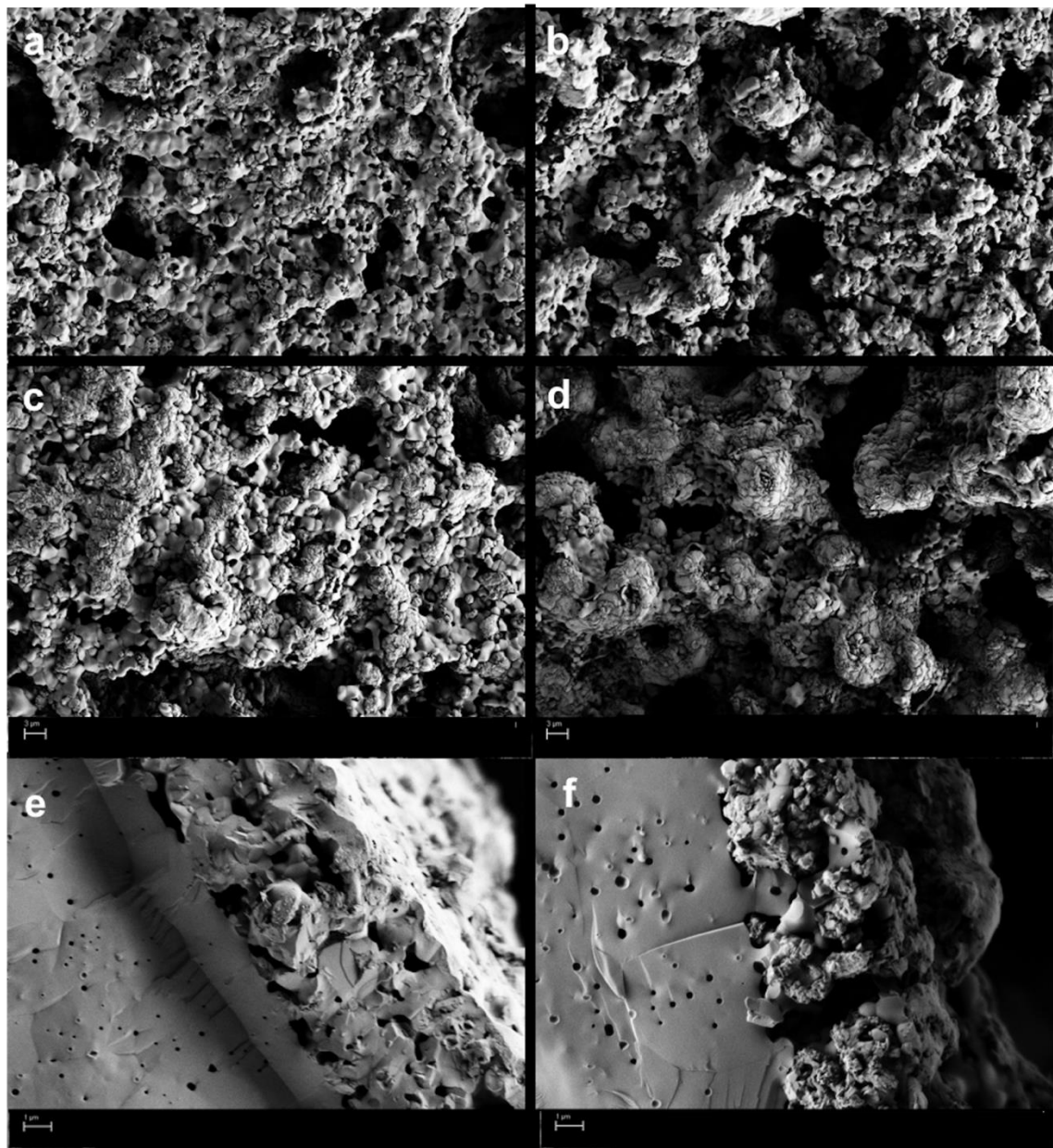


Figure 3.7. Ex-situ FE-SEM images of anode surfaces after H₂O exposure (a-ALT doped, b-undoped), O₂ exposure (c-ALT doped, d-undoped), and anode cross sections after O₂ exposure (e-ALT doped, f-undoped).

Additional insight into environmental redox degradation mechanisms can be inferred from impedance measurements following each redox cycle. Benchmark EIS data for redox cycles run with O_2 are shown in Figure 3.8.

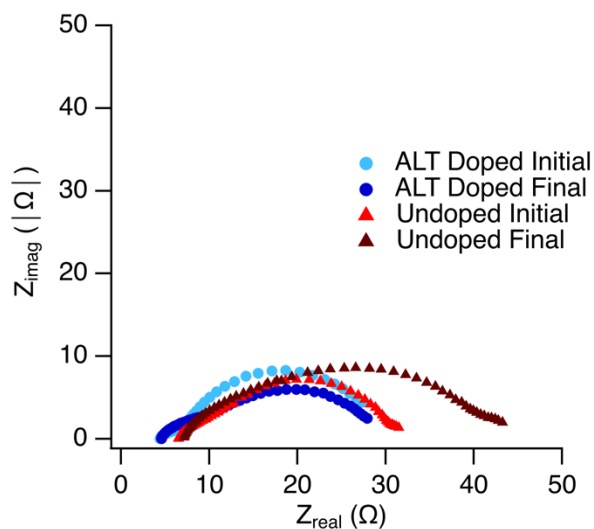


Figure 3.8. Nyquist plots of electrochemical impedance data acquired after initial and final redox cycles for undoped and ALT doped cells.

These data show favorable performance for ALT doped samples. Overall changes in polarization resistances are evident for EIS data acquired at the start and end of redox cycling. Redox cycling also leads to changes in the measured series resistances. EIS data were fit using a circuit consisting of a resistor and two parallel RQ elements connected in series as shown in Figure 3.9.

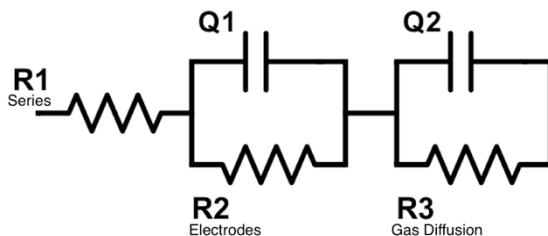


Figure 3.9. Circuit diagram of resistor and two parallel RQ elements in series used to fit experimental EIS data. R1 is attributed to the series resistance, R2 to the resistance at the electrodes, and R3 to resistance due to gas diffusion.

The selection of a specific equivalent circuit was based on both low associated uncertainties in fit parameters as well as assumed physical relevance of the chosen model circuit. The three resistive elements of the circuit are assigned to bulk or series resistance (R1) at high frequency, resistance at the electrodes (R2) at intermediate frequencies, and resistance due to gas diffusion (R3) at low frequencies.

Little difference was observed in fits for EIS performed following oxidation with H₂O, but differences are more apparent in cells that were subjected to O₂ oxidation. Representative EIS fits are shown in Figure 3.10 with corresponding calculated resistance values reported in Table 3.1. Initial values for the series resistance were $\sim 4 \Omega$ for ALT doped anodes and $\sim 5 \Omega$ for undoped anodes. These values are consistent given results reported in previous publications with similarly prepared electrodes.^{59,85,100} Over the course of a redox cycling experiment, series resistance values remained consistently lower for ALT doped samples and both type of cells showed only a small increase in R1 over the course of an experiment. These results suggest that bulk connectivity was maintained

between the electrolyte and electrodes with doped anodes showing consistently better cohesion across the electrolyte-anode interface.

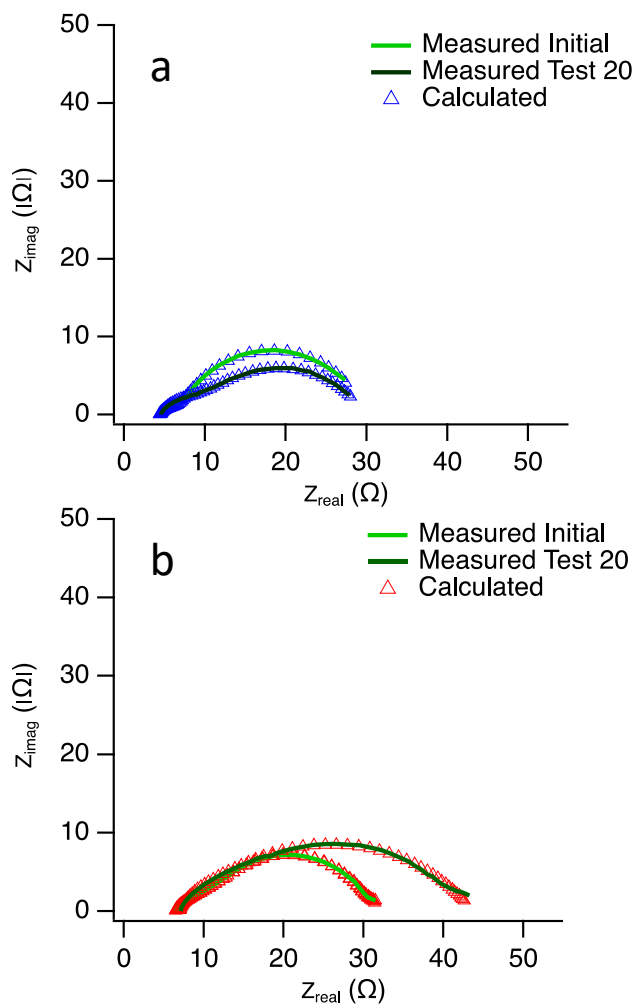


Figure 3.10. Fits of electrochemical impedance data using ZSimpWin software for ALT doped cell (a) and undoped cell (b). Data was modeled using an $R(RQ)(RQ)$ circuit where resistance values are attributed to bulk resistance, resistance at the electrodes, and mass transport respectively.

Table 3.1. Resistance values derived from electrochemical impedance data fits using an R(RQ)(RQ) circuit.

	ALT Doped Cell			Standard Cell		
Trial Number	R1 (Ω)	R2 (Ω)	R3 (Ω)	R1 (Ω)	R2 (Ω)	R3 (Ω)
0	4.16	3.37	22.2	5.82	16.6	10.4
20	4.25	5.05	24.3	6.65	34.7	2.36

Given that the cathodes were the same for all types of cells, we attribute changes in R2 to the changes in charge transfer rates and activation overpotential at the anode. While R2 increases by less than 2 Ω over the course of an experiment for cells with ALT doped anodes, it more than doubles for cells with undoped anodes from 16.6 Ω to 34.7 Ω . The steady growth of R2 in cells with undoped anodes reflects a loss of triple phase boundaries and Nickel surface area^{97,99} as the anode particles agglomerate under the aggressive environmental redox cycling. This result is consistent with the degree of microstructure degradation observed in the post-mortem FE-SEM images. This irreversible loss of catalytic activity is suppressed in cells with anodes doped with ALT as the anchoring and strengthening secondary phases endow the anode cermet benefits that preserve microstructure and catalytic activity.^{34,100}

Similar to the minimal change in R2 values seen in cells with ALT doped anodes, little change is seen in the values of R3 throughout the course of an experiment. For undoped cells however, R3 decreases by more than a factor of four from 10.4 Ω to 2.4 Ω . Because R3 is associated with low frequency mass transfer properties, this quantity serves as an indirect measure of anode porosity. A decrease in R3 is therefore consistent with the

more open (degraded) microstructure observed in the FE-SEM images (Figure 3.7d.) Predictably, overall total resistance, or polarization resistance, was also lower for ALT doped samples due to the ability of ALT to preserve the electronic percolation of the Ni-YSZ anode microstructure. This electrochemical data suggests that minimal modifications to the traditional cermet anode foundation has the potential for a technological solution to the redox problem apparent in standard Ni-YSZ anodes.

While these data show that addition of ALT helps preserve anode performance during repeated environmental redox cycling, we note here that changes in equivalent circuit parameters change in qualitatively different ways for anodes subject to electrochemical redox cycling. For example, the drop in R_3 associated with anode porosity, observed for undoped cells, is not apparent in undoped cells subjected to electrochemical redox cycling. A comparison of resistance values of cells subjected to electrochemical and environmental redox cycling is included in the Supporting Information (Table S1).

The loss of triple phase boundaries is arguably the main degradation mechanism for standard, undoped, cells subject to environmental redox cycling. This result stands in contrast to cells subject to electrochemical redox cycling¹⁰⁰ where a loss in connectivity between the electrode and electrolyte (delamination) is the main factor leading to cell degradation, supporting that different types of redox cycling impact cell degradation mechanisms. The addition of ALT is beneficial under both circumstances; maintaining cross sectional connectivity under electrochemical cycling and maintaining catalytic activity and anode microstructure under environmental cycling. ALT addition promotes

mechanical resilience and durability to anodes under both types of redox stress that otherwise initiate catalyst degradation.

Conclusions

Spectroscopic and electrochemical data presented in this study suggest that secondary phases in ALT doped Ni-YSZ cermet anodes directly drive improved cell durability and resilience to environmental redox cycling. Oxidizing the anodes using H₂O and O₂ resulted in some amount of cell degradation for cells with both ALT doped and undoped anodes, however, ALT doped anodes proved much more resilient. While O₂ oxidation caused undoped anodes to repeatedly drop to below 50% of their initial $I_{\max}$, doped anodes only degraded ~25% of undoped anodes. Raman spectroscopy was used to monitor the reduction and oxidation of Ni throughout a cycle, while electrochemical methods were used to monitor changes in cell potential, current output, and changes in resistance. The benefits of strategically adding small amounts of secondary phase materials to standard Ni-YSZ SOFC anodes is relevant for the design and fabrication of more durable and efficient electrodes for SOFC purposes.

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CHAPTER FOUR

MITIGATING CARBON FORMATION WITH Al_2TiO_5 ENHANCED SOLID OXIDE
FUEL CELL ANODESContribution of Authors and Co-Authors

Manuscript in Chapter 4

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MITIGATING CARBON FORMATION WITH Al_2TiO_5 ENHANCED SOLID OXIDE
FUEL CELL ANODES

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Abstract

Spectroscopic and electrochemical techniques were used to examine the benefits of adding small amounts of aluminum titanate (Al_2TiO_5 or ALT) to standard NiO-YSZ based SOFC anodes operating with methane at 800 °C. Combining small amounts (4% by mass) of ALT with NiO-YSZ leads to the formation of secondary phases that improve anode carbon tolerance via multiple reaction mechanisms. Raman data show that carbon forms on both ALT doped and undoped anodes at OCV and with applied bias as evidenced by the vibrational band of highly ordered graphite at 1560 cm^{-1} . However, ALT doped anodes limited the amount of carbon that forms on both the surface and within the bulk resulting in improved performance for up to 12 hours of exposure to CH_4 . Results show that ALT enhanced anodes accumulate $\sim 25\%$ less carbon on the surface under open circuit conditions and that increasing polarizations to 50 % of the maximum current and beyond results in no observable carbon accumulation. These observations are used to deduce possible mechanisms that describe how secondary phases suppress carbon accumulation.

Introduction

Solid oxide fuel cells (SOFCs) are a promising bridging technology as societies transition from traditional fossil fuel feedstocks to power production strategies based on renewable fuel sources. SOFCs are devices capable of producing high power and current outputs with energy conversion efficiencies approaching 90% in combined heating and power (CHP) applications.^{12,23,109} For CHP related applications, however, SOFCs *must* be able to leverage their fuel flexibility and operate with a variety of fuels including H₂, CH₄, syngas, biogas, and higher molecular weight hydrocarbons.^{12,23,108–110} This capability differentiates SOFCs from other types of fuel cells such as polymer electrolyte membrane fuel cells (PEMFCs) that can operate only with sources of clean H₂ because of their easily poisoned precious metal catalysts. Carbon containing fuels, however, carry with them the risk of carbon accumulation (or coking) and eventual electrode failure.

SOFCs are solid state devices consisting of two electrodes separated by an ionically conducting electrolyte. The high operating temperatures (~700-900°C) required for oxide diffusion through the electrolyte enable SOFC fuel flexibility and the use of relatively inexpensive electrocatalyst materials such as elemental nickel for anodes and MIEC perovskites for cathodes. As an electrocatalyst, Ni is inexpensive, electronically conducting, stable under *operando* conditions, and highly effective at activating CH bonds.^{4,111} In functioning anodes, Ni particles form an electronically percolated network with ionically conducting yttria stabilized zirconia (YSZ) to create a porous cermet structure that allows for high Ni surface areas, extensive three phase boundaries and facile

fuel delivery and product removal. However, unless conditions in the SOFC are managed carefully, Ni catalysts are susceptible to carbon accumulation or ‘coking’ when exposed to carbon containing fuels.^{21,111,112} These carbon deposits consist of either carbon filaments, highly ordered graphite or disordered graphite,^{24,113,114} all of which can be detrimental to the cells as carbon accumulation impedes gas transport and blocks catalytic sites, limiting cell performance.^{109,115,116} Eventually, accumulated carbon reacts with the Ni itself in a process known as metal dusting that results in irreversible anode microstructure disintegration.^{117,118}

The thermodynamics of carbon formation show that increasing temperature significantly affects the amount of carbon that accumulates on a Ni cermet anode.¹⁰⁸ One approach to mitigate carbon accumulation is to introduce steam into the fuel feed when using hydrocarbon based fuels.^{112,119,120} Increasing the steam content above a steam to carbon ratio of 1.5 suppresses carbon formation at high temperatures.¹¹⁹ However, large amounts of steam can also limit device performance by decreasing operating voltage and increasing the risk of oxidizing the Ni catalyst.¹⁰⁸ Therefore, materials-focused solutions are often preferred as alternative strategies to minimize carbon accumulation. These approaches can involve replacing the nickel altogether with alternative materials such as copper, ceria, or oxide conducting perovskites.^{67,121–126} While showing limited success, these materials are often unable to match the performance of Ni-based anodes, motivating efforts to improve anode carbon tolerance simply through modifying the conventional Ni-YSZ anode structure. One strategy for doing so is to dope Ni based anodes with small

amounts of secondary metals that can lower barriers to fuel oxidation, increase operational stability and improve tolerance toward carbon exposure.^{74,80,127}

Recent reports have shown that small addition ($\leq 5\%$ by mass) of aluminum titanate (Al_2TiO_5 / ALT) to Ni-YSZ anodes in electrolyte supported SOFCs improves the thermal expansion match between the Ni-based anodes and the YSZ electrolyte. ALT also appears to prevent Ni particle coarsening.^{16,105,106} Additionally, ALT doped anodes show a variety of other benefits including increased electrochemical performance in cells operating with H_2 , improved mechanical strength, and increased resilience to both electrochemical and environmental redox cycling.^{16,34,39,100} During anode processing, ALT reacts with the NiO and YSZ to form nickel aluminate (NiAl_2O_4) and zirconium titanate ($\text{Zr}_5\text{Ti}_7\text{O}_{24}$). Upon reduction, these materials separate, forming elemental Ni and oxides of aluminum and titanium. The literature contains few reports describing how – or even if – these secondary phases will confer the same benefits to SOFCs operating with carbon containing fuels as they do when H_2 is the fuel source. Nickel aluminate on its own is a well-studied spinel that has previously shown resistance towards coking.^{128–130}

Upon reduction NiAl_2O_4 reduces to Ni metal and Al_2O_3 . Corundum ($\alpha\text{-Al}_2\text{O}_3$), the most stable form of alumina,¹³¹ is commonly used in general catalysis applications because its surface is inert and the material possesses good mechanical strength in both dense and porous forms.¹³² Several studies have examined the effects of alumina addition to Ni, in both general catalysis and in SOFC applications and observed improvements in reforming rates of hydrocarbon fuels and improved carbon tolerance compared to nickel deposited on other supports.^{129,130,133–135} Others credit a barrier layer mechanism as the main reason to

why less carbon is observed on Al_2O_3 doped Ni surfaces.^{115,136} Barrier layers that minimize carbon formation have also been proposed for other SOFC-relevant catalyst systems such as ceria.^{122,137} While low amounts of Al_2O_3 addition in SOFCs reduce the amount of carbon deposition, higher levels have been shown to have the opposite effect. This result has been explained by the surface's increased acidity related to the inverse spinel structure of nickel aluminate where close to half of the Al^{3+} ions are expected in tetrahedral coordination.^{74,132}

In addition to Al based compounds, reports suggest that TiO_2 doped Ni-based catalysts also suppress carbon formation through increased reforming activity.^{74,138} Many prior experimental and theoretical studies on $\text{TiO}_2/\text{H}_2\text{O}$ interactions suggest that water adsorbs and dissociates on a reduced TiO_2 surface.^{139–141} As a reducible metal oxide, TiO_2 possesses a variety of oxidation states and the large number of oxygen vacancies that can form across a TiO_2 surface in a reducing atmosphere serve as steam adsorption sites and provide oxygen species for the oxidation of reforming hydrocarbons.^{74,138,139} If carbon forms on a nickel surface, the water adsorbed to TiO_2 can, in principle, remove the carbon through a surface gasification reaction.

The discussion above illustrates that small amounts of dopants added to improve traditional Ni-YSZ cermet anode performance can lead to a complicated, multi-pathway reaction mechanisms. Missing in most studies, however, are *operando* measurements that directly measure carbon appearance and disappearance in devices as a function of fuel identity, applied polarization and temperature. Experiments described in this work use *operando* vibrational Raman spectroscopy and electrochemical methods to determine how a combination of alumina and titania based secondary phases in low percentage doped,

ALT infiltrated NiO-YSZ anodes affect carbon formation by methane at 800 °C compared to carbon formation on conventional undoped anodes. Results show that ALT decreases carbon formation on the anode surface at OCV as well as under polarized conditions. Spectrochronopotentiometry methods are also used to evaluate the ability of the secondary phases to limit carbon formation within the bulk of the cell during longer methane exposure times.

Findings presented below demonstrate conclusively that adding small amounts of ALT to traditional Ni-YSZ cermet electrodes (4% by mass) significantly improves device performance and suppresses carbon accumulation. Furthermore, the data support a picture where the secondary phases that form play an active catalytic role in reducing the amount of carbon that does accumulate. Taken together, these findings demonstrate that secondary phases can markedly improve SOFC anode performance, and suggest that improved formulations of well-established electrode materials will help transition SOFC technologies into productive solutions for electrical power production throughout the world.

Experimental Section

Complete SOFCs were constructed using commercially purchased 8YSZ electrolytes from Fuel Cell Materials (0.3 mm thick). Aerosol sprayed anodes were made from a mixture of 8YSZ (34 wt.%, Tosh Corp.), NiO (66 wt.%, JT Baker), and cornstarch. Anodes were dried overnight and then sintered to 1250 °C for two hours with a ramp rate of 10 °C per minute. ALT enhanced anodes were infiltrated with a solution of aluminum

nitrate and titanium lactate dissolved in deionized water at stoichiometric ratios to produce Al_2TiO_5 . The solution was added by pipetting to achieve a 4 wt.% loading relative to anode mass, for which the dopant loading corresponds to prior results suggesting optimal performance for infiltrated ALT. Organics were removed between each loading by heating the cells at 400 °C for two minutes. All cells (doped and undoped) were then heated to 1400 °C with a ramp rate of 5 °C per minute and a 1-hour dwell time at the high temperature. This temperature was chosen to form the requisite secondary phases in ALT doped anodes as established in prior studies.³⁴ Cathodes were applied on the opposite side of the anodes using LSM-YSZ paste (Fuel Cell Materials, 50%/50% LSM/YSZ). The paste was applied in a 12.5 mm diameter using a Kapton-tape mold to create a thickness of ~0.06 mm. Cells were then sintered at 1150 °C with a ramp rate of 1 °C per minute and dwell time of 1 hour.

Gold wire current collectors (Alfa Aesar) were attached using silver mesh (Alfa Aesar) and gold paste (Heraeus) and platinum mesh (Alfa Aesar) and platinum paste (Heraeus) to the anodes and cathodes, respectively. The cells were attached (cathodes faced down) to a 2.5 mm diameter alumina tube (Sentro Tech) and secured with layers of ceramic paste (Aremco Products Inc) to provide a gas tight seal. The alumina tube assembly was then covered with a quartz tube, sealed with a rubber stopper and placed inside of a tube furnace. Further details about this experimental setup can be found in previous publications.^{43,51} Raman spectra were acquired with a Renishaw InVia spectrometer operating with a 30 mW, 488 nm Ar-ion laser with 10 second exposures. Backscattered light was directed through an edge filter with a 150 cm^{-1} cut-off to allow Stokes scattered

radiation to be measured by the charge coupled device detector. Electrochemical measurements, including linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS), were measured using a Princeton Applied Research VersaStat MC. LSV measurements were carried out between 0% and 80% of the maximum current to avoid damage to the cells and were collected using a sweep rate of 0.1 V/sec. EIS data were measured with an AC voltage amplitude of 0.01 V over a frequency range of 100 000 Hz to 0.1 Hz. All cell potentials were measured in reference to the reduction of O₂ on the cathode, resulting in measured OCV with negative values.

All cells were heated to 800 °C $\pm$ 5 °C at a 1°C per minute ramp rate with 20 sccm Ar on the anode and 20 sccm Air on the cathode. Once at temperature, gas flows were increased to 100 sccm Ar and 85 sccm Air. The anodes were reduced with 100 sccm H₂ for 1 hour while simultaneously monitoring Raman kinetics and OCV. Following initial reduction, benchmark LSV and EIS measurements were collected under H₂. All EIS data were graphed in Nyquist and/or Bode plots and modeled using ZSimpWin 3.60 software. For carbon cycling experiments, shown schematically in Figure 4.1, cells were exposed to 20 sccm of CH₄ for 15 minutes while Raman spectra were collected. CH₄ flow was then turned off for 3 minutes to allow the anode gas lines to clear prior to oxidizing the cell at OCV using H₂O (3 %) in Ar. Oxidation continued until cells reached the Ni/NiO equilibrium at $\sim$ 0.73 V and NiO appeared in the Raman spectra. Carbon cycling experiments were repeated with CH₄ exposure under OCV as well as galvanostatic polarizations of 10%, 25%, 50%, and 75% of initial max current ($I_{\max}$). Longer-term carbon durability and spectrochronopotentiometry (SCP) tests were performed by exposing cells

to CH_4 for up to 12 hours with intermittent potentiostatic EIS measurements at an overpotential of 500 mV. SCP was used to electrochemically oxidize the cells after 2 hours and then again after 12 hours to evaluate carbon build up in the bulk of the cell over time.

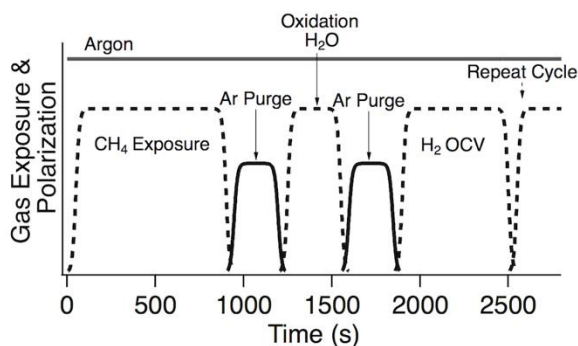


Figure 4.1. Cycling experiment for 15 minute CH_4 exposures. After exposure to CH_4 inlet gas lines were purged with Ar prior to oxidation with H_2O (3 % in Ar) and subsequent H_2 reduction.

Ex-situ Raman mapping experiments were performed on cells subjected to 2 hours of 20 sccm CH_4 at a 500 mV overpotential. Following CH_4 exposure, cell conditions were isolated with Ar over both the anode and cathode. Raman signals were tracked during cool down to ensure no leaks were present in the cell that would lead to non-electrochemical carbon oxidation. A Renishaw HSES motorized stage was used to collect spectra across each cell cross section at intervals of $\sim 8 \mu\text{m}$. Carbon intensities of ALT enhanced and undoped cells were then compared at the edge of the anode, in the center of the anode, and at the electrolyte-anode interface.

Results and Discussion

Experiments described in this work sought to investigate how SOFCs with ALT enhanced NiO-YSZ anodes behaved relative to undoped cells under a variety of operational conditions using CH₄ as a fuel. Cells with ALT enhanced anodes have shown superior initial power and reduced degradation rates when operating with H₂, but the question of how – or even if – ALT affects SOFC anode carbon tolerance remains unknown. Coupling electrochemical methods and *operando* vibrational spectroscopy is a particularly effective way to address this question given that carbon accumulation in functioning SOFCs gives rise to a strong, readily discernible Raman response centered at 1560 cm⁻¹. In the results presented below, Raman and electrochemical data show that carbon build up occurs quickly on both ALT-enhanced and undoped anodes, but ALT doping limits the amount of both surface and bulk carbon in the cells. As seen in Figure 4.2, carbon formed on cells show signals from the “G” vibrational mode corresponding to highly ordered graphite (1560 cm⁻¹), the “D” vibrational mode corresponding to disordered graphite (1350 cm⁻¹), and the “2D” vibrational mode associated with vibration-phonon coupling (2699 cm⁻¹). Since the G vibrational mode or G-band is the most prominent feature in all Raman spectra, G-band intensity was used as the primary indicator of carbon formation throughout this work.

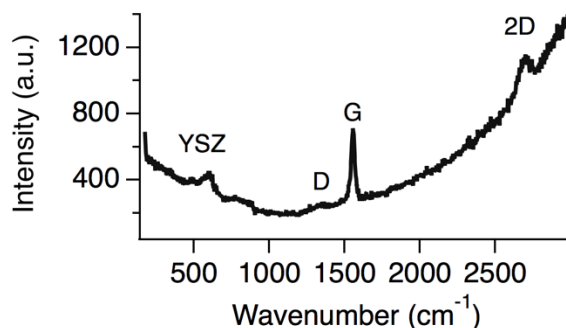


Figure 4.2. Representative Raman spectrum of reduced Ni-YSZ showing YSZ and carbon signatures present on the anode after exposure to CH₄. The G-band (~ 1560 cm⁻¹) appears as the most prominent carbon feature and was therefore used as the primary indicator of carbon build up.

Carbon buildup on the anode surfaces was studied using Raman spectroscopy under OCV and polarizing conditions of 10 %, 25 %, 50 %, and 75 % of maximum cell current ($I_{\max}$). Each cell was exposed to CH₄ for 15 minutes before Raman scans were acquired (10 second acquisitions). Under OCV conditions less carbon formed on ALT-enhanced cells compared to undoped cells as shown in Figure 4.3. In addition to differences in the absolute amount of carbon that formed, the kinetics of carbon appearance were also slightly delayed on ALT-enhanced samples. Figure 4.4a shows the intensity of the G-peak as a function of time in a representative Raman kinetics scan where spectra were taken every 10 seconds with a 10 second exposure time for clear signal. The G-peak signal first appears in pure cells after 30 seconds of CH₄ exposure, while similar G-peak intensity is not seen on ALT-enhanced anodes consistently until ~ 20 seconds later (~ 50 seconds). (Given experimental flow rates and the volume of the SOFC assembly, we estimate gas residence times above the anode to be ≤ 20 sec.)

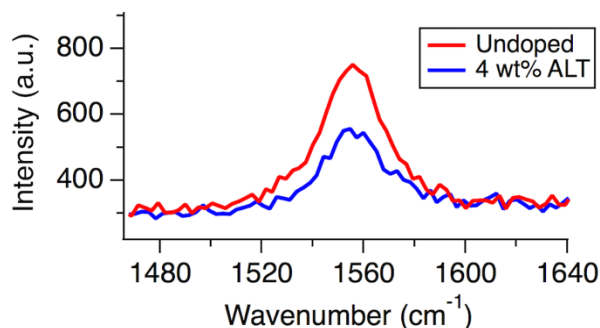


Figure 4.3. Sample Raman data of ALT enhanced anode surface and undoped anode surface following 15 minutes of CH_4 exposure at OCV conditions.

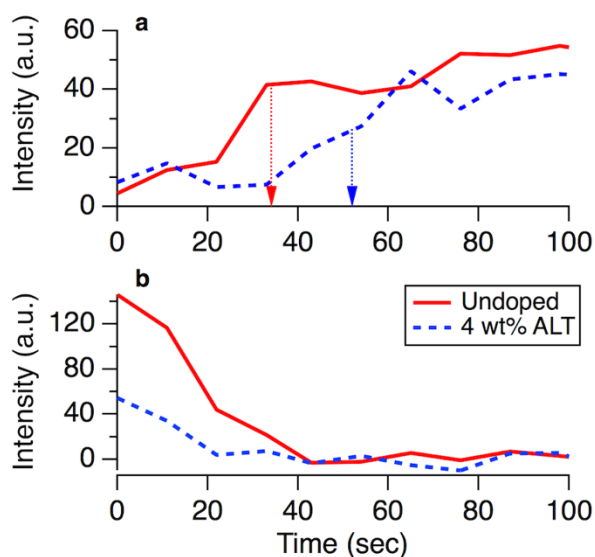


Figure 4.4. Carbon appearance when exposed to CH_4 (a) and disappearance (when exposed to 3% H_2O in Ar) (b) on anode surfaces as a function of time and intensity of the carbon G-peak (1560 cm^{-1}).

Similarly, the lower amounts of surface carbon on ALT enhanced cells leads to faster carbon removal when exposed to steam (Figure 4.4b). These carbon removal kinetics are also reflected in the appearance of NiO in the Raman spectrum. All Raman measurements verified that carbon removal preceded Ni oxidation, consistent with

previous reports.⁸⁰ Figure 4.5 shows a full experimental cycle where cells are exposed to CH₄ for 900 seconds prior to purging and oxidation by steam. ALT enhanced cells reach a Ni-NiO equilibrium potential (-0.73 V) more than 100 seconds sooner than the time required for undoped cells, implying that less carbon accumulates on ALT enhanced anodes than on traditional Ni-YSZ anodes and supporting results from the Raman spectroscopy experiments.

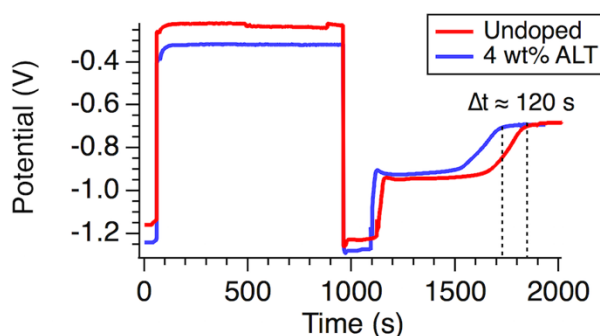


Figure 4.5. Representative potential trace of carbon cycling experiments (as shown in Figure 1). Cells are exposed to CH₄ for 900 seconds with subsequent gas purging and oxidation using H₂O. ALT enhanced cells reach Ni-NiO equilibrium, at 0.73 V, over two minutes prior to cells with no added dopant.

Changes in the kinetics data resulting from ALT infiltration can arise from several different mechanisms. One mechanism is that of a barrier layer. Secondary phases formed on the surface of the anode can block anode active sites and in turn, suppress Ni-catalyzed C-H bond activation and subsequent carbon accumulation in these areas. This description, as proposed in previous reports,^{115,128,142} could partially explain differences in carbon intensity observed on ALT enhanced anodes versus undoped anodes. However, since dopant levels are relatively low (4 wt %) compared to the relative amount of carbon suppression (25%) observed in Figure 4.3, barrier layers are likely not enough to fully

explain the observed differences. Simply stated, the amount of secondary phase material formed is not sufficient to block large areas of the anode and therefore a barrier originating from ALT (or the secondary phases that form) is unlikely to be the sole reason for reduced carbon formation. Also, a substantive anode barrier would significantly limit cell performance by blocking catalytic sites in direct contrast to the *performance improvement* observed in cells having ALT-enhanced anodes as evidenced in initial LSV and EIS benchmark measurements discussed below. Further, cohesive barrier layers are not readily observed in any microscopy from prior studies of ALT addition. Therefore, we propose that alternative mechanisms are the primary contributors to decreased carbon deposition on anodes fabricated with ALT.

Candidate mechanisms include the reforming activity of Al- and Ti-containing secondary phases that will oxidize carbon before observable amounts accumulate. This mechanism is based on numerous studies that report reforming activity of both Al_2O_3 and TiO_2 ,^{74,133,134,136,138,140,141,143} two compounds known to form when ALT-enhanced anodes are reduced.^{34,131} When Ni reacts with ALT the main secondary phase formed is NiAl_2O_4 . However, small amounts of Ni can also react with TiO_2 to create NiTiO_3 .¹³¹ Reduction of these materials results in an anode consisting of Ni metal and Al_2O_3 and TiO_2 . The latter two materials can endow the anode with enhanced reforming capabilities. Additionally, in the presence of Y_2O_3 , TiO_2 can react with ZrO_2 to form a $\text{Zr}_5\text{Ti}_7\text{O}_{24}$ superstructure when the anode is processed.^{144,145} Preliminary impedance measurements performed with this material suggest that it has MIEC properties,⁵⁹ presumably due to mixed valence states of

titanium. MIEC capabilities would expand the triple phase boundary in ALT enhanced anodes and improve overall performance relative to undoped anodes.

Both undoped and ALT enhanced cells confirmed that increasing polarization decreases carbon formation.¹¹⁰ Figure 4.6 shows an example of the changes in G-peak intensity as a result of polarization for an undoped cell. When normalizing G-peak intensities (Figure 4.7), data show that higher overpotentials (higher % of $I_{\max}$) preferentially suppress carbon formation in ALT enhanced cells. Cells with undoped anodes, in comparison, still showed ~25 % of OCV carbon formation at these same polarizations.

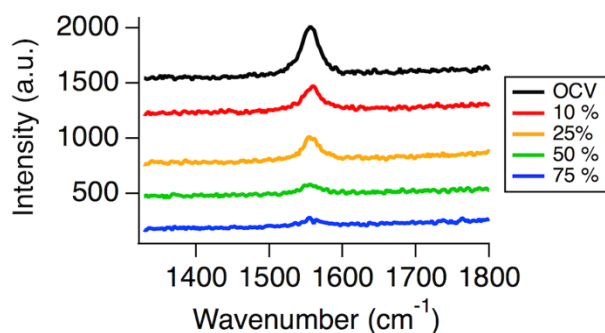


Figure 4.6. Relative intensity of G band for undoped cell at OCV and varying polarization conditions.

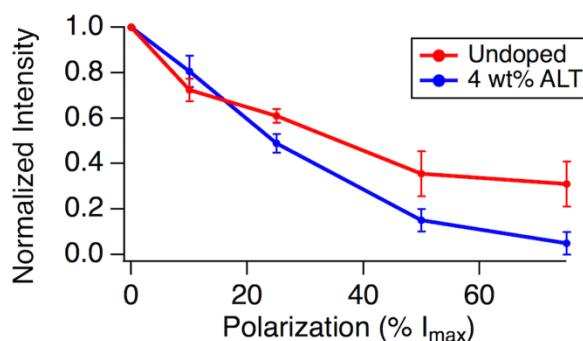


Figure 4.7. Normalized G band intensities for ALT enhanced and undoped anodes at OCV and varying polarizations. Close to no carbon accumulation is seen in doped samples at polarizations beyond 50 % of maximum current.

While the Raman measurements reported in Figures 4.3-4.7 illustrate the ability of ALT-enhanced anodes to suppress carbon accumulation, these results are necessarily limited in their value due to the anode's relatively short exposure times to methane. To examine whether or not the improved carbon tolerance of ALT-enhanced anodes was sustained over longer periods, spectrochronopotentiometry (SCP) methods were used to compare the relative amounts of carbon formation within the anode microstructure in cells operating with methane for 2 and 12 hours under an applied overpotential of 500 mV. Figure 4.8 shows representative electrochemical oxidation SCP traces from ALT-doped and undoped Ni-YSZ cells after 2 hours of CH_4 exposure and after 12 hours of CH_4 exposure. Following operation for 2 hours and 12 hours, the fuel supply was turned off while the cell continued to operate under galvanostatic conditions. Under these circumstances, the only 'fuel' remaining was the carbon already deposited on the anode. Previous studies have directly correlated carbon disappearance from the anode with a steep rise in applied potential as the oxidation half-reaction responsible for current generation

changes from carbon oxidation to nickel oxidation.⁹⁷ Several characteristics stand out in the SCP traces. First, the applied overpotential takes less time to rise to a value consistent with Ni oxidation with ALT-enhanced cells relative to undoped cells. We interpret this result to signify less overall carbon accumulation on the ALT-enhanced cells.

Second, the functional form of the SCP potential is qualitatively different between the ALT-enhanced and undoped anodes. SCP data from ALT-enhanced anodes after both 2 and 12 hours of operation show a steep rise with well-defined ‘equivalence points’ that occur 700 and 725 seconds after the fuel has been turned off. This result implies that electrochemically accessible carbon accumulated in a well-defined and relatively narrow region within the anode. In contrast, SCP data from undoped anodes rises almost monotonically suggesting a spatially broader distribution of carbon throughout the anode that takes much longer to oxidize. While 800 seconds are required for surface Ni to oxidize in ALT enhanced cells, 1400 seconds are required for undoped cells. Using the methods first reported in Kirtley et al.⁵⁹ to calculate electrochemically accessible carbon and the time required for SCP traces to reach 90% of maximum potential rise, we estimate that ALT enhanced cells have ~35% less carbon than undoped cells after 2 hours of CH₄ exposure (7.2×10^{-5} moles C and 1.1×10^{-4} moles C for ALT enhanced and undoped, respectively) and ~75 % less carbon after 12 hours of CH₄ exposure. (7.9×10^{-5} moles for undoped vs. 2.3×10^{-4} moles for ALT enhanced). This result implies that carbon continues to accumulate in the undoped cells but not in cells enhanced with ALT. Raman data showed steady G-peak intensities following the first ~60 minutes of CH₄ exposure in both types of

cells, implying that any carbon that continued to accumulate in the bulk anode microstructure did so beyond the sampling depths accessible to Raman measurements.

Following 12 hours of CH_4 exposure, 1400 seconds were required to see NiO in ALT enhanced cells upon oxidation indicating only a modest buildup of carbon. The time required to cross 0V potential did not drastically change for ALT enhanced cells between 2 and 12 hours of CH_4 exposure suggesting that reforming activity and increased oxygen conductivity attributed to secondary phases limits the amount of carbon that accumulates throughout the anode microstructure. A more quantitative comparison of electrochemically accessible carbon that formed in the anodes showed that operating for 12 hours (compared to 2 hours) resulted in only 10% additional carbon formed on the ALT-enhanced anodes. In comparison, 2500 seconds were required for Ni oxidation after 12 hours of CH_4 exposure in the undoped cell. Relative to the 2 hour measurement, quantitative analysis showed that anodes without ALT accumulated more than 2x more carbon during 12 hours of continuous exposure.

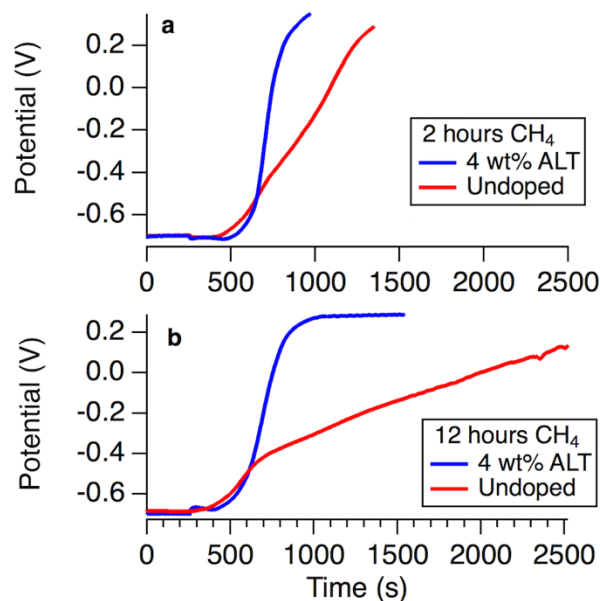


Figure 4.8. SCP traces for ALT enhanced and undoped cells acquired after 2 hours of CH₄ exposure (a) and after 12 hours (b). While more time was required to see NiO in the Raman spectrum for both types of cells after the 12 hour CH₄ exposure, this difference was much more pronounced in undoped cells suggesting further carbon build up with time.

These findings were supported by ex-situ Raman mapping scans across the cross-sections of each type of cells (Figure 4.9). Cells used for Raman mapping were cooled under Ar directly following 2 hours of CH₄ exposure at an applied overpotential of 500 mV, and the amount of carbon formed on each anode was measurably different. G-peak intensities were monitored during cool-down to verify that the amount of observable carbon remained constant, within the limits of temperature dependent spectral intensities. Carbon accumulation maps were generated from Raman data acquired every ~8 μm from the anode edge to the electrolyte-electrode interface. While carbon was noticeable in all spectra from undoped cells, graphite signal was more difficult to locate across the ALT enhanced cells illustrating ALT-enhanced anodes' reduced susceptibility to carbon

accumulation. Figure 4.9 shows a comparison of highest intensity carbon points close to the edge and center of both cell types. G-peak intensities shown at the edge of each line scan are more than double in undoped anodes compared to ALT enhanced anodes. Towards the center of the electrodes the G-peak intensities on undoped anodes decrease in intensity by $\sim 50\%$, while for ALT enhanced anodes this decrease was closer to $\sim 70\%$.

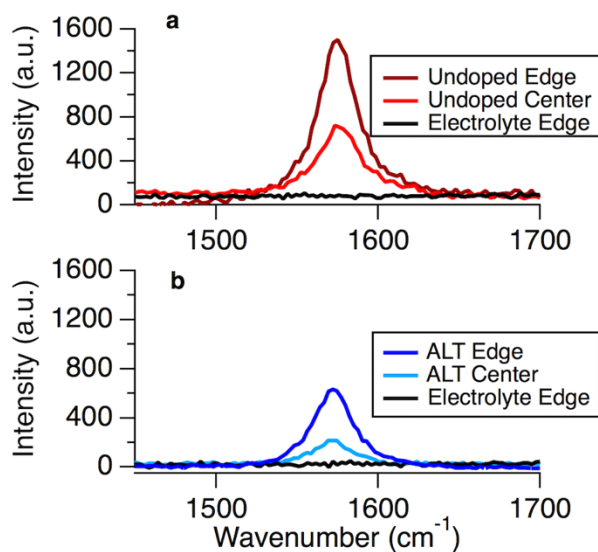


Figure 4.9. Ex-situ Raman mapping scans of anode-electrolyte cross sections. ALT enhanced cells show less carbon accumulation both close to the edge of the anode and within the anode bulk.

Spectroscopic data were correlated directly with overall cell performance using LSV and EIS measurements throughout the course of the SCP experiments to identify cell condition and performance losses as a result of carbon build-up. Raman data in Figure 4.7 show that at $\sim 50\% I_{\max}$, carbon accumulates on both ALT-enhanced and undoped anodes, although the amount of carbon accumulation in ALT-enhanced anodes is considerably less. Figure 4.10 shows representative current and power outputs of cells after initial reduction

and after operating with CH₄ with a 500 mV overpotential for 2 and 12 hours. ALT-enhanced cells consistently outperformed standard, undoped cells, an observation observed previously with pure H₂ and observed for this first time in this study with CH₄. Operation with CH₄ led to decreased performance from undoped cells and performance continued to worsen over time. In contrast, ALT-enhanced cells showed no such degradation, even after 12 hours of operation with CH₄. From these results, we surmise that while a limited amount of carbon forms within the electrochemically active regions in ALT enhanced anodes - as evidenced by the SCP data – most of the carbon that accumulates does so outside of the electrochemically active region leaving cell performance largely unaffected. With the undoped anodes, carbon appears to block electrochemically active sites throughout the electrode microstructure.

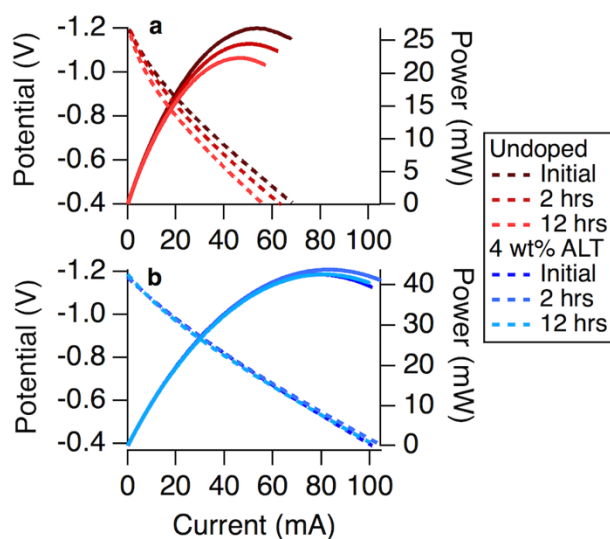


Figure 4.10. LSV comparison of ALT enhanced and undoped cells after initial reduction and after SCP at 2 hours and 12 hours. ALT enhanced cells show better performance and stability after CH₄ exposure and oxidation as compared to undoped cells.

EIS data were also acquired at OCV initially and following each SCP oxidation. Representative Nyquist plots and corresponding Bode plots are shown in Figure 4.11. Bode plots are shown to quantify and highlight visual differences that appear in the Nyquist data. Fitting parameters for the Nyquist plots using a LR(RQ)(RQ) equivalent circuit are listed in Table 4.1. Here, the first resistor (R1) corresponds to the bulk resistance assigned to the high frequency Z_{Real} intercept, the second resistor (R2) corresponds to the electrochemical electrode resistance, and the third resistor (R3) corresponds to the resistance due to gas diffusion.⁶⁹ At OCV, Nyquist data (Figure 4.11a) show much smaller polarization resistance values for cells with ALT enhanced anodes suggesting better overall cell connectivity. This result argues against secondary phases blocking anode active sites as a major mechanism responsible for suppressed carbon formation and instead supports ALT's reaction products with Ni-YSZ (NiAl_2O_5 and $\text{Zr}_5\text{Ti}_7\text{O}_{24}$) as having the ability to function as sintering and reforming aids with possible contributions to improved current collection from a zirconium titanate secondary phase.^{16,105} Bulk resistances (R1) actually improve for both types of cells over the course of 12 hours of operation, implying that carbon accumulation does not result in anode delamination or any sort of oxide ion blocking between the electrolyte and the anode. This result is consistent with previous reports showing that small amounts of carbon can help improve percolation of the electronically conductive Ni phase enabling electrons to quickly reach the current collector.^{110,146} R2 values increase for both types of cells at OCV following CH_4 exposure but the increase is much more pronounced for the undoped anodes. For both types of cells this result likely reflects a loss in catalytic activity resulting from carbon accumulation at triple phase

boundaries. These dramatic changes seen in the Nyquist plot for ALT enhanced cells are emphasized by the appearance of a medium frequency arc at 158 Hz, shown in the Bode plot (Figure 4.11b). This evolution implies that charge transfer mechanisms change as secondary phases become active in the cell resulting in increased reforming and ion/electron transport activity. R3 values (at low frequencies) show a predictable increase for both types of cells as carbon accumulated in the anode microstructure impedes mass transfer. Since cathodes are identical for both ALT enhanced and undoped samples, the overall lower R2 and R3 values for ALT enhanced cells are assumed to result directly by the conductive and reforming properties of the secondary phases in the ALT-enhanced anodes.

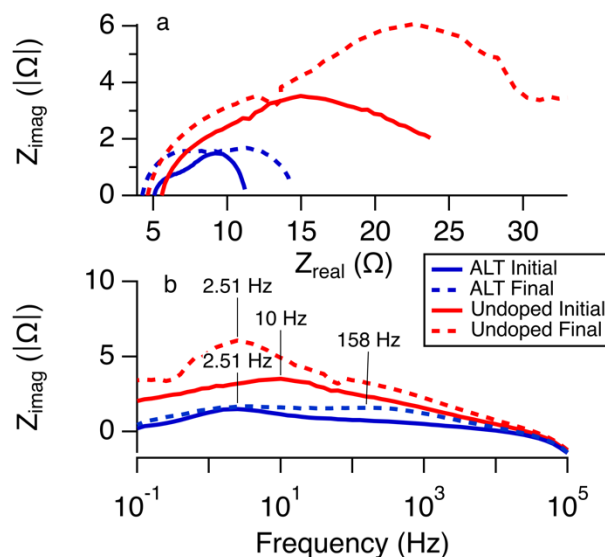


Figure 4.11. EIS data acquired at OCV before and after carbon exposure shown in a Nyquist plot (a) and Bode plot (b). Key frequencies are highlighted in the Bode plot to emphasize the structural differences seen in the Nyquist arcs.

Table 4.1. Resistance value fits of EIS data collected at OCV

	Undoped			4 wt% ALT Doped		
	R1(Ω)	R2(Ω)	R3(Ω)	R1(Ω)	R2(Ω)	R3(Ω)
Initial OCV (0 hrs)	4.98	8.4	20.6	4.82	3.2	3.27
Post SCP (12 hrs)	4.12	21.44	21.8	4.03	6.05	4.67

Conclusion

The work described above shows that ALT doping of standard Ni-YSZ SOFC anodes yields increased tolerance to coking from hydrocarbon fuels. Characterization of these systems has provided insight into how the secondary phases formed following ALT doping prevent carbon from accumulating in functioning devices. In this work we conclude that secondary phases have the ability to prevent carbon deposition by several different mechanisms. Past research has credited similar observations to the creation of barrier layers that prevent carbon deposition. While we maintain that barrier layers may, indeed, prevent carbon accumulation, these effects are small and cannot account for the improved performance and durability observed in ALT-enhanced anodes during operation. Specifically, results presented in this work point to different secondary phases formed from ALT decomposition serving both as a reforming substrate (Al_2O_3) and as a mixed ion-electron conducting material ($\text{Zr}_5\text{Ti}_7\text{O}_{24}$). Spectroscopic data shows that less carbon forms on the surface of the ALT enhanced anodes under both OCV and polarized conditions. Spectrochronopotentiometry as well as ex-situ Raman mapping also show that ALT doping

limits the amount of carbon that accumulates within the bulk of the anode and that the majority of carbon that forms within the ALT enhanced anodes does so outside of the electrochemically active regions. In conclusion, this work highlights how small changes to SOFC anode composition and processing can have substantial effects on the stability and performance of the overall cell.

Acknowledgment

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CHAPTER FIVE

WHAT DOES CARBON TOLERANT REALLY MEAN? *OPERANDO*
VIBRATIONAL STUDIES OF CARBON ACCUMULATION ON NOVEL SOLID
OXIDE FUEL CELL ANODES PREPARED BY INFILTRATION

Contribution of Authors and Co-Authors

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WHAT DOES CARBON TOLERANCE REALLY MEAN? *OPERANDO*
 VIBRATIONAL STUDIES OF CARBON ACCUMULATION ON NOVEL SOLID
 OXIDE FUEL CELL ANODES PREPARED BY INFILTRATION

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Abstract

Operando Raman spectroscopy and electrochemical techniques were used to examine carbon deposition on niobium doped SrTiO₃ (STN) based SOFC anodes infiltrated with Ni, Co, CGO and combinations of these materials. Cells were operated with CH₄/CO₂ mixtures at 750 °C. Raman data shows that carbon forms on all cells under operating conditions where Ni is present as an infiltrate. Additional experiments performed during cell cool down, and on separate material pellets (not under electrochemical potential), show that chemically labile oxygen available in the CGO infiltrate will preferentially oxidize all deposited surface carbon as temperatures drop below 700 °C. These observations highlight the benefit of CGO as a material in SOFC anodes but more importantly, the value of *operando* spectroscopic techniques as a tool when evaluating a material's carbon tolerance. Solely relying on *ex-situ* measurements will potentially lead to false conclusions about the studied materials' carbon tolerance and improperly inform

efforts to develop mechanisms describing electrochemical oxidation and material degradation mechanisms in these high temperature energy conversion devices.

Introduction

High temperature energy conversion systems such as solid oxide cells (SOCs) are an attractive technology for efficient energy conversion as they can operate in both fuel cell and electrolysis mode creating a self-contained energy system with net zero emissions when coupled with renewable fuel sources. When operated as a solid oxide fuel cell (SOFC), these devices have a higher electrical efficiency relative to commercially available low temperature proton exchange membrane fuel cells (PEMFCs), and can approach efficiencies of 90% in combined heat and power applications.^{8,52–55} Their real advantage, however, is their fuel flexibility. Because SOFCs typically operate at temperatures above 600°C with non-precious metal catalysts, they can use a wide range of carbon-containing fuels including CH₄, syngas, biogas, and higher molecular weight hydrocarbons. In order to leverage this advantage, however, SOFC anodes must be resistant to carbon accumulation (also known as coking) during operation. The traditional SOFC anode uses Ni as its electrocatalyst, and in SOFCs anode coking can take the form of carbon filaments, highly ordered graphite or disordered graphite. While small amounts of carbon have proven to be beneficial in some circumstances,^{22,110,114,147} more extensive carbon accumulation leads to electrode failure by both impeding gas transport and blocking catalytically active sites, thereby limit the cell performance.^{113,114} Additionally, irreversible metal dusting caused by carbon reacting with the Ni itself can occur leading to complete anode

disintegration.¹¹⁸ As a result of Ni's susceptibility to carbon-induced degradation, development of carbon tolerant, conducting materials has become a priority for SOFC development and high temperature materials research.

Commercial SOFC anodes are typically composed of a Ni-YSZ cermet in order to provide both electrical and ionic conductivity as well as a thermal expansion coefficient match to the electrolyte. As an electrocatalyst Ni is affordable, stable under typical operating conditions, and offers exceptional electrical conductivity and catalytic activity compared to other anode candidates.^{4,8,58,111} Despite these benefits, however, Ni's high efficiency for C-H bond activation leaves the anode susceptible to carbon accumulation. Adding steam to the fuel mitigates carbon formation^{119,120} but at the risk of oxidizing the Ni and limiting overall performance by decreasing the device's operating voltage. Additionally, Ni has been shown to drive carbon accumulation even under conditions not predicted by thermodynamics including for steam to carbon ratios > 1 .¹⁴⁷ Another alternative for mitigating carbon formation is to reform the hydrocarbon fuel upstream of the fuel cell. This additional fuel processing, however, lowers overall cell efficiency.¹⁰⁹ Consequently, numerous efforts have been devoted to developing materials-based solutions that prevent – or at least limit – carbon accumulation on fuel cell anodes. These tactics have ranged from complete replacement of the original Ni-YSZ cermet to more subtle material modifications.^{74,80,127}

Materials such as copper, ceria, and mixed ionic electronic conducting (MIEC) perovskites are unable to match Ni's catalytic activity, but these materials have shown promise in their ability to operate directly with hydrocarbons fuels.^{67,123,124,148} While high

anode catalytic activity is important, improved carbon tolerance could arguably compensate for performance losses. Perovskite materials stand out as possible replacements for Ni-YSZ cermet anodes. One example is donor-doped, strontium titanate (SrTiO_3 , STO). Doped-STO materials have relatively high electronic conductivity and stability under reducing atmospheres, as well as tolerance to both carbon and sulfur.^{29,149–}

¹⁵¹ STO's main drawback is its low electrocatalytic activity, ionic conductivity and correspondingly poor performance as a fully functional anode. A number of studies have added electrocatalytically active infiltrates such as Pd or Ni, together with oxygen ion conducting CGO to STO electrodes and have reported reasonable performance compared to state of the art Ni-YSZ anodes.^{151,152}

The studies described below investigate whether or not niobium doped-STO (STN) anode scaffolds infiltrated with mixtures of nano-sized catalysts are truly carbon-tolerant. The use of nano-sized catalysts has multiple benefits although their effects are limited by coarsening at SOFC-relevant operating temperatures. In principle, cermet anodes would be most efficient if they consisted of a percolated network of nano-scale catalyst particles.^{153,154} Material combinations of Ni, Co and CGO were used as catalysts as these materials have demonstrated carbon tolerance under open circuit and single atmosphere conditions in previous work.¹⁵⁵ Additionally, CGO based catalysts have been one of the most extensively studied anode materials for SOFCs operating directly with hydrocarbon fuels.^{22,123,156–158} Many studies have claimed good performance with Ce based systems with little to no reported carbon accumulation.^{32,121,125,159–162} These same studies, however, base

their claims largely on indirect or *post mortem* analyses of whether or not carbon is observed on the decommissioned anodes.

Findings presented in this work employ *operando* vibrational Raman spectroscopy to explore directly carbon formation on functioning STN electrodes infiltrated with CGO, Ni and Co and combinations of these materials at 750 °C under varying atmosphere and electrochemical conditions. Data show that in anodes containing infiltrated Ni, either by itself or in combination with other nanocatalysts, carbon accumulates when exposed to CH₄. Carbon persists on STN anodes infiltrated solely with Ni when the anode is cooled to room temperature. On STN anodes co-infiltrated with either Ni-CGO or Ni-Co-CGO, however, any observed carbon that forms at operational temperatures disappears as the cell cools. Additional experiments using simple material pellets show that while carbon can be homogenously distributed throughout an anode at operating temperatures, oxygen available in CGO remains chemically labile during cool down and oxidizes deposited carbon leading to the false impression that the anodes were resistant to carbon accumulation during operation. These findings, therefore, highlight the importance of using *operando* optical techniques when drawing conclusions about a material's carbon tolerance.

Experimental

The SOFCs used in this work were electrolyte-supported cells. The Sc₂O₃, stabilized ZrO₂ electrolyte (Nippon Shokubai Co., Ltd, Japan) of ca. 150 µm thickness was laser cut to 26 mm diameter. Onto this electrolyte, a Sr_{0.94}Ti_{0.9}Nb_{0.1}O₃ (STN) porous

backbone was deposited through spray deposition. The slurry for the deposition was prepared using STN powder (prepared in the lab through solid state mixed oxide method), PVP_{10,000} dispersant/binder and ethanol solvent. After deposition, the backbone was sintered in air at 1200 °C for 8 hours. Subsequently, a La_{0.6}Sr_{0.4}CoO₃ (LSC) (Kusaka, Japan) – Ce_{0.9}Gd_{0.1}O₂ (CGO) (Rhodia GmbH, Germany) composite cathode was screen-printed on the opposite side of the electrolyte and sintered in air at 930 °C for 24 hours. Anode electrocatalysts comprised of Ni or Co or Ni-Co and CGO were added to the STN backbone by infiltration. The infiltration solutions were prepared in the following way: at first, a 3M CGO aqueous solution was prepared using corresponding metal nitrates. To this solution, nitrate precursors of the Ni or Co or Ni-Co metals were added in the ration of 90:10 by weight. The procedure for infiltration is described elsewhere.¹⁶³ After infiltration, the cells were calcined at 350 °C for 2 hours to decompose the metal nitrates. Finally, a cathode current collection layer, LSC, was screen-printed on the LSC-CGO cathode. A schematic diagram of the completed cells can be seen in Figure 5.1 together with an SEM image of the infiltrated anode. A corresponding list of the complete fuel cell samples is shown in Table 5.1 below.

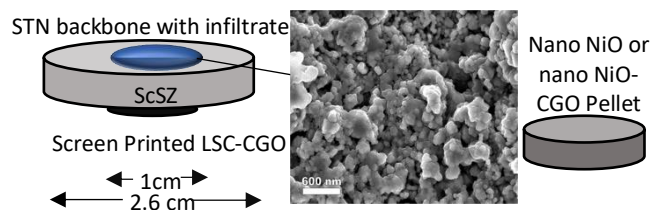


Figure 5.1. Schematic representation of membrane electrode assemblies (with accompanying SEM image) and chip materials used for experiments.

Table 5.1. Summary of membrane electrode assemblies with catalyst loading percentages and the weight gained by infiltration.

Sample Name	Catalyst	Loading (wt. %)	Weight gain (mg)
Ni	Ni	100	0.50± 0.2
Ni-CGO	Ni; CGO	10; 90	0.78± 0.08
Co-CGO	Co; CGO	10; 90	0.63± 0.24
Ni-Co-CGO	Ni; Co; CGO	5; 5; 90	0.58± 0.33
Ni-Co-CGO	Ni; Co; CGO	10; 10; 80	0.40± 0.12
Ni-YSZ	Ni; YSZ	40; 60	n/a

Current collectors consisting of gold wire (Alfa Aesar) attached to a gold mesh (Alfa Aesar) were attached to both electrodes with gold paste (Heraeus). The cells were then attached to a 2.6 mm diameter YSZ tube using ceramic paste (Aremco Products Inc). The YSZ tube was enclosed in a quartz tube and sealed with a rubber stopper. Detailed descriptions of the experimental set up can be found in previous publications.^{51,114} The assembly was then placed into a tube furnace for heating. Raman spectra were acquired using a Renishaw InVia spectrometer coupled to a 30 mW, 488 nm Ar-ion laser with 30-60 second exposures. Backscattered light was directed through an edge filter with a 150 cm⁻¹ low frequency cut off. Table 5.2 presents Raman modes and main peak assignments of the materials discussed in the Results section below. Electrochemical measurements were collected using a Princeton Applied Research VersaStat MC.

Table 5.2. Raman modes and peak assignments of materials present in Results below. Frequencies are accurate to $\pm 3 \text{ cm}^{-1}$.

Phase/Species	Raman Modes	Main Peak(s) Room Temperature (cm^{-1})
YSZ	F_{2g}	619
CGO	F_{2g}	463
NiO (Nano)	LO	500
NiO (Micron)	2LO, (2M)	1090, (1490)
STO	TO	415, 780
C (Graphite)	E_{2g}	1350, 1585, 2700

All cells were heated to $750 \text{ }^{\circ}\text{C} \pm 5 \text{ }^{\circ}\text{C}$ at a ramp rate of $1 \text{ }^{\circ}\text{C}/\text{min}$ under 20 sccm Ar on the anode and 20 sccm Air on the cathode. Once at temperature, gas flows were increased to 100 sccm Ar and 85 sccm Air. Anodes were then reduced under 100 sccm humidified H_2 (3% H_2O) and anodes were considered fully reduced when the open circuit voltage stopped changing (-1.10 V). Once the anode was reduced, benchmark electrochemical measurements were performed including linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) with humidified H_2 . EIS measurements were collected with an AC voltage amplitude of 0.001 V over a frequency range of 1 MHz to 0.1 Hz . LSV measurements were carried out between 100% and 20% of the measured OCV in order to avoid cell damage and were collected using a sweep rate of $0.1 \text{ V}/\text{sec}$. Carbon exposure experiments were performed under 4 different anode atmospheres of varying CO_2 and CH_4 compositions totalling a flowrate of 100 sccm: 70% CO_2 / 30 % CH_4 , 50 % CO_2 /50% CH_4 , 25 % CO_2 /75% CH_4 , and 100% CH_4 . As polarization conditions can influence carbon deposition^{164,165} in addition to CH_4 - CO_2 ratios, EIS measurements were collected under each gas composition at 3 fixed current conditions including polarization of 85%, 40%, and 10% of the maximum current density

obtained by the LSV. The effects of STN infiltration and carbon accumulation on the electrochemical performance of the cells will be addressed in a future report. Raman kinetic measurements were collected for each set of conditions with 30 second exposure times. Carbon removal between sets was carried out using humidified Ar followed by reduction and benchmark measurements under humidified H₂. This procedure was performed between different gas compositions even when carbon was not observed. All cells were cooled under Ar in order to preserve the chemical composition of species across the anode for post-operation *ex-situ* Raman spectroscopy.

Materials used for chip studies (Figure 5.1) included commercially available nano-NiO and CGO powders (JT Baker). Pellets were pressed with a 1.27 cm diameter from either 100% NiO powder or mixture of 10 wt. % CGO (Gd_{0.2}Ce_{0.8}O_{1.95}) and 90 wt. % NiO. Pellets were sintered at 1400 °C with a ramp rate of 5 °C/min and a 1 hour dwell time. Chips from sintered pellets were attached to a closed YSZ disc using a small amount of ceramic paste (Aremco Products Inc). The final assembly for heating was equivalent as to described above. Chips were heated to 750 °C ± 5 °C before being exposed to 100 sccm of CH₄ for 10 minutes to match the exposure times in full cell experiments. Clear evidence of carbon accumulation based on Raman spectra was apparent within ~3 minutes. Chips were then cooled under a pure Ar environment with Raman spectra being acquired continuously to monitor compositional changes occurring under the inert atmosphere.

Results

Operando observations of differences in carbon tolerance.

Experiments described in this work sought to investigate the carbon tolerance of nano-infiltrated STN-based SOFC anodes exposed to different CH₄/CO₂ mixtures under different applied overpotentials. The different infiltrated nanoparticle samples included pure Ni, Ni-CGO, Co-CGO, and bimetallic Ni-Co-CGO. Coupling electrochemical methods with *operando* Raman spectroscopy has proven to be an effective method for measuring carbon tolerance,⁵⁹ as any accumulated carbon will give rise to a strong Raman vibrational feature at 1560 cm⁻¹ as shown in Figure 5.2. This vibrational mode corresponds to highly ordered graphite on the cell surface and is often referred to as the “G-band”. In addition to this feature, Raman vibrational modes at 1350 cm⁻¹ and 2699 cm⁻¹ assigned to disordered graphite (“D-band”) and vibration-phonon coupling (“2-D band”), respectively, also appear in Figure 5.2. (The lower frequency feature at ~600 cm⁻¹ is due to the YSZ substrate.) Raman bands assignments and frequencies relevant to the present study are cited in Table 5.1. Correlating carbon accumulation on anodes with changes in EIS and voltammetry data has provided insight into the effects of carbon on electrochemical oxidation, mass transport and material degradation.^{120,155,165}

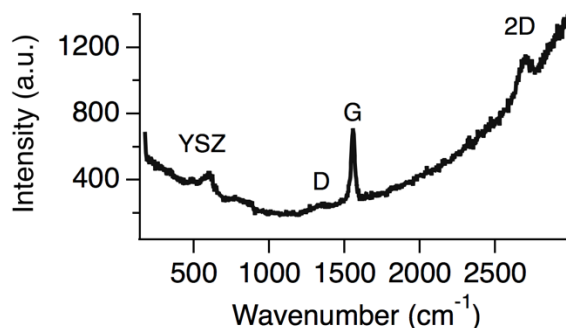


Figure 5.2. Representative Raman spectrum of reduced Ni after exposure to CH₄. The G-band visible at 1560 cm⁻¹ is used in this study to confirm carbon accumulation. This spectrum was acquired at 750° with an acquisition time of 30 sec.

All experiments in this work were performed at 750 °C and carbon accumulation was monitored using mixtures of CO₂ and CH₄ at ratios of 30:70, 50:50, 75:25, and 0:100% CH₄. Every sample was exposed to the gas ratios at 85%, 40%, and 10% of each cell's maximum current ($I_{\max}$) for 10 minutes each. These electrochemical conditions will be referred to as high, medium and low current conditions, respectively. In previous reports, a 10 minute exposure to CH₄ has shown significant carbon accumulation on traditional Ni-YSZ cermet anodes.^{108,110,114} Continuous Raman measurements were performed to track the growth of the G-band. Mixtures of CO₂ and CH₄ did not lead to any spectroscopically observable carbon on any of the cell surfaces; carbon was only observed with 100% CH₄ conditions. These results indicate that addition of CO₂ to the inlet fuel stream suppresses carbon accumulation and is consistent with several past studies showing that at temperatures above 700°C, CO₂ in the incident fuel leads to dry reforming reactions that remove deposited carbon.^{108,166,167} Dry reforming is thermodynamically favored at temperatures above 730°C assuming standard state partial pressures of reactants and

products. As no carbon was observable even at the lowest CO₂ ratios (25%) in the current studies, our observations implies that CO₂ dry-reforming occurred faster than CH₄ decomposition.

Figure 5.3 shows Raman kinetic traces comparing carbon accumulation rates on all cells exposed to pure CH₄ at high, mid and low currents. The kinetic traces are a compilation of Raman scans collected every 30 seconds where the height of the G-band is measured individually from each spectrum. Changes in the kinetic data between cells having the same anode composition and tested at different current densities are the result of the different electrochemical polarization conditions driving more or fewer oxides to the anode. Comparing different samples operating with the same polarization conditions illustrate how effectively the infiltrated nanoparticles catalyze C-H bond activation.

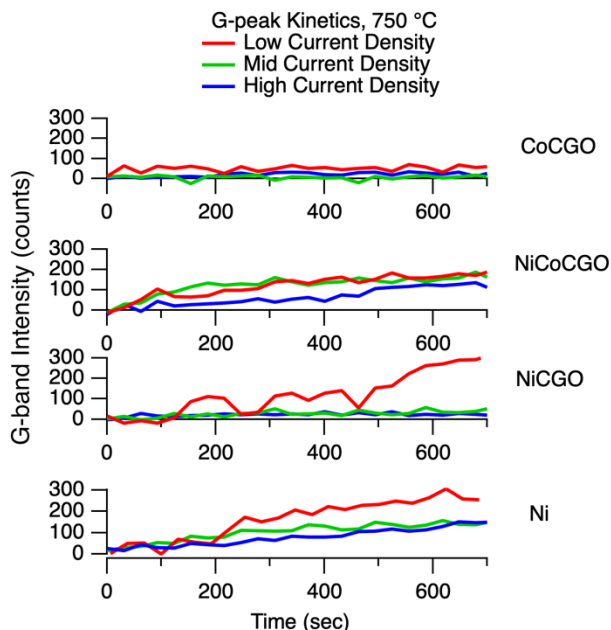


Figure 5.3. Representative Raman kinetic traces of G-band appearance at 100% CH₄ conditions under all studied polarizations. CH₄ exposure started at time 0. While Co-CGO samples showed no sign of carbon accumulation under any conditions, carbon was continuously visible in Ni containing samples.

Data in Figure 5.3 show clearly that carbon accumulation occurred in all samples where Ni was present, even in combination with other infiltrates. This result emphasizes Ni's strong propensity towards C-H bond activation even when present only in small amounts. Samples infiltrated solely with Ni consistently showed the most carbon under all polarization conditions with counts exceeding 300 under low current conditions. (The "counts" label refers to the G-peak Raman intensity. Previous work from our lab has shown G-peak intensities correlate linearly with the amount of electrochemically accessible accumulated carbon).¹¹⁰ Note that the low nanoparticle loadings on the STN scaffolds did not provide sufficient percolation for the nanoparticles themselves to serve as a SOFC anode.

Co-infiltrated Ni-CGO samples repeatedly showed little carbon formation at high and mid polarization, but increased carbon accumulation at low polarizations with counts just below 300. Comparing the Ni only and Ni-CGO samples illustrates that addition of CGO to the anode microstructure decreases the amount of deposited carbon. This effect can be attributed both to CGO's relatively high ionic conductivity under reducing conditions, as well as its oxygen storage capacity (OSC). This effect was also observed for the bimetallic infiltrated sample, Ni-Co-CGO. While slight carbon accumulation was observed under each polarizing current, counts never exceeded 200 for these samples. With low current conditions Ni-Co-CGO anode showed even less carbon accumulation compared to Ni-CGO but carbon was nevertheless present. Co-CGO infiltrated anodes showed no signs of any observed carbon accumulation, even with 100% CH₄ conditions at low currents. While Co has been cited as a carbon tolerant electrocatalyst,^{115,168} Co-CGO's poor electrochemical performance identified in these studies and illustrated in Figure 5.4, however, implies that Co has very little catalytic activity towards C-H bond activation. These findings caution against complete replacement of Ni with Co in the quest to develop high efficiency, carbon tolerant SOFC electrode materials.^{122,125,126}

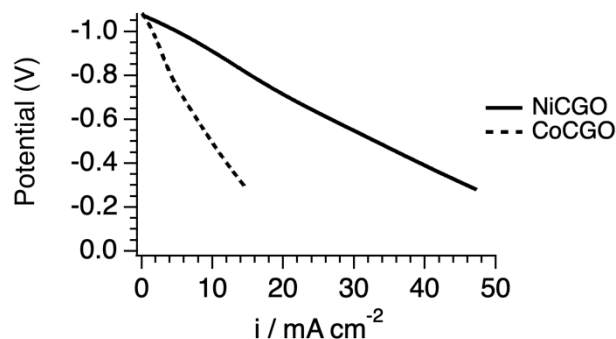


Figure 5.4. Representative LSV traces of cell with Co-CGO anode compared to Ni-CGO anode measured in humidified H_2 at 750°C .

Infiltrated STN ceramic electrodes studied in this work were fabricated to decouple the electrocatalytic phase from the electronic conducting phase. This strategy has become popular in the quest to develop carbon tolerant MIEC materials for SOFC electrodes.^{154,169,170} Infiltrates were added to the porous STN backbone in order to improve the materials' electrocatalytic capability. In order to compare carbon's tendency to accumulate on infiltrated STN electrodes relative to traditional Ni-YSZ cermet anodes comprised of μm sized Ni and YSZ particles,^{171–174} equivalent experiments were performed using internally manufactured, electrolyte supported SOFCs having a Ni-YSZ cermet anode. Under pure methane conditions and low polarization a standard Ni-YSZ anode showed more than double the counts of G-band intensity in the Raman spectra compared to the Ni based, nano-infiltrated anodes shown in Figure 5.3. Traditional Ni-YSZ cermets also showed evidence of carbon deposition at low current conditions when exposed to a mixture of 75% CH_4 and 25% CO_2 (Figure 5.5). While nano-infiltrated anodes show Raman signal only within the limit of noise (~ 20 counts) with this CH_4/CO_2 balance, an average of 60 counts was seen for G-peak formation in the standard Ni-YSZ anode.

Admittedly, the Ni-YSZ cermet anode had considerably higher Ni content than the Ni-infiltrated STN electrode, leading to greater susceptibility for carbon accumulation. Nevertheless, this comparison served its purpose in comparing carbon tolerances between the infiltrated ceramic electrodes designed to be carbon tolerant and a traditional SOFC anode. Furthermore, these studies show that even those electrodes having low Ni-content are susceptible to coking.

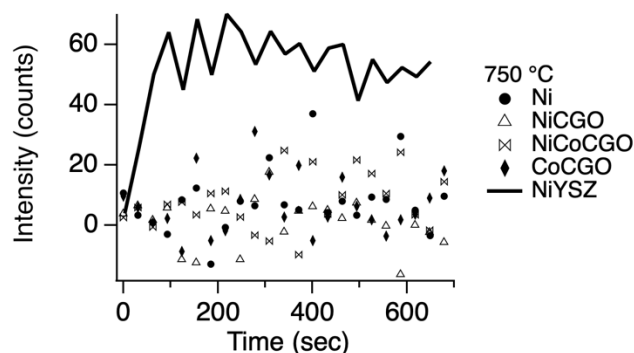


Figure 5.5. Raman kinetics of G-band intensity upon exposure to a fuel mixture of 75% CH₄ and 25% CO₂. While nano-infiltrated catalysts do not show any sign of carbon deposition, a standard Ni-YSZ anode shows a stable G-band intensity of ~60 counts.

Carbon disappearance during cooling.

Raman spatial sampling was used to examine the homogeneity of carbon deposition on the nano-infiltrated anodes with measurable G-band intensity. Figure 5.6 shows a representative Raman spectrum collected at various locations across a Ni-CGO anode following final benchmark measurements at low current, 100% CH₄ conditions at 750°C. The spectra show a homogenous distribution of carbon across the anode surface regardless of measurement location. While carbon is clearly present across the anodes at operating temperatures, *no carbon signal was observed on these same samples after cool down under*

argon. Based on these findings, any analysis of the infiltrated STN electrodes used in this work based on *ex situ*, *post-mortem* analyses would conclude that all electrodes other than the Ni-only infiltrated anode are carbon tolerant, despite the *operando* vibrational spectroscopy data that shows clear carbon accumulation on the Ni-CGO and Ni-Co-CGO during operation. Following disassembly and *post-mortem* analysis, Raman signal from the STN-itself and anode infiltrates (CGO, primarily) were still visible, and *ex-situ* SEM analysis showed no obvious changes in anode microstructure suggesting that carbon removal occurred without significant changes to other anode materials. In order to investigate this observation further, two Ni-Co-CGO cells were independently heated up to 750 °C and exposed to CH₄ at low current conditions. Following carbon exposure and G-band appearance, fuel environments over *both* electrodes were switched to Ar in order to prevent carbon removal due to imperfect seals between the anode and cathode chambers and/or continued oxide diffusion through the electrolyte. Cells were cooled under these conditions and G-band intensities were monitored in order to identify any changes in accumulated carbon as the temperature returned to ambient conditions.

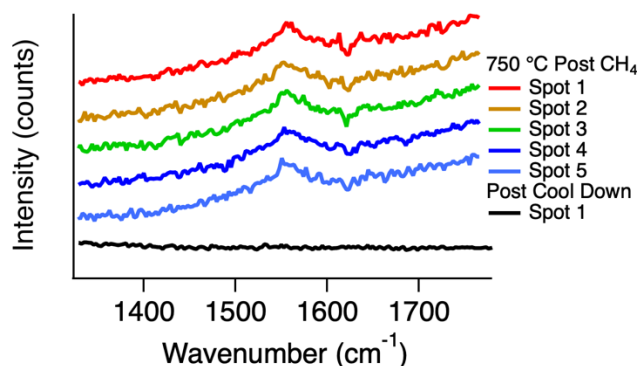


Figure 5.6. Raman measurements with 30 sec exposure time collected at various locations across Ni-CGO anode surface (average of 1 mm spacing) including close to fuel inlet, close to current collector, and anode edge and centre.

Figure 5.7 shows the changes in G-band intensity as a function of temperature as the Ni-CGO cells cooled. Cells were cooled at a rate of $\sim 2.5^{\circ}\text{C}/\text{min}$ and the total time in Figure 5.7 (including top right inset) amounts to a ΔT of $\sim 120^{\circ}\text{C}$. After 25 minutes (1500 sec) of cooling (anode temperature of $\sim 690^{\circ}\text{C}$), very little intensity was observed in the G-band. A challenge when making these measurements was maintaining an optimal focus for the Raman excitation laser. As the temperature cooled, thermal expansion changed the sample height sufficiently to become a second source of signal loss. The microscope field of view was re-focused after 27 minutes to re-optimize G-band signal. While some signal was measurable (~ 80 counts) this number continued to decrease upon continued cooling (inset, Figure 5.7). Because traditional Ni-YSZ and infiltrated Ni-only anodes both repeatedly show visible anode coking in *post-mortem* analyses when cooled under equivalent conditions, carbon removal on the infiltrated samples must be explained by differences in material composition between the Ni-only, Ni-YSZ cermet anode and the nano-co-infiltrated STN. As STN is not catalytically active towards CH activation,¹⁵¹

carbon related changes must be due to the infiltrates. In order to investigate whether carbon removal upon cool down was a result simply of Ni particle size, chip studies of nano-sized NiO were conducted. Co was not considered for these studies as Co-CGO infiltrated samples had proved carbon tolerant during operation. Figure 5.8 shows Raman spectra of a NiO chip comprised of nano-sized particles. The peak at 500 cm^{-1} , a signature of nano-NiO,^{42,175} confirms that the particles did not undergo significant coarsening during sintering. Figure 5.8 shows clearly that carbon deposition occurs at $750\text{ }^{\circ}\text{C}$, and carbon remains during cool-down *and* during *post mortem* analysis. Therefore, carbon loss upon cool down cannot be attributed to differences in catalyst size.

Based on these observations, we attribute carbon disappearance from Ni-CGO and Ni-Co-CGO infiltrated anodes to the CGO itself. This material is the only apparent oxygen source in the infiltrated STN anodes as Ni and Co are both reduced to pure metal catalysts at the start of the study and then preserved as zero-valent elemental materials during cool-down. CeO₂ based materials are widely used in a variety of catalyst applications because of their oxygen storage capacity. Ceria's well-known, labile Ce⁴⁺/Ce³⁺ mixed valence at high temperatures and low P_{O2} leads to MIEC capabilities.^{176,177} Below 700°C , CGO is nearly a pure ionic conductor^{176,178,179} and these conditions, where little electronic conductivity is observed, could explain the observed Raman kinetics and the oxidation of carbon in the studied samples when temperatures approached $700\text{ }^{\circ}\text{C}$ and below. Electronic conductivity would enable materials to remain reduced, while lack of electronic conductivity but continued ion conductivity could, conceivably provide a path leading to carbon oxidation. The potential of CGO to oxidize carbon by active lattice oxygen species,

even under low partial pressures of oxygen has been reported elsewhere.^{25,180} Additionally, synergistic effects with Ni have been found to enhance the ability of ceria to oxidize carbon.¹⁸¹

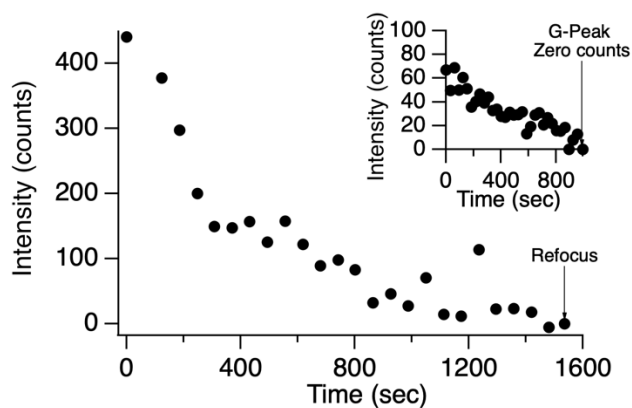


Figure 5.7. Representative Raman kinetics of G-band intensity during cell cool down following Ni-CGO anode exposure to CH₄ at near OCV conditions. The inset shows kinetics following a Raman re-focus after the initial 1600 seconds.

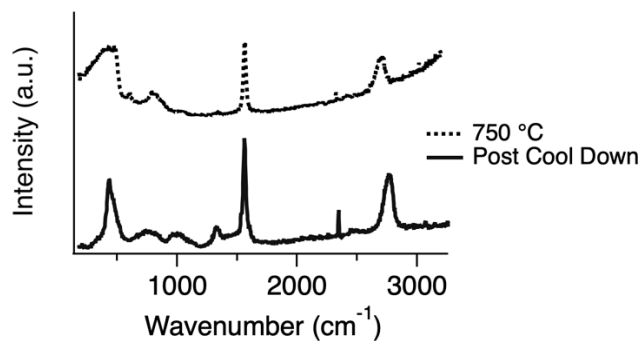


Figure 5.8. Raman extended scans showing surface of nano-NiO chip after exposure to CH₄ at temperature and post cool down.

To investigate the role of CGO in C-removal, a sample consisting of nano-sized NiO (90%) and CGO (10%) was prepared and subjected to the same testing procedure as the nano-NiO chip described above. The results for the NiO-CGO chip show clearly that

G-band intensity decreases dramatically between 700 °C and 675 °C, with no measurable G-band intensity at 650 °C (Figure 5.9). Carbon disappearance coincides with a dramatic increase in the intensity of the CeO₂ F_{2g} Raman peak at 460 cm⁻¹. Figure 5.10 shows measurements comparing the chip's surface composition prior to heat up (top trace) where NiO and CGO signals are prominent, after CH₄ exposure at 750 °C showing clear G-band intensity (middle trace), and after cool down (bottom trace). Curiously, the bottom trace of Figure 5.10 shows no sign of Ni oxidation eliminating any suspicion of surface oxidation due to a leak or oxide flux through the sample. This result instead suggests a mechanism for carbon removal that utilizes the labile oxygens in CGO, but these same species are not sufficiently labile to oxidize Ni. Smaller CeO₂ nanoparticles support this theory as they exhibit even greater relative oxygen storage capacity given to their larger relative surface areas.¹⁸² Comparing redox potentials of the CO₂/C_(s) couple with that of NiO/Ni, thermodynamics predict that carbon would be preferentially oxidized when compared to Ni¹⁸³ as the equilibrium potential for the NiO/Ni couple is less favourable (-0.73 V) compared to that of the CO/CO₂ product couple (-0.99 V).^{8,22} These predictions have been experimentally validated by several *in situ* studies.^{59,80,184} We assume that had more carbon accumulated on the samples, such as the amounts seen on Ni-YSZ cermet-based cells, complete carbon oxidation might not have been possible, but a decrease in *post mortem* Raman signal compared to *operando* signals would still be expected. Studies claiming that CeO₂-based catalysts are carbon tolerant^{32,121,125,137,160,162} should therefore consider carefully the chemistry that can occur during cool-down and how changes in catalyst

reactivity might impact *post mortem* analyses relative to what is observed in direct, *operando* measurements.

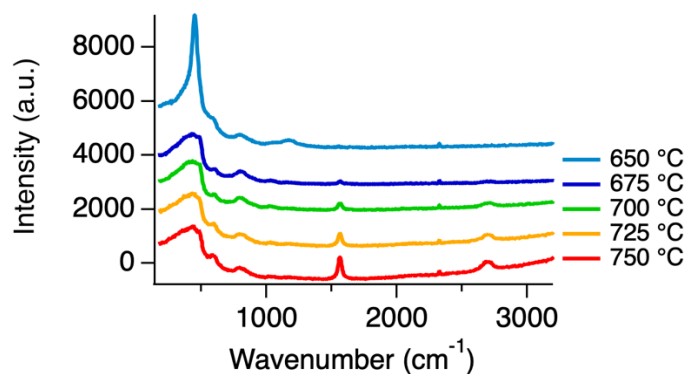


Figure 5.9. Raman extended scans of nano NiO (90%) CGO (10%) chip taken during cool down to track changes in the g-band at $\sim 1560 \text{ cm}^{-1}$.

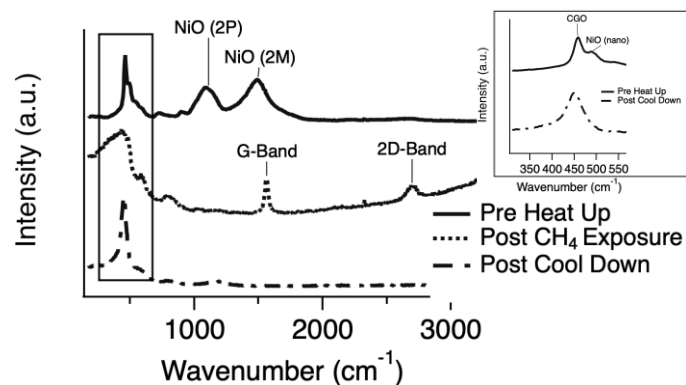


Figure 5.10. Comparison of Raman extended scans of nano NiO (90%) and CGO (10%) chip prior to heat up, at $750 \text{ }^{\circ}\text{C}$ after CH_4 exposure and post cool down. Raman g-band present at temperature is not visible post cool down.

Conclusions

Operando spectroscopic data presented above demonstrate that assumptions about SOFC electrode properties based on *ex-situ* measurements may fail to capture relevant surface chemistry that occurs when carbon containing fuels are being electrochemically

oxidized. Vibrational Raman data show the importance of acquiring real-time, materials-specific information about SOFC electrodes in order to determine anode carbon tolerance. In the present work a novel anode design based on infiltration of Ni, Co, and CGO into an STN backbone was investigated. All anodes tested in this study proved carbon tolerant when CO_2 was present in the fuel stream in combination with CH_4 . Under pure CH_4 conditions all anodes except for ones infiltrated with Co-CGO showed that carbon accumulated at 750°C . Carbon accumulation on the surface of these samples, however, was much less than that observed in Ni-YSZ cermet anodes. While the current study has proven that carbon will accumulate where Ni is present, quantifying the amount of carbon based on Ni particle size remains a challenge for future work. In addition to confirming carbon formation on the infiltrated STN anodes, results also demonstrated that CGO in the anode functioned as an oxygen reservoir upon cool down. This behavior led to oxidation of the surface carbon present during cool down. While questions remain about how to improve the electrochemical performance of the studied cells to make them competitive with conventional SOFC materials, the increase in carbon tolerance can help drive future studies.

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CHAPTER SIX

OPERANDO CHARACTERIZATION OF METALLIC AND BIMETALLIC
ELECTROCATALYSTS FOR SOFC FUEL ELECTRODES OPERATING UNDER
INTERNAL METHANE REFORMING CONDITIONS

Contribution of Authors and Co-Authors

Manuscript in Chapter 6

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Contributions: Collected and analyzed all data, generated figures and wrote manuscript in preparation for publication.

Co-Author: Märtha M. Welander

Contributions: Collected and analyzed all data. Assisted in figure generation. Edited and commented on manuscript.

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Contributions: Contributed important insight into performing experiments and interpreting results. Edited and assisted in the preparation of the manuscript.

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Contributions: Contributed important insight into performing experiments and interpreting results. Edited and assisted in the preparation of the manuscript.

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Contributions: Contributed important insight into performing experiments and interpreting results. Edited and assisted in the preparation of the manuscript.

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Contributions: Contributed important insight into performing experiments and interpreting results. Edited and assisted in the preparation of the manuscript.

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OPERANDO CHARACTERIZATION OF METALLIC AND BIMETALLIC
ELECTROCATALYSTS FOR SOFC FUEL ELECTRODES OPERATING UNDER
INTERNAL METHANE REFORMING CONDITIONS

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Abstract

Operando Raman spectroscopy, electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV) were used to study the electrochemical performance and carbon tolerance of SOFCs with niobium doped SrTiO₃ (STN) anodes infiltrated with combinations of Ni, Co, and CGO. Cell anodes were exposed to environments of humidified H₂, pure CH₄ and combinations of CO₂ and CH₄ at operating temperatures of 750 °C. Under pure CH₄, data show that carbon forms on all cell anodes containing Ni. In cells with CGO, deposited carbon results in a decreased polarization resistance highlighting the benefits of CGO to the electrocatalytic activity of the triple phase boundaries. Co-only containing anodes show no sign of carbon deposition in the Raman spectra. The absence of observable carbon together with low frequency processes observed in the EIS suggest that Co may play a role in oxidizing carbon before measurable amounts accumulate.

Introduction

Solid oxide fuel cells (SOFCs) are high-temperature electrochemical cells that convert chemically stored energy into electrical energy with very high efficiencies. Current state of the art (SoA) SOFCs use a nickel/YSZ (Ni/YSZ) composite fuel electrode for $\text{H}_2/\text{H}_2\text{O}$ and CO/CO_2 reactions because of their affordability, high electrical conductivity and high catalytic activity.¹⁸⁵ These composite electrodes, however, can experience degradation during unintended reduction and oxidation (redox) cycles, are prone to carbon deposition and electrode poisoning by common fuel impurities including sulfur.^{184,186–189} Consequently, materials-driven research has focused on developing more robust fuel electrodes.¹¹⁵ One way to overcome challenges associated with SoA electrodes is to decouple the functionalities of the fuel electrode by separating the electronically conductive phase from the electrocatalytic phase. This method of decoupling allows a porous backbone with higher redox tolerance to be infiltrated separately with the electrocatalytic material. One example of such a backbone is donor-doped SrTiO_3 (ST). ST based materials have previously been shown to tolerate oxygen-, carbon-, and sulfur-containing atmospheres, have high electronic conductivity and high redox stability.^{29,149,190–192} Studies described in this chapter examine the use of Nb-doped strontium titanate (STN) as the electrode backbone having different infiltrated nanoparticle catalysts including Ni, Co, Gd-doped ceria (CGO) and catalyst mixtures. STN has previously been shown to have high redox stability when used as SOFC fuel electrodes, especially when compared to conventional Ni/YSZ fuel electrode materials.¹⁹¹ However,

in order for STN to become a viable alternative to the composite electrode several challenges must be overcome as STN, on its own, lacks both adequate electrocatalytic activity and ionic conductivity to function as a fuel electrode, thus motivating the need for catalyst infiltration.

Previous studies have shown how successful infiltration of STN electrodes with different metal nanoparticles, including Ni, Co and Fe increases an electrode's electrocatalytic activity.¹⁹³ However, due to a lack of ionic conductivity, only the electrocatalytic nanoparticles present at the interface between the electrode and the electrolyte, were considered part of the triple phase boundary (TPB). The lack of ionic conductivity throughout the anode microstructure could be compensated for by co-infiltration of CGO, a mixed ionic and electronic conductor under conditions commonly found in SOFCs.¹⁹⁴ The introduction of CGO into the structural matrix has in previous studies been found to successfully decrease the polarization resistance of these STN electrodes.¹⁹⁵

The studies described below investigated the electrochemical performance of infiltrated STN based fuel electrodes, in the full SOFC configuration. The STN-based fuel electrodes were infiltrated with CGO and either nickel or cobalt as Ni-CGO, Co-CGO, or Ni-Co-CGO. Several reports have proposed that combinations of Ni, Co, and CGO would give rise to synergistic effects, achieved from the respective favorable properties of the base-metal and secondary-metal.^{196,197} Similar fuel cells have been investigated previously by T. Ramos et al.¹⁵⁰ where promising performance and low resistances were observed under operation at 850°C in 4% H₂O/H₂. These studies, however, do not report on the

performance of these new SOFC fuel electrodes when operating with carbon-containing fuels. What makes SOFCs attractive for commercial development is their fuel flexibility that enables them to operate with fuel including natural gas, syn-gas, biogas and higher molecular weight hydrocarbons.^{24,124} To leverage the advantage of fuel flexibility, the SOFC fuel electrodes must be resistant to carbon accumulation, also known as coking, during operation. While small amounts of carbon can sometimes improve cell performance,^{22,110,114,147} more extensive carbon accumulation will result in electrode failure.^{113,114,118} Coke-induced degradation in SOFC electrodes has been studied mostly with *in situ* electrochemical data and with subsequent *ex situ* measurements performed after the cell has cooled down and disassembled. Even though *ex situ* studies have provided useful information concerning the conditions responsible for sustained and stable SOFC operation, they leave many questions unanswered regarding coking mechanisms and coking's direct impact on electrochemical performance. These open questions motivate the need for direct or *operando* studies that directly correlate material changes during operation with a device's electrochemical performance.^{114,198–201}

Results presented below uses galvanostatic electrochemical impedance spectroscopy (EIS) an linear sweep voltammetry (LSV) in combination with Raman spectroscopy at *operando* conditions to monitor cell performance and surface behavior of novel STN based anodes under humidified hydrogen, and different methane containing atmospheres at 750°C. Results focus primarily on changes in electrochemical data under conditions where carbon was observed on the cell surfaces and compare changes in carbon accumulation with changes in electrochemical performance.

Experimental

The SOFCs investigated in the present work were electrolyte-supported cells. The Sc_2O_3 stabilized ZrO_2 electrolyte (Nippon Shokubai Co., Ltd, Japan) of ca. 150 μm thickness was laser cut to 26 mm diameter. On to this electrolyte, a $\text{Sr}_{0.94}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_3$ (STN) porous backbone was deposited through spray deposition. The slurry for the deposition was prepared using STN powder, prepared in the lab through solid state mixed oxide method, PVP_{10,000} dispersant/binder and ethanol solvent. After deposition, the backbone was sintered in air at 1200 °C for 8 hours. Subsequently, $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ (LSC) (Kusaka, Japan) – $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ (CGO) (Rhodia GmbH, Germany) composite cathode was screen printed on the opposite side of the electrolyte and sintered in air at 930 °C for 24 hours. Anode electrocatalysts comprising of Ni or Co or Ni-Co and CGO were added to the STN backbone by infiltration. The infiltration solution was prepared in the following way: At first A 3M CGO aqueous solution was prepared using corresponding metal nitrates. To this solution, nitrate precursors of the Ni or Co or Ni-Co metals were added in the ratio of 90:10 by weight. The weight of the cells was measured prior to infiltration and after infiltration, in order to determine the weight gain (Table 6.1). The procedure for the infiltration is described elsewhere.^{155,193} Finally, a cathode current collection layer, LSC, was screen-printed on the LSC-CGO cathode. A schematic representation of the completed circular cells can be seen in Figure 6.1.

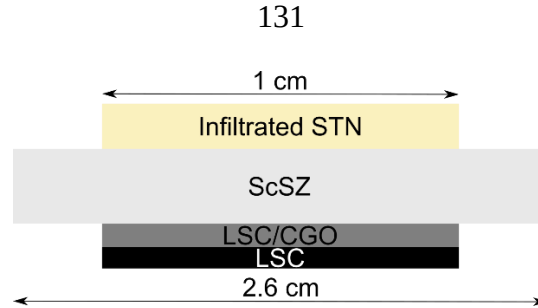


Figure 6.1. Schematic representation of the fuel cell assembly tested in these studies. Notably, the thickness of these layers is not to scale.

Table 6.1. Summary of electrode infiltrations with catalyst loading weight percentages and the weight gained by the infiltration.

Infiltrate	Catalyst	Catalyst loading (wt. %)	Weight gain (mg cm⁻²)
Ni	Ni	100	0.63± 0.25
Ni-CGO	Ni; CGO	10; 90	0.99± 0.10
Co-CGO	Co; CGO	10; 90	0.80± 0.31
Ni-Co-CGO	Ni; Co; CGO	5; 5; 90	0.74± 0.42

Cell microstructure was investigated from a fractured cross-section using scanning electron microscopy (SEM) (ZEISS Merlin, Carl Zeiss, Germany). Prior to investigation the samples were coated with a thin layer of carbon, in order to avoid charging defects. The microstructure of the samples was investigated directly after infiltration as well as after being tested in order to investigate structural changes that occurred. To analyze the distribution of nanomaterials through the electrodes, all electrodes were investigated at four to five randomly chosen spots between the electrode surface and the electrode-electrolyte interface.

Current collectors consisting of gold mesh (Alfa Aesar) were attached to both electrodes with gold paste (Heraeus). The total area of the current collecting layer was kept at around 0.5 cm². The cells were then attached to a 2.6 cm diameter YSZ tube using an alumina-based ceramic paste (Aremco Products Inc). The YSZ tube was enclosed in a

quartz tube and sealed with a rubber stopper. Detailed descriptions of the experimental set up can be found in previous publications.^{43,51} The assembly was then placed into a tube furnace for heating. Raman spectra were acquired using a Renishaw InVia spectrometer coupled to a 30 mW, 488 nm Ar-ion laser with 30-60 second exposures. Backscattered light was directed through an edge filter with a 150 cm^{-1} low frequency cut off. All electrochemical measurements were collected using a Princeton Applied Research VersaStat MC.

All cells were heated to $750^{\circ}\text{C} \pm 5^{\circ}\text{C}$ at a ramp rate of $1^{\circ}\text{C}/\text{min}$ under 20 sccm Ar on the anode and 20 sccm Air on the oxygen electrode. Once at temperature, gas flows were increased to 100 sccm Ar and 85 sccm Air. Fuel electrodes were reduced under 100 sccm humidified H_2 (3% H_2O) and fuel electrodes were considered fully reduced once the open-circuit voltage stabilized at -1.10 V. Once the fuel electrode was reduced, benchmark LSV and OCV EIS measurements (with humidified H_2) were performed. OCV EIS measurements were collected with an AC voltage amplitude of 10 mV over a frequency range of 1 MHz to 0.1 Hz. LSV measurements were collected using a sweep rate of 0.1 V/sec. In order pass through the maximum power on the power-curve and still avoid too high overpotentials, the minimum cell voltage during the LSV was set to be 20% of the measured OCV value. Carbon exposure experiments were performed under four different fuel electrode atmospheres of varying CO_2 and CH_4 compositions totaling a flow rate of 100 sccm: 30 % CH_4 / 70% CO_2 , 50 % CH_4 / 50% CO_2 , 75 % CH_4 / 25% CO_2 , and 100% CH_4 . Experiments at each gas composition involved galvanostatic polarization and collection of 10 EIS measurements at three varying current conditions, including 85% of

maximum current, 40% of maximum current, and 10% of maximum current. Galvanostatic impedance spectra were recorded between 0.1 Hz and 1MHz with 10 points/decade applying a 1mA amplitude. The frequency range was specifically chosen in order to obtain temporal resolution between the spectra. To track the cell performance after exposure to the various fuel environments reference LSV and OCV EIS data were collected in humidified H₂ in between each CH₄/CO₂ atmosphere. Raman kinetic measurements were collected independently for each set of conditions with 30 second exposure times. Carbon removal between each set of experiments where carbon collected on the anode surfaces was carried out using humidified Ar followed by reduction and benchmark measurements under humidified H₂. This procedure has proven effective at rapidly removing carbon from SOFC anodes with minimal degradation to the anode's microstructure from repeated environmental redox cycling.^{80,184,202,203}

Results

In order to monitor the stability of the electrode microstructure and inform interpretation of the electrochemical results, the electrodes were examined by SEM before and after testing in the SOFC assembly with particular attention focused on changes in electrode porosity and the structure and distribution of infiltrated materials. Representative images of a Ni-CGO infiltrated electrode microstructure before and after testing are shown in Figure 6.2. The data illustrate how the infiltrated nanoparticles tended to agglomerate into larger particles during SOFC operation.^{155,193,195} This behavior was common to all infiltrates used in these studies and resulted in spherical nanoparticles of 100-200 nm

diameters after operation. Some separation of the metal infiltrates from the CGO was also observed. Previous reports have shown that infiltrated CGO will evolve into to sponge-like structures^{149,204} and similar structures in Figure 6.2b are ascribed to this form of CGO. The images shown in Figure 6.2 were acquired from the active electrode areas that have been covered by the current collector during the experiment and were therefore not left directly exposed to the anode's gas phase atmosphere.

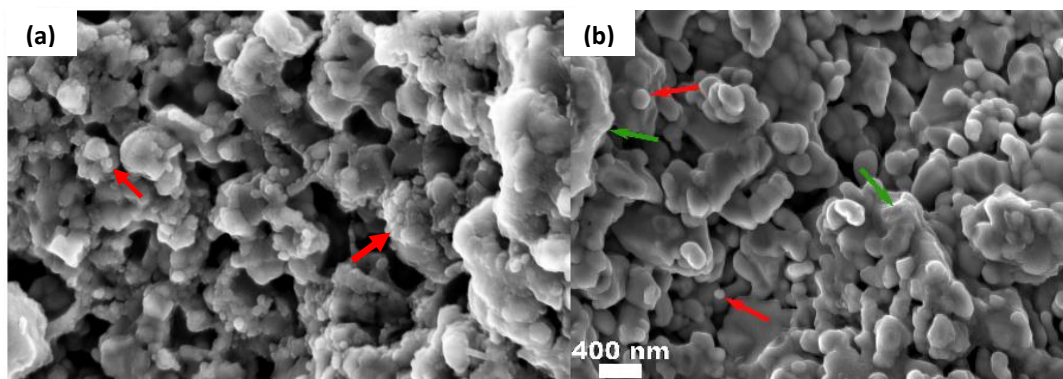


Figure 6.2. Ni-CGO infiltrated STN94 anode before testing (a) and post testing (b). Notably, examples of the metal infiltration structures are indicated with red arrows, and CGO (b) is indicated with green arrows.

Electrochemical performance was evaluated with LSV to measure current and power densities. Figure 6.3a shows the initial LSV characterization for all the tested cells after reduction in 3% $\text{H}_2\text{O}/\text{H}_2$ at 750°C . The corresponding power density curves for the individual cells are shown in Figure 6.3b with listed values for current and power reported in Table 6.2. These measurements show considerable variations in both the maximum current densities and the maximum power densities, even for cells with identical infiltrations. Differences in performance between cells with identical infiltrations are attributed to variations in the catalyst loading (Table 6.1), illustrating the need to carefully

control infiltration procedures for optimal (and reproducible) performance. Cell-to-cell variability notwithstanding, the Ni-only and the Co-CGO infiltrated electrodes consistently underperformed the Ni-CGO and Ni-Co-CGO electrodes. The low performance of the nickel infiltrated electrodes is readily explained by the lack ionic conductivity as no CGO infiltrate was present in this cell to facilitate oxide transport away from the electrolyte and into the anode microstructure. As a result, the only sites for electrochemical oxidation would have been at the electrolyte-nanoparticle interface without the STN scaffold playing any significant role. The low performance of the Co-CGO infiltrated electrodes, however, was in direct contrast to previous studies performed on symmetric cells under OCV conditions where results predicted near equivalent electrocatalytic performance of cobalt and nickel.¹⁵⁵ The variation from *in situ* data, illustrates the importance of *operando*, full cell testing as results predicted by *in situ* testing may differ significantly when a cell is polarized and oxygen ions are being transported to the triple phase boundary.

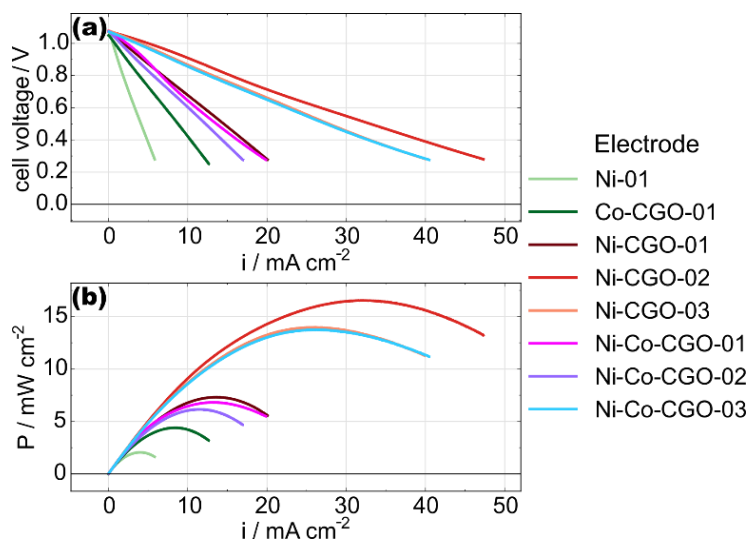


Figure 6.3. Initial LSV of all the tested cells, measured in 3% H₂O/H₂ at 750°C.

Table 6.2. Initial maximum power densities and corresponding currents for data shown in Figure 3 at 750°C in H₂O/H₂.

Sample	i / mA·cm⁻²	P_{max} / mW·cm⁻²
Ni-01	4.0	2.1
Co-CGO-02	8.6	4.4
Ni-CGO-01	13.6	7.3
Ni-CGO-02	31.8	16.5
Ni-CGO-03	26.1	13.9
Ni-CGO(avg. ± s.d.)	23.9±7	12.6±3
Ni-Co-CGO-01	13.3	6.8
Ni-Co-CGO-02	11.3	6.2
Ni-Co-CGO-03	26.1	13.8
Ni-Co-CGO (avg. ± s.d.)	16.9±6	8.9±3

Following initial reduction, the cells were exposed to different compositions of methane-carbon dioxide mixtures at polarizations of 10, 40, and 85% of maximum current (where the maximum current refers to data measured initially with 3% H₂O/H₂) for 15 minutes each. Following polarization at each fuel composition, benchmark LSV measurements were acquired in 3% H₂O/H₂ in order to track changes in electrode performance. Discussion of the electrochemical data presented below focuses on the Ni-Co-CGO infiltrated systems as a representative example. Figure 6.4 and Table 6.3 show how performance evolved after exposure to each of the fuel compositions for a Ni-Co-CGO infiltrated electrode. Maximum current density and maximum power density both increased over the course of the experiment. Note that a full experiment in this case is defined as the polarization of a cell at the three various currents under each of the CH₄/CO₂ fuel compositions (starting with 30% CH₄ / 70% CO₂ and ending with 100% CH₄). For the Ni-Co-CGO cell shown in Figure 6.4, the measured power and current densities increased by a factor of ~2 between the initial measured LSV (with 3% H₂O in H₂) and the

final measured LSV (post polarization in 100% CH₄). Because the measured OCV remained constant, this increase must be explained by a decrease in overall cell resistance. This trend was observed for all cells containing both nickel and CGO. Ni only and Co-CGO infiltrated electrodes did not experience this same increase in performance but instead showed a stable performance initially and after exposure to a 50% CH₄/ 50% CO₂.

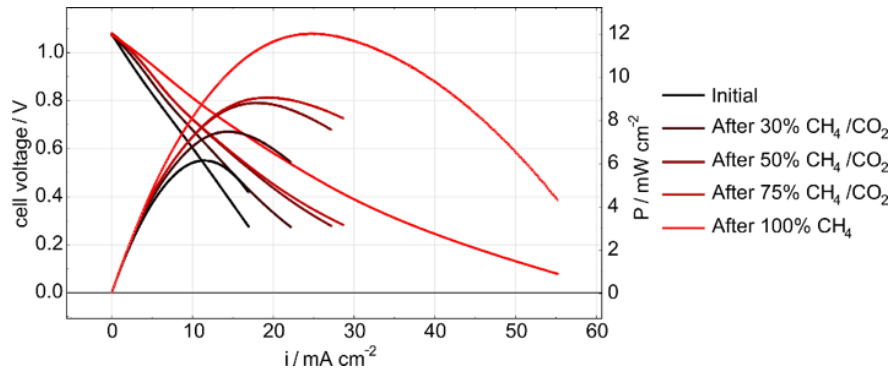


Figure 6.4. LSV curves for a cell with a Ni-Co-CGO anode measured in 3% H₂O/H₂ after operation for 15 minutes with each CH₄/CO₂ atmosphere at 750°C. The LSV curves (left axis) are plotted together with the calculated power curves (right axis).

Table 6.3. Maximum power densities and corresponding currents for a cell with a Ni-Co-CGO anode (seen in Figure 4) after exposure to each CH₄/ CO₂ atmosphere (in 3% H₂O/H₂).

	$i / \text{mA} \cdot \text{cm}^{-2}$	$P_{\text{max}} / \text{mW} \cdot \text{cm}^{-2}$
Initial	11.3	6.2
After 30% CH ₄ /CO ₂	14.2	7.5
After 50% CH ₄ /CO ₂	18.2	8.8
After 75% CH ₄ /CO ₂	19.9	9.1
After 100% CH ₄	24.7	12.0
Overall Increase	13.5	5.9

That the increased performance observed in the figures above is a result of lowered resistance within the cell is supported by complementary impedance data shown in Figure 6.5. Figure 6.5a shows that the serial resistance of the cell remains constant while the

polarization resistance decreases during the experiment. The decreasing polarization resistance suggests that changes in cell performance are due to reactions at the electrodes and not from changes in electrolyte structure or composition. The Bode plot displayed in Figure 6.5b further illustrates that the low-frequency contribution is changing the most. This part of an impedance spectrum is generally assigned to adsorption of reactive species to the STN fuel electrode.¹⁹³

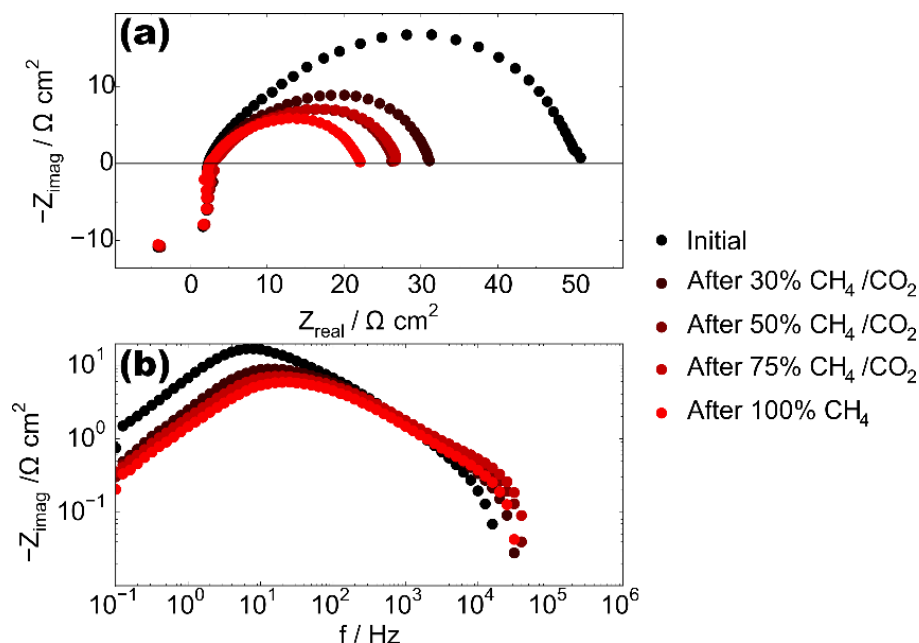


Figure 6.5. Impedance data for a cell with a Ni-Co-CGO anode measured in 3% $\text{H}_2\text{O}/\text{H}_2$ after exposure to each $\text{CH}_4 / \text{CO}_2$ atmosphere at 750 °C in a) the Nyquist representation and b) in the Bode representation.

Electrode performance was also measured during exposure to the CH_4/CO_2 atmospheres (in addition to the post-exposure data recorded with $\text{H}_2\text{O}/\text{H}_2$ reported in Figures 6.4 and 6.5). Initial LSV data obtained in each of the CH_4/CO_2 atmospheres for a Ni-Co-CGO cell are shown in Figure 6.6. As methane content is increased (lowering the

effective pO_2), the OCV increases as do the maximum current and power densities (Table 6.4). This increase in performance can be attributed to an increase in the amount of usable fuel within the fuel stream as methane concentration is increased. Furthermore, lowering the pO_2 can change the oxidation state of ceria from Ce^{4+} to Ce^{3+} thereby increasing CGO's electrocatalytic activity and electronic conductivity.^{115,205} A lower pO_2 and an increase in the OCV can also positively influence STN's conductivity by further reducing the STN and enhancing electronic conductivity through the electrodes (even when the pO_2 returns to pre-reducing levels).¹⁹¹

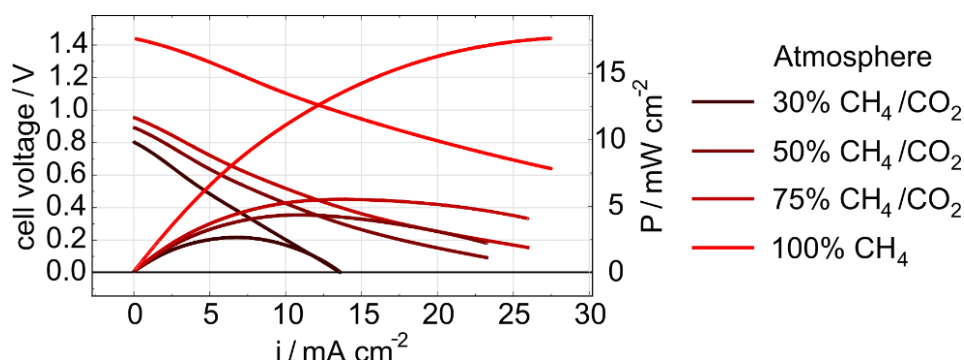


Figure 6.6. LSV and power density curves of a cell with a Ni-Co-CGO anode measured in 30% CH_4/CO_2 , 50% CH_4/CO_2 , 75% CH_4/CO_2 , and 100% CH_4 at 750°C.

Table 6.4. Measured maximum power densities and corresponding currents for a cell with a Ni-Co-CGO anode (seen in Figure 6) in 30% CH_4/CO_2 , 50% CH_4/CO_2 , 75% CH_4/CO_2 , and 100% CH_4 at 750°C

Atmosphere	$i / mA \cdot cm^{-2}$	$P_{max} / mW \cdot cm^{-2}$
30% CH_4/CO_2	6.8	2.6
50% CH_4/CO_2	11.2	4.3
75% CH_4/CO_2	13.7	5.5
100% CH_4	27.4	17.6

During galvanostatic polarization, electrochemical impedance spectroscopy experiments were performed continuously under each of the CH_4/CO_2 atmospheres (~ one spectrum collected per minute for 10 minutes). Figure 6.7 shows the impedance response

of the cell with a Ni-Co-CGO infiltrated anode, at 750°C in 100 % CH₄, under the strongest polarization (85% $I_{\max}$) conditions. Three dominant features are visible; a high frequency inductive loop, a process having a characteristic frequency at ~100 Hz, and a low frequency contribution below 1 Hz. Due to the chosen frequency range, only part of this low frequency process is visible. The most noticeable changes to the overall impedance are associated with the electrochemical reactions ~ 100 Hz (Figure 6.7b). The loop observed at the highest frequencies is an artifact arising from the potentiostat.

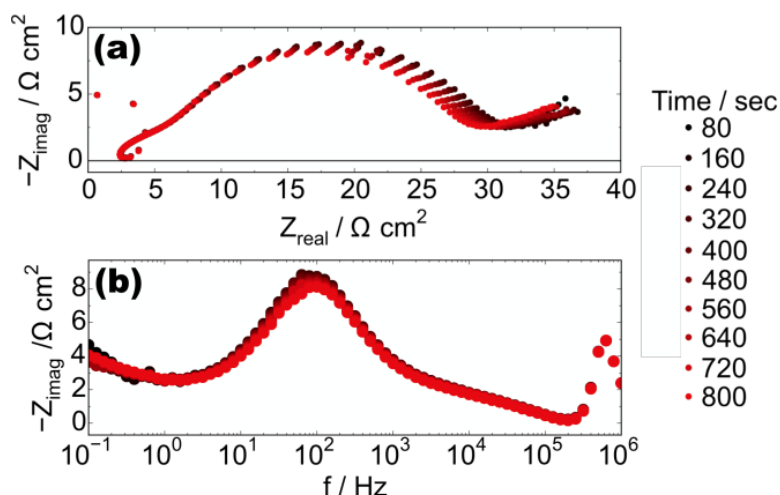


Figure 6.7. Impedance spectra recorded during the strongest polarization (85% $I_{\max}$ / 5.5 mA) of the Ni-Co-CGO cell in 100% CH₄ at 750°C; a) plotted as Nyquist plots and b) plotted as Bode plots.

The chosen impedance range (1 MHz and 0.1 Hz) was motivated by a need to acquire EIS data continuously and did not allow for low enough frequencies to obtain the DC resistance from all infiltrated electrodes. In particular, the frequency range was not suitable for electrodes infiltrated with Co (Ni-Co-CGO and Co-CGO) at 100% CH₄ conditions, suggesting that when Co is present an additional reaction occurs below 0.1 Hz.

To estimate the total polarization resistance of the Co-doped electrodes, the Nyquist data were fit to an L-R-R₁Q₁-R₂Q₂-R₃Q₃-R₄Q₄ circuit (Figure 6.9). In order to validate the area specific resistance obtained through the impedance fitting, the DC resistance of the cell was also calculated from the polarization and current data. The DC resistance was calculated from a linear regression of the three cell voltages applied in the galvanostatic measurements and plotted together with the impedance response. Since the DC resistance is calculated from only three points, the value has a larger uncertainty than one would normally associate with impedance data. The uncertainty was estimated by calculating the slope between the two points obtained at 85% $I_{\max}$ and 40% $I_{\max}$. The slope obtained between the 40% $I_{\max}$ and the 10% $I_{\max}$ then marks the other boundary of the error-zone for the DC resistance (schematically shown in Figure 6.8). The calculated DC resistance shown in Figure 6.9 is lower than the area specific resistance obtained from the fitting of the impedance spectra. This mismatch was observed for all nickel containing electrodes. In order to reach the calculated DC resistance, an inductive process, resulting in a “negative impedance”, is required at low frequencies. Inductive loops, like the one drawn schematically in Figure 6.9, have been assigned previously to reactions in which several electron transfer reactions take place. With this interpretation in mind, the inductive loop included in Figure 6.9 is assigned to intermediate species (as yet undefined) competing for adsorption sites, with their coverages depending on the applied overpotential.^{206,207}

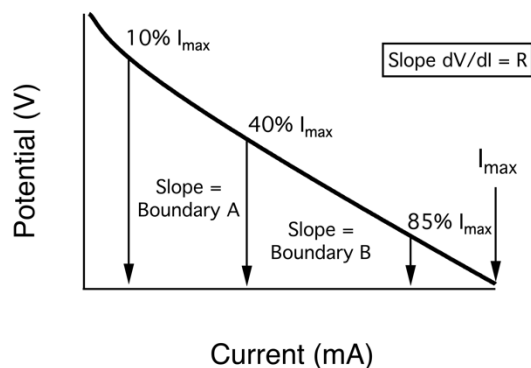


Figure 6.8. Schematic representation of the locations of currents used to calculate slope and DC resistance error boundaries in Figure 9.

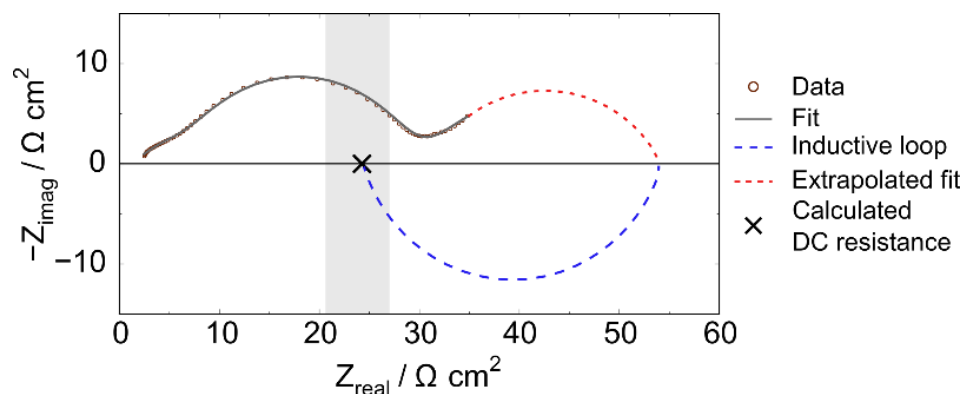


Figure 6.9. Fitting of the first impedance spectra recorded during the strongest polarization (85% $I_{\max}$) of the Ni-Co-CGO cell in 100% CH_4 at 750°C. Notably, the calculated DC resistance is also seen at 24 $\Omega \cdot \text{cm}^2$.

A tentative explanation for inductive loop's origin can be found in a cascade of possible reactions taking place when only methane is present in the fuel stream such as when methane reacts with oxygen ions to form carbon monoxide and hydrogen. The carbon monoxide is assumed to be the reaction intermediate causing the inductive loop, but once carbon monoxide is oxidized into CO_2 , it drives the dry reforming process.^{208,209}

Previous results obtained from symmetric cell testing can be used to further narrow the electrochemical processes occurring on Co-containing electrodes.¹⁵⁵ These previous

studies found that the Co infiltrated electrodes did not experience any carbon deposition, while the Ni-infiltrated electrodes did. Ni-Co-CGO infiltrated electrodes experienced some carbon accumulation, but significantly less carbon than Ni-CGO or Ni-only infiltrated electrodes.¹⁹⁵ Taken together, these results indicate that several different mechanisms may result in the lack of carbon observed on cobalt containing electrodes. These mechanisms include the potential for Co to actively remove deposited carbon or simply Co's ability to block carbon formation. While it is possible that Co is simply inactive to C-H bond activation, previous work suggests that Co can be an effective catalyst under some circumstances.^{193,197,210,211} For the purposes of this study Co-C activity is assumed in order to propose a possible mechanism that explains the features seen in the EIS spectrum above. However, questions about cobalt's active role remain and further research on the catalytic activity of Co in the infiltrated STN anode systems is warranted. If cobalt does actively remove surface carbon, the additional process observed below 0.1 Hz in the EIS could relate to Co-C interactions and electrochemical data would suggest that the Co-CGO and Ni-Co-CGO infiltrated electrodes are capable of suppressing carbon accumulation. The competition for adsorption sites between intermediate species, like CO and adsorbed C, may be responsible for the inductive loop inferred in the impedance data. Combining nickel with cobalt would therefore enable the catalyst to utilize both the desirable properties of nickel (e.g. CH bond activation), running the dry-reforming process, as well as the desirable properties of cobalt, carbon tolerance and/or the ability to remove deposited carbon actively.

In order to provide materials specific information that complemented electrochemical behavior, *operando* Raman spectroscopy was used to determine whether or not carbon was accumulating on the infiltrated, STN anodes. Raman spectra acquired simultaneously with the EIS data in Figure 6.7 (with a functioning Ni-Co-CGO anode), are shown in Figure 6.10. The appearance of carbon on the cell surface is evident by the vibrational mode at 1560 cm^{-1} , referred to as the “G-band”. Figure 6.10 shows that carbon starts to accumulate on the anode surface within minutes of exposure to CH_4 . With incident fuel feeds that also contain CO_2 , no observable carbon accumulates on the anode.

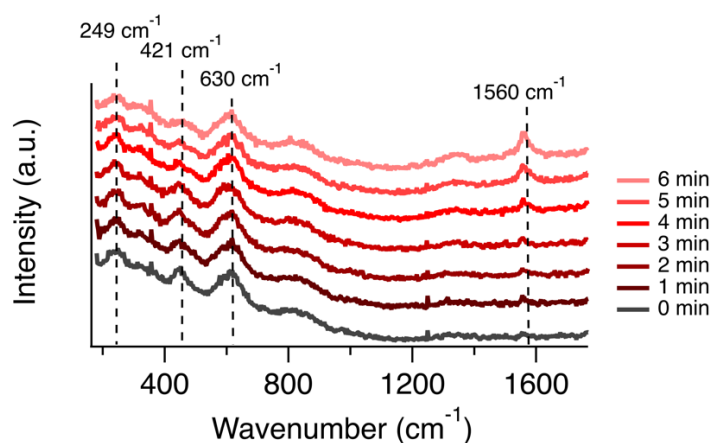


Figure 6.10. Raman spectra recorded during the strongest polarization ($85\% I_{\max}$) of the Ni-Co-CGO cell in $100\% \text{CH}_4$ at 750°C . Notably, the spectra are vertically shifted for clarity.

To see how changes in the electrochemistry correspond to changes in carbon accumulation, Figure 6.11 plots G-band intensity alongside the total polarization resistance as a function of time for all types of cells at each of the three polarizations conditions. Figure 6.11a-c corresponds to the Ni-only infiltrated cell. Here, polarization resistance increases with the increasing Raman G-band intensities by several $\Omega\text{-cm}^2$, especially at

lower polarizations. An increase in carbon deposition, associated with polarization conditions closer to OCV, is therefore shown to limit electrochemical activity in the Ni infiltrated cells.

Figure 6.11d-f, shows the same data for a Ni-CGO infiltrated electrode. Under high polarization conditions no sign of carbon deposition is apparent and the polarization resistance remains fairly constant, also supporting a lack of any carbon deposition. At the middle polarization, however, a minor increase in the G-band intensity is observed alongside a slight decrease in polarization resistance. This same trend is observed at the lowest polarization where the carbon deposition increases from 0 to 500 counts during the 15 minute exposure and the polarization resistance simultaneously drops by ~20%. These observations are in direct contrast to the Ni-only infiltrated electrodes where polarization resistance increases with carbon deposition. For the Ni-CGO infiltrated electrode the cell experiences a decrease in polarization resistance when carbon is present suggesting that deposited carbon improves connectivity within the anode microstructure.

A similar trend is observed for the bimetallic Ni-Co-CGO infiltrated electrode, shown in Figure 6.11g-i . An increase in the G-band intensity is observed under all the polarization strengths, with absolute intensities falling between those of the pure Ni and the Ni-CGO sample. While absolute intensities cannot be correlated quantitatively with the absolute amount of accumulated carbon, previous studies have quantified general increases in G-band intensity with increasing amounts of electrochemically accessible carbon. The increase in G-band intensity observed in Figures 6.11g-I is followed by a

decrease in the polarization resistance, further supporting the hypothesis that deposited carbon helps increase the connectivity of the anode microstructure.

No carbon deposition was observed on the Co-CGO infiltrated electrodes under any polarizations (Figure 6.11j-l). A lack of observable carbon strengthens the hypothesis that Co has the ability to oxidize carbon to CO that then desorbs or prevent carbon from depositing in the first place. Minor changes in the total polarization resistance were observed under both the strongest and middle polarization strength, while the polarization resistance showed quite a significant drop under low current conditions. A drop in the polarization resistance, drawing from findings with Ni-containing anodes, suggests that carbon might be depositing but at amounts below the detection limit of the spectrometer under conditions close to OCV.

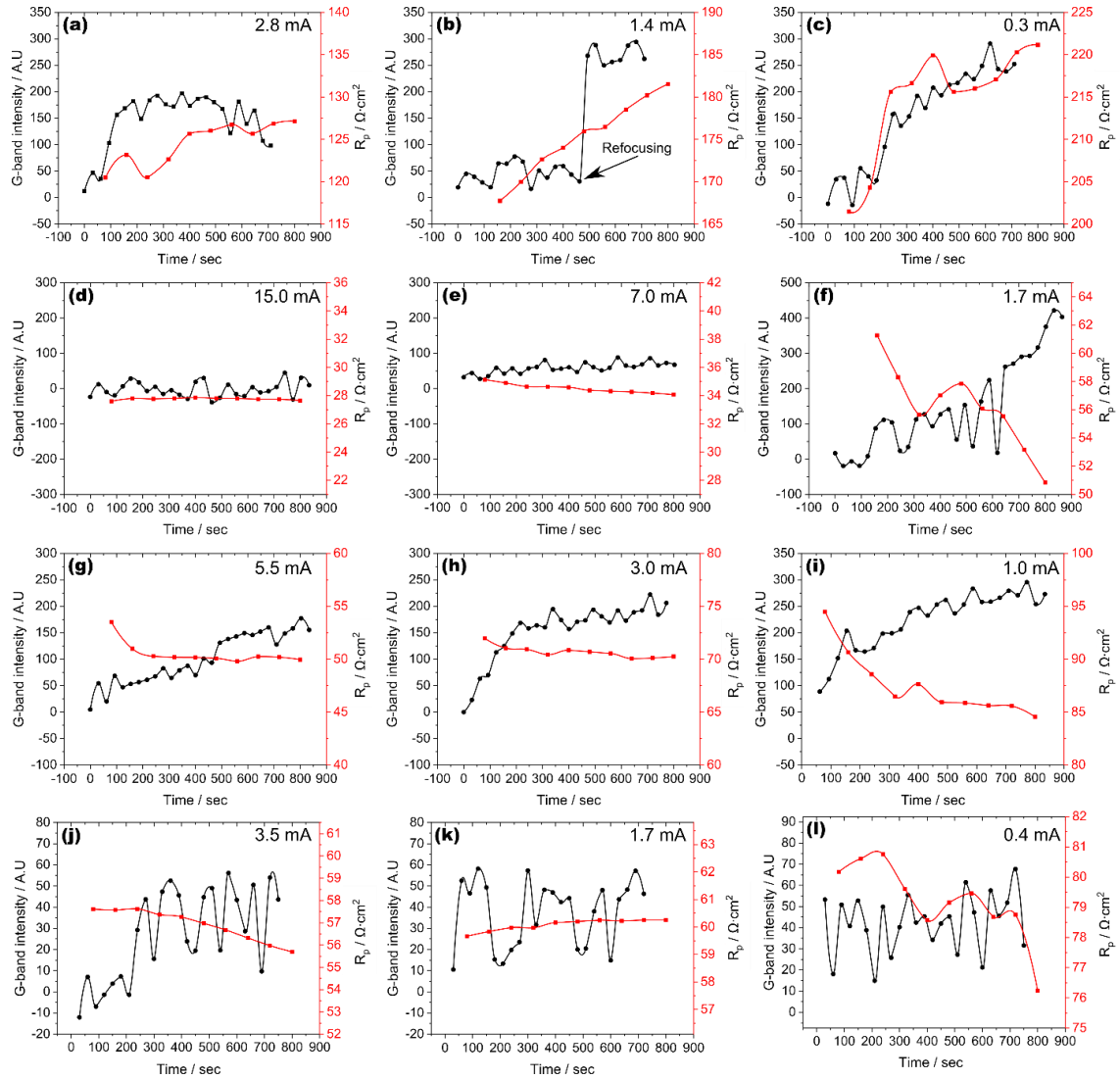


Figure 6.11. The G-band intensity plotted together with the total polarization resistance found by galvanostatic EIS, under different polarization strengths in 100% CH₄ at 750°C. a) Ni infiltrated electrode under 85% $I_{\max}$, b) Ni infiltrated electrode under 40% $I_{\max}$, and c) Ni infiltrated electrode under 10% $I_{\max}$. d) Ni-CGO infiltrated electrode under 85% $I_{\max}$, e) Ni-CGO infiltrated electrode under 40% $I_{\max}$, and f) Ni-CGO infiltrated electrode under 10% $I_{\max}$. g) Ni-Co-CGO infiltrated electrode under 85% $I_{\max}$, h) Ni-Co-CGO infiltrated electrode under 40% $I_{\max}$, and i) Ni-Co-CGO infiltrated electrode under 10% $I_{\max}$. j) Co-CGO infiltrated electrode under 85% $I_{\max}$, k) Co-CGO infiltrated electrode under 40% $I_{\max}$, and l) Co-CGO infiltrated electrode under 10% $I_{\max}$.

In summary, Figure 6.11 shows that the cell resistance decreases as carbon accumulates on both the Ni-CGO and Ni-Co-CGO infiltrated electrodes, correlating to the electronic conductivity of graphitic carbon. As carbon accumulates within the electrodes, the electrode's overall electronic conductivity increases. Deposited carbon can also activate previously isolated areas of the electrode, thereby increasing the triple phase boundary areas and improving conversion efficiency. Similar results showing the positive impact of small amounts of carbon on the electrode performance have been reported elsewhere.^{110,114,147,212} Ni-only infiltrated electrodes accumulated carbon above this beneficial point, and therefore experienced an increase in the polarization resistance. Taken together, these *operando* Raman-EIS studies illustrate that the effect of carbon accumulation on performance is largely dependent on the type of electrode infiltration and the amount of total accumulated carbon. Bi-metallic infiltration using Co and Ni as well as Ni-CGO seems promising as polarization resistances decrease with lower carbon accumulation amounts.

Conclusion

The studies presented in this work utilize *operando* Raman spectroscopy coupled with electrochemistry to monitor the performance of alternative fuel electrodes for SOFC operation. The studies are the first of their kind to monitor infiltrated STN anodes operating with a hydrocarbon fuel. Raman spectroscopy showed that carbon accumulated on all nickel containing electrodes when exposed to 100% CH₄, but that performance degradation was only experienced by the Ni-only infiltrated electrodes. In combination with the

electrochemical data, Raman spectroscopy suggested that small amounts of carbon accumulation increase cell performance in electrodes with CGO containing matrices (Ni-CGO and Ni-Co-CGO infiltrated electrodes). CGO therefore plays an important role in the electrocatalytic activity and the TPBs in these alternative fuel electrodes. Electrochemical measurements further show that Ni-containing electrodes experience an inductive loop, possibly attributed to the competition for adsorption sites between intermediate species when using pure methane as fuel. Moreover, cobalt-containing electrodes were found to experience an additional process below 0.1 Hz, a process that could potentially be the oxidation of solid carbon into CO. While performance of these alternate anodes lags that of state of the art Ni-YSZ, limited coking and the positive effects observed from limited coking make them promising candidates for further research and development.

CHAPTER SEVEN

CONCLUSIONS AND FUTURE DIRECTIONS

Conclusions

Experiments contained in this thesis were designed to investigate the benefits of adding small amounts of ALT to state of the art Ni-YSZ SOFC anodes as well as to evaluate the performance of infiltrated STN-based anodes where the electronically conductive phase is separated from the electrocatalytic phase. Both research objectives consider the effects of how subtle changes to already well established fabrication and processing methods of SOFC electrodes may improve the performance of the electrodes in the hopes of developing commercially viable systems to match the increasing demand for electrical power. Experiments used a combination of *operando* Raman spectroscopy coupled with electrochemical techniques to directly couple material changes, and the role of dopants and secondary phases, with changes observed in cell performance. This work represents collaborative efforts with the Sofie Research Group in the Department of Mechanical and Industrial Engineering at Montana State University as well as The Department of Energy Conversion and Storage at the Technical University of Denmark.

Chapter 2 shows that ALT addition to Ni-YSZ anodes improves cell resilience toward electrochemical redox cycling under *operando* conditions at 800 °C. The increased redox tolerance is a direct result of increased connectivity at the electrode-electrolyte interface, which otherwise is prone to delamination in undoped systems.^{8,213} While

irreversible degradation occurred in cells both with and without ALT over time, ALT doped cells showed much greater resilience and survived on average twice as long as cells without ALT. Similar to electrochemical redox cycling, ALT addition also benefits a cell's tolerance toward environmental redox cycling. This phenomenon is shown in Chapter 3. In standard SOFC systems electrochemical redox cycling will affect the anode-electrolyte interface primarily as oxide ions are transported through the electrolyte to the anode. Environmental redox cycling, on the other hand, will mainly damage the surface of the electrode. Studies investigating environmental redox cycling used both O_2 and H_2O as oxygen sources. Oxidation using H_2O proved more gentle than O_2 and did not result in complete cell failure for either type of cell. Degradation amounts for cells without ALT were however greater than cells with ALT. Under O_2 oxidation undoped cells consistently reached cell failure in the allotted experimental time, while cells with ALT did not degrade much more than under H_2O conditions. Post mortem FEM images as well as experimental EIS data attribute this to changes in charge transfer rates and activation over potentials at the anode as a result of a loss of TPBs and catalyst surface area. Undoped cells therefore experience a greater propensity toward Ni particle agglomeration as a result of environmental redox cycling, which was spared in cells doped with ALT. The ability of ALT to prevent particle coarsening under standard reducing conditions with H_2 has been demonstrated in previous work.^{16,34} Taken together, spectroscopic, electrochemical, and post mortem FEM imaging results are promising and demonstrate the efficacy of adding ALT to Ni-YSZ anodes in order to improve cell durability and resilience to both electrochemical and environmental redox cycling.

Addition of ALT to SOFC anodes was also found to reduce carbon deposits with CH_4 fuel. Chapter 4 describes experiments designed to investigate how carbon formation and oxidation mechanisms compare in cells with and without ALT. The spectroscopic and electrochemical data show that suppressed carbon formation in ALT doped cells can be explained by several different mechanisms. While barrier layers may in part contribute to these observations by preventing Ni catalyzed C-H bond activation in the first place and thereby subsequent carbon accumulation, a more likely explanation is that carbon formation is suppressed by the reforming ability of the secondary phases. Both Al and Ti based oxides have reforming capability and can therefore oxidize carbon formed within the anodes. Additionally, zirconium titanate likely possesses MIEC capability that can expand the TPBs of the anode and improve overall cell performance.¹⁴⁵ Chapter 4 uses spectrochronopotentiometry (SCP) methods to monitor carbon oxidation at all TPBs since Raman spectroscopy alone will only provide a measure of the relative amounts of carbon deposited on each type of anode. SCP showed that in addition to less carbon formation on ALT doped anodes, carbon forms in a well-defined, narrow region that remains relatively unchanged between 2 and 12 hours of exposure time. Anodes without ALT, however, accumulate more than 2 times more carbon during 12 hours of exposure to CH_4 . This behavior was true for anodes held at OCV as well of those that were polarized during exposure. These results are promising and warrant future experiments with carbon containing fuels on anodes with alternative oxide dopants.

Chapters 5 and 6 recognize the roles of Ni, Co, and CGO infiltration on the electrochemical performance and carbon tolerance of STN based anodes. Five different

infiltration combinations were studied: Ni, Co, Ni-CGO, Co-CGO, and Ni-Co-CGO. Ni-CGO and Ni-Co-CGO consistently showed greatest cell performance under both H_2 and CH_4 conditions (Chapter 6). Additionally, limited amounts of carbon buildup in these cells lowered overall polarization resistance by activating previously isolated areas of the electrode and increasing the active catalytic surface area. Carbon was shown to form on all cells where Ni was present under pure methane only conditions. However, these cells show promise when compared to SoA Ni-YSZ electrodes as much less carbon was observed in comparison. Results also show that CGO present in the anodes functioned as an oxygen reservoir upon cool down to oxidize surface carbon present (Chapter 5). This observation merits future studies of these novel anodes at slightly lower operating temperatures where CGO carbon oxidation is active.

Collectively, the data obtained from the experiments summarized above demonstrate that with properly designed experiments, Raman spectroscopy and electrochemistry methods provide valuable information that can identify material and compositional changes responsible for enhanced catalytic activity and performance in SOFC systems. While experiments do not fully replicate industry conditions, the experimental insight obtained is enough to help guide the development of more durable SOFC electrodes.

Future Directions

High Temperature Proton Ceramic Fuel Cells

The work defined within this dissertation established the role played by aluminum titanate doping in improving redox and carbon tolerance in Ni-YSZ systems, as well as the effect of separating the functionalities of the fuel electrode through infiltration of STN anode backbones on performance and carbon tolerance in relation to Ni-YSZ systems. Both objectives aimed to study mechanisms responsible for enhanced performance, durability, and resilience of SOFCs. As energy conversion technologies are constantly being improved to meet the increasing demand for clean energy, ceramic fuel cells become increasingly viable as operating temperatures and system costs are reduced. With these goals in mind, high temperature proton ceramic fuel cells (PCFCs) have begun to garner widespread interest.²¹⁴⁻²¹⁷ PCFCs are less mature technology compared to oxide-conducting SOFC devices, but the low activation energy associated with proton transfer (compared to oxide transport) make them useful for mid temperature applications in the range from 300-500 °C.²¹⁸ Additionally PCFCs have also illustrated remarkable coking and sulfur tolerance, but performance lags far behind SOFCs. To bridge this gap, the community needs data describing electrochemical oxidation and reduction mechanisms *and* new generations of materials with higher durability and greater catalytic activity.²¹⁵

Barium based perovskite-type materials, including barium zirconate $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-x}$ (BZY) and barium cerate $\text{BaZr}_{0.7}\text{Ce}_{0.2}\text{Y}_{0.1}\text{O}_{3-x}$ (BZCY), are currently used as PCFC electrolytes as they exhibit good protonic conductivity under hydrogen

atmosphere at intermediate temperatures.^{219–222} Barium cerates exhibit higher proton conductivities but are chemically unstable in the presence of acidic gases (such as CO or water vapor), while the barium zirconates offer greater chemical stability but lower proton conductivities.²²¹ The ratio of Ce:Zr is therefore a key control factor in the tradeoff between chemical stability and conductivity.²²³ One of the first steps to developing new electrochemical conversion technologies is to optimize and then streamline processing of materials used for the different fuel cell components. Therefore, the development of practical PCFCs has focused great efforts on lowering both the sintering temperature and sintering time of the electrolyte materials, where densification of zirconium and volatilization of barium have otherwise proved problematic.^{216,218,223–225} The fundamental structure-property relationships of these materials are only partially understood and very little research has focused on material specific properties that exist during PCFC operation.²¹⁸ Detailed material characterization methods are therefore necessary to fully understand chemical stability of the materials and how they react to environments present under *operando* conditions. Much of the work presented throughout this dissertation has shown that Raman spectroscopy is an effective means of providing insightful analysis of material properties and material changes in functioning, high temperature devices. While BZY Raman measurements have previously been recorded these are often inconsistent,^{218,226–228} and a more thorough understanding of how vibrational signals change as temperature and fuel compositions are varied is required.

Work described in this section used Raman spectroscopy to evaluate materials changes of BZY under exposure to dry and humidified fuels *in situ*. Experiments were

carried out in a Linkam CCR100 high temperature controlled stage that could raise sample temperatures up to 1000 °C under controlled atmospheres. BZY ($\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-}$) was purchased from Fuel Cell Materials and ball milled for 24 hours with 1 wt. % of NiO (also Fuel Cell Materials) as a sintering aid. The powder was freeze dried and calcined at 1200 °C for 8 hours. The powder was then pressed into 1 inch pellets which were sintered at 1400 °C for 10 hours with a ramp rate of 1 °C/min. Following initial Raman analysis at room temperature, 120 mg samples were placed into the Linkam CCR1000 for heat up. Samples were heated to 400 °C under 50 sccm Ar atmosphere with Raman data collected every 50 °C.

Undoped barium zirconate adopts a cubic $\text{Pm}\bar{3}\text{m}$ unit cell. When doped with yttrium the structure shifts slightly towards the tetragonal unit cell. While this structure has no theoretical Raman bands predicted by group theory, a broad feature can be seen experimentally at $\sim 720 \text{ cm}^{-1}$ that is assigned to defects induced by yttrium addition into the lattice.^{226,227} For the BZY samples prepared, this broad feature was present both at room temperature and after heat up to 400 °C (Figure 7.1). The figure suggests that the material is stable under both dry H_2 and humidified H_2 conditions as no obvious changes are observed in the Raman spectrum. Interestingly, when conditions were reversed and the sample was first exposed to humidified H_2 at operating temperature a new feature appeared in the spectrum at 548 cm^{-1} (Figure 7.2). This new feature appears to become stronger with time and remains as the sample is cooled back down to room temperature. The conditions of the 548 cm^{-1} peak are limited to a temperature range between 400 and 450 °C, and

requires that the sample is first exposed to humidified H_2 with no prior reduction under dry fuel conditions.

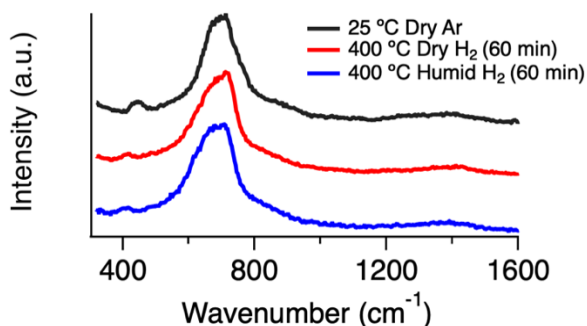


Figure 7.1. Raman spectra collected of BZY at room temperature at operating temperature after exposure to dry and humidified H_2 , showing a main Raman band $\sim 720 \text{ cm}^{-1}$.

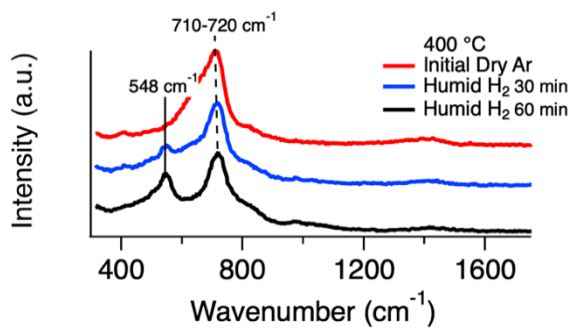


Figure 7.2. Raman spectra of BZY collected at $400 \text{ }^\circ\text{C}$. Upon exposure to humidified H_2 a new vibrational band at 548 cm^{-1} appears. The ratio between this and the initially present $\sim 720 \text{ cm}^{-1}$ band shifts during longer fuel exposures.

In order to characterize material changes responsible for the appearance of the 548 cm^{-1} Raman feature, X-ray photoelectron spectroscopy (XPS) was used. Samples in which the 548 cm^{-1} peak had appeared and samples in which it had not were both analyzed by XPS. Figure 7.3 shows a sample survey scan of the material. Survey scans were identical for both types samples, indicating that no new materials or contaminants were present in

either sample, and that samples contained all expected peaks for the material composition. Multiplex scans were acquired for the main Ba, Zr, O, and Y peaks. Major differences were observed in the O 1s peak of the two sample types. Figure 7.4 shows that the O 1s signal was split into a doublet and that the ratios of the two observed peaks differed by 10% between the two samples. XPS analysis determined that the oxygen species present at the lower binding energy (~ 529 eV) corresponds to Y_2O_3 while the peak present at higher binding energy (~ 531 eV) corresponds to BaO.²²⁹ In the sample where the 548 cm^{-1} feature was not present, the ratio of the higher to lower binding energy peaks was calculated to be 0.88 while for the sample with the 548 cm^{-1} feature present the ratio was calculated to be 0.78. This result suggests that the sample which was initially subject to humidified H_2 caused more Ba to oxidize to BaO compared to samples which were initially subject to dry fuel. Barium zirconate material instability under humidified conditions, and specified temperatures, can therefore be attributed, in part, to the oxidation of the barium metal. These findings are suggestive and represent, to our knowledge, the first direct *in situ*, materials specific measurements carried out with PCFC materials. Whether or not these changes in Ba oxidation state and binding lead to mechanical or catalytic changes remain to be tested.

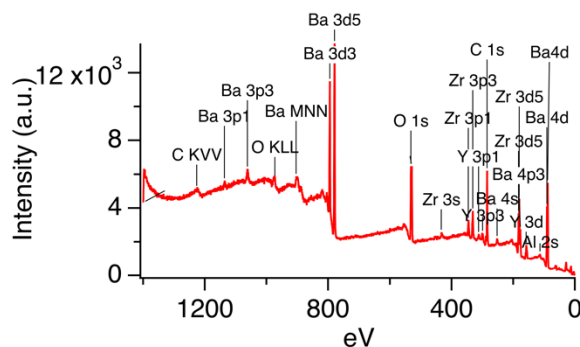


Figure 7.3. XPS survey scan of BZY material.

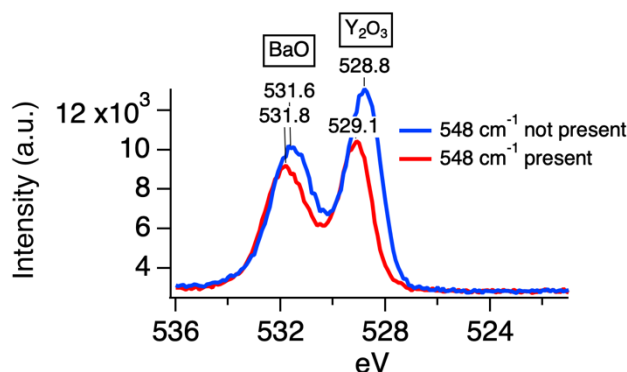


Figure 7.4. XPS oxygen 1s multiplex scans for samples with the 548 cm^{-1} Raman feature (red) and samples without (blue).

The connection between intrinsic material properties (oxygen absorption capacity and mass transport), structure, and stress tolerance of BZY and BZCY materials should be further investigated before the use of these material in full configuration PCFCs. Cells can then be studied with the assembly described in Chapter 1 to determine if observed material changes correlate with changes in electrochemical performance when the cells are run in fuel cell mode. The ultimate goal of this research will be to establish the parameters or ‘windows of stability’ where BZY and BZCY based PCFCs can function optimally with

the results described above providing the foundation for experimental design to determine basic material stability. Results derived will enhance the understanding of proton conducting ceramics as promising candidates for SOFC type applications.

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APPENDIX A

SUPPORTING INFORMATION FOR CHAPTER THREE

Supporting Information

FE-SEM images below are presented to strengthen the conclusion that ALT addition stabilizes the Ni-YSZ microstructure under environmental redox cycling and prevents the formation of increased porosity leading to cell degradation. Figure A1.1 shows low magnification images to compliment results shown in Figure 3.7. Lower magnification images show large areas of anode surfaces where drastic differences are noticeable between doped and undoped anodes exposed to various oxidants. Oxidation using H₂O leaves both doped and undoped anodes fairly intact while O₂ oxidation results in severe particle agglomeration in undoped anodes, something that is prevented by the addition of ALT. Additionally, anode surface images of cells exposed to electrochemical redox cycling are shown in Figure A1.2. These images show minimal surface degradation supporting the difference in degradation mechanism between undoped cells exposed to environmental versus electrochemical redox cycling.

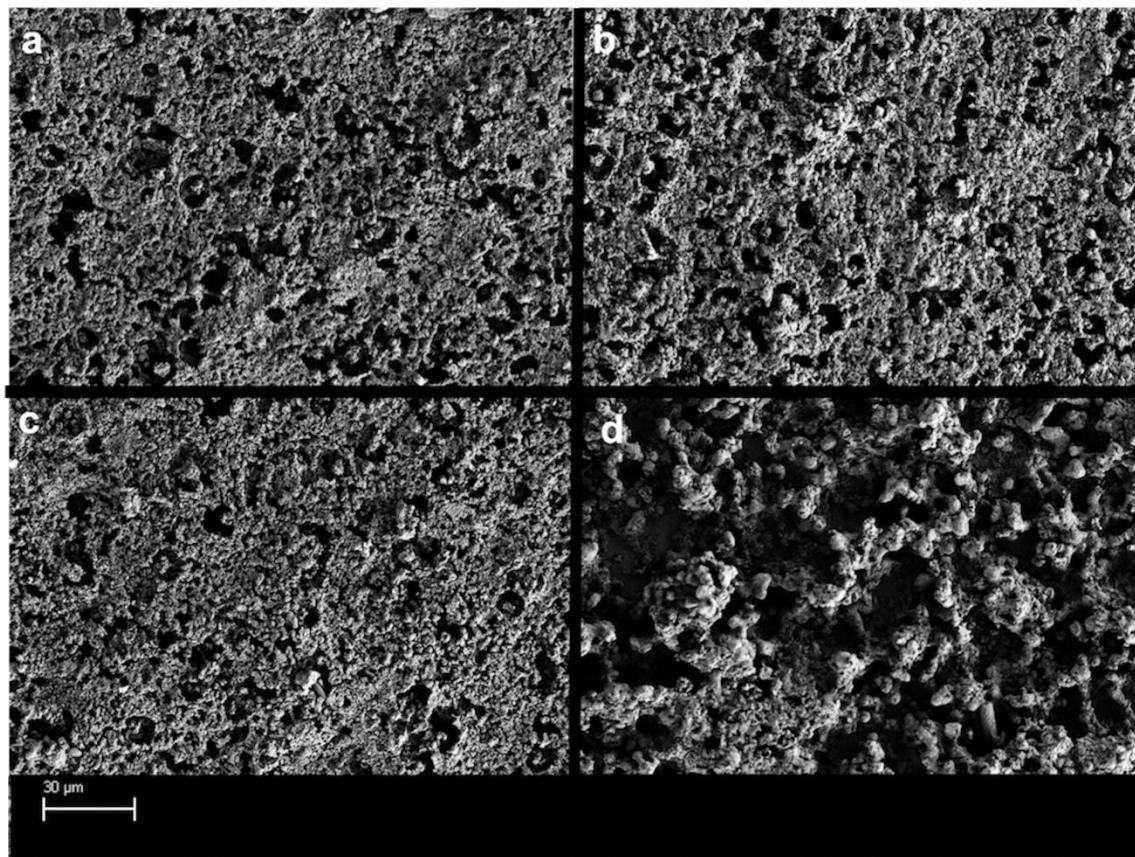


Figure A1.1. Ex-situ FE-SEM images of anode surface after H₂O exposure (a-ALT doped, b-undoped) and O₂ exposure (c-ALT doped, d-undoped)

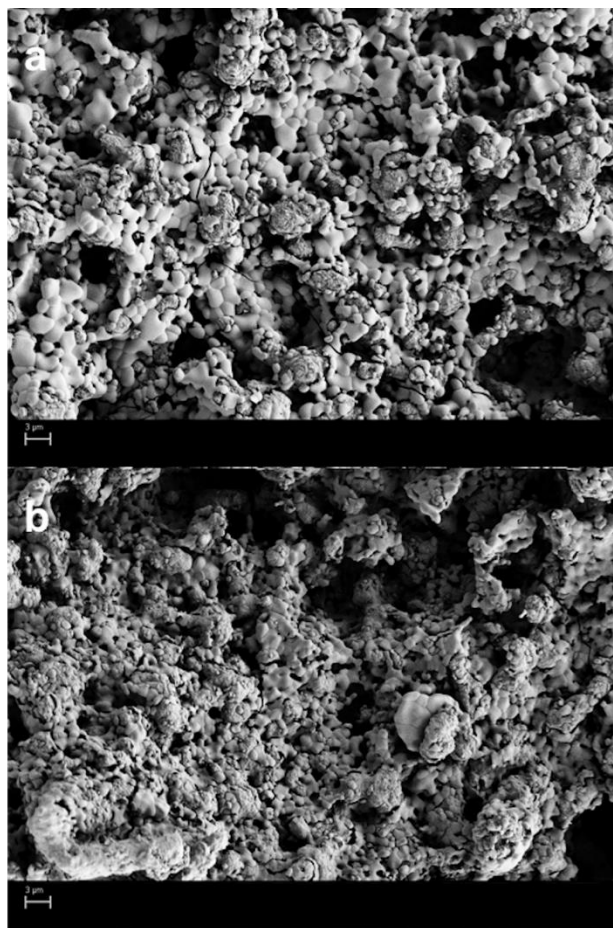


Figure A1.2. Ex-situ FE-SEM of anode surfaces exposed to electrochemical redox cycling (a-ALT doped, b-undoped)