

CHLORINE INDUCED DEGRADATION OF SOFCS OPERATING ON
CARBON CONTAINING FUELS

by

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of

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in

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ABSTRACT

Chlorine present in green and synthetic fuels such as biogas and syngas can accelerate degradation of solid oxide fuel cell (SOFC) nickel-based anodes. Chlorine contamination has been studied in SOFCs where H_2 was the primary fuel but little attention has focused on deleterious, cooperative effects that result from Cl-contamination in predominantly carbon-containing fuels. Experiments described in this work examine degradation mechanisms in SOFCs with Ni-YSZ cermet anodes operating with a biogas surrogate and exposed to 110 ppm Cl (delivered either as CH_3Cl or HCl). Operando Raman spectroscopy is used to directly observe the the anode's catalytic activity as evidenced by observable carbon accumulation, and electrochemical impedance and voltammetry measurements report on overall cell performance. Studies performed at 650 °C and 700 °C show that Cl suppresses carbon accumulation and causes slow but steady cell degradation. Prolonged exposure to Cl results in and irreversible device failure. These results differ markedly from recent reports of Cl contamination in SOFCs operating independently with H_2 and CH_4 .

INTRODUCTION

US energy usage has doubled since 1960, and with predictions for world energy usage to increase again by 20% by 2040 alternative energy devices that take advantage of solar radiation and wind energy are being developed with renewed fervor. [1] The most fundamental challenge with such devices is intermittent supply and inadequate storage media. [2] More traditional power production methods using fossil fuels are still necessary to keep pace with the increased demand for electricity. The efficiency of traditional electricity sources, mainly coal and natural gas power plants, has plateaued over the last 40 years. [1, 3–5] Lowering greenhouse gas emission while also producing more electricity necessitates a solution that would produce continuous, distributed power at high efficiencies with a small, scalable form factor device, while producing few greenhouse gases. Fuel cells can accomplish these goals while also operating as electrolyzers utilizing excess electricity to produce high energy content fuels. [6–11] Fuel cells do not require large power plant installations enabling distributed electricity generation, reducing losses due to electrical transmission. Examples of fuel cell commercialization already exist in countries like Japan. For almost a decade, Tokyo Gas has been marketing and selling their “ENE-FARM” fuel cell power production units throughout Japan for use by individual homes needing combined heat and power. [12, 13] The units themselves consist of low temperature polymer electrolyte fuel cells (PEFCs) operating on pure hydrogen produced from a separate gas reformer unit and claim 95% efficiency when operating with liquid petroleum (LP) gas. These types of fuel cells were used in early NASA missions due to their simplicity and benign products (water). Fuel cells in general (Figure 1.1) operate with a porous anode and

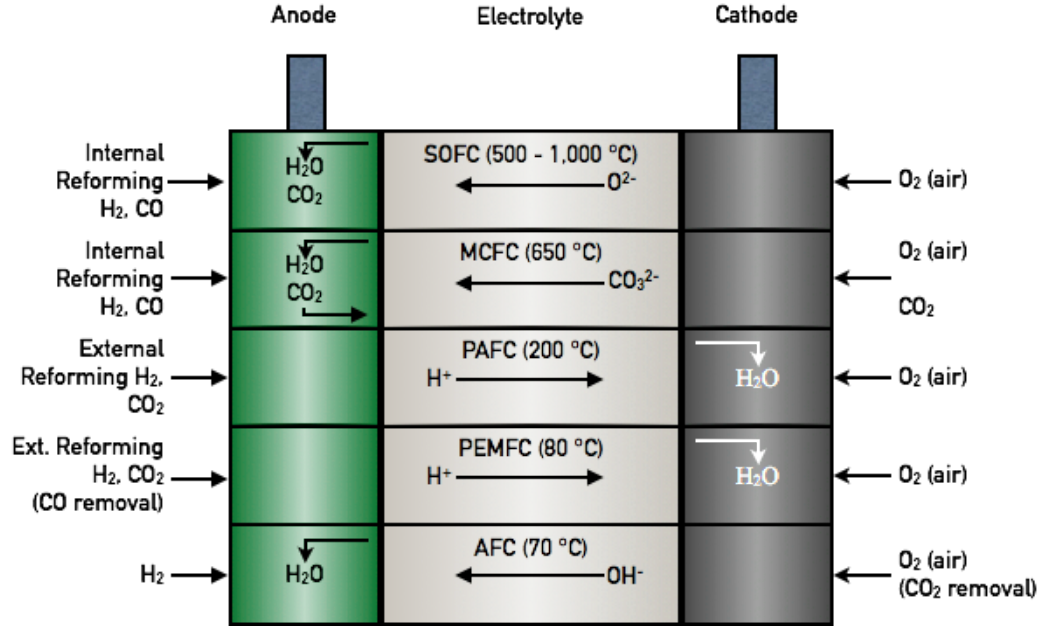


Figure 1.1: Fuel cell types, operating temperatures and gas treatments required for operation.

cathode separated by a dense membrane electrolyte. [14] The electrolyte transports charged species such as H^+ or O^{2-} due to potential difference and concentration gradients between the electrodes. Fuel cells in general work on the basic premise of interrupting electron flow of a redox reaction. The two half reactions for PEM fuel cells are shown in equation 1.1a and equation 1.1b and overall reaction in equation 1.1c. Molecular hydrogen is oxidized at the anode, producing electrons that power the external load. The oxidized hydrogen (protons) flow through the dense electrolyte and are reduced to water at the cathode by the same electrons that powered the external load.



While some commercial SOFC systems exist, widespread deployment of fuel cell systems as electricity producing devices is hampered by several considerations including cost and durability. [15–25] Low temperature fuel cells are particularly susceptible due to expensive electrocatalysts and the necessity of high purity fuels needed for operation. [17, 26–30] PEFCs are easily poisoned by a variety of contaminants including CO, that are difficult to remove from incident fuel streams, necessitating expensive reformers and filters or a short fuel cell operating life. High temperature fuel cells, on the other hand, are less susceptible to CO poisoning, use cheaper electrocatalysts, and can operate directly on commonly available, carbon-containing fuels without the need for a reformer. Specifically, solid oxide fuel cells (SOFCs) (Figure 1.2) can operate on fuels such as natural gas and syngas, making them an ideal power generating technology to transition away from fossil fuel consuming power plants and toward a more sustainable and secure power production infrastructure. [7, 11, 21, 31–35] However, technical challenges specific to SOFCs prevent these devices from being integrated into traditional power generating schemes. SOFCs operate in extreme conditions with both reducing (cathode) and oxidizing (anode) environments at very high temperatures, limiting the use of cheap materials for cell, interconnect, and rig construction. [6, 8, 20, 21, 36–40] Given the stringent requirements for operation, SOFCs are traditionally constructed of a cermet anode structure such as nickel-yttria stabilized zirconia (Ni-YSZ) with a dense YSZ electrolyte and a perovskite cathode, typically lanthanum strontium manganate

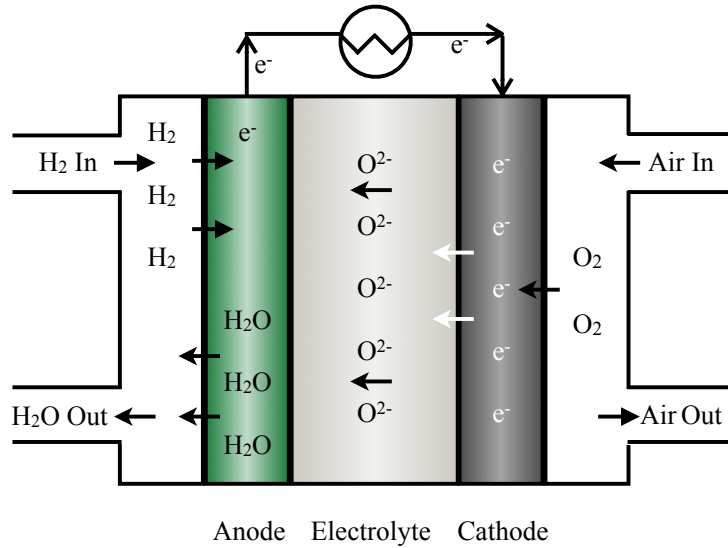


Figure 1.2: SOFC schematic showing operation on hydrogen.

(LSM) or lanthanum strontium cobalt ferrite (LSCF). (Figure 1.2) [39, 41–43] When operating on hydrogen, the complete electrochemical reaction is seen in equation 1.1c. In SOFCs, molecular oxygen at the cathode, usually provided as air, is reduced to O^{2-} (oxide) (Equation 1.1b). Oxide then diffuses through the dense electrolyte by way of oxide vacancies throughout the cubic zirconia lattice. Pure zirconia (ZrO_2), under relevant conditions, has a monoclinic structure and is an ion conducting insulator. [44, 45] Doping zirconia with yttria, however, not only stabilizes the cubic lattice, but also introduces oxide vacancies, endowing YSZ with oxide conductivity. Other ions of similar size, such as scandium, can also be used to stabilize the cubic zirconia lattice however, at most usable SOFC temperatures (690 °C–1000 °C), YSZ has a higher ionic conductivity. (Figure 1.3). [45–52] Oxides diffuse through the electrolyte from the cathode to the anode where they oxidize fuel to produce electrons, powering an external load.

In order for the oxidation reaction to occur at the anode, all three components (fuel, oxides, and electrons) must be present at a single location, called the triple

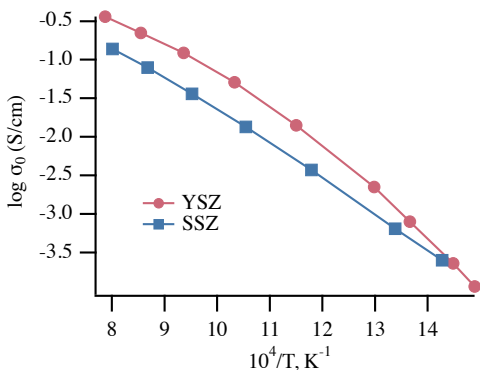


Figure 1.3: Comparison of the ionic conductivity of YSZ vs SSZ.

phase boundary (TPB) (Figure 1.4) While contaminants will adsorb anywhere along the nickel surface, non-fuel species at the TPB effectively stop electrochemical oxidation of fuel. [53–64] One solution to this type of contamination is to use a “mixed ionic-electronic conductor” (MEIC or MIEC) such as gadolinium doped ceria (GDC) or LSCF. [18, 39, 65–67] The advantages to such a material is that reactions can occur anywhere along the two-dimensional boundary between the material and a pore, greatly increasing reaction area over the one-dimensional TPB and removing bottlenecks. Significant effort has been dedicated toward developing and characterizing MIEC materials in recent years. [18, 39, 65–71] However, these materials are not as stable as cermet structures for use in SOFCs that are expected to operate for 10,000 hours or longer. At higher temperatures (i.e. above 800 °C) ion migration causes ion deficient regions, reducing conductivity throughout the electrode. Reactions between mobile ions and YSZ form insulating layers between phases preventing both electronic and ionic conduction. Such degradation methods are slow compared to degradation caused by contaminants however.

In addition to the challenges posed by high temperature materials degradation, various fuels used by SOFCs also contain contaminants that will prematurely degrade

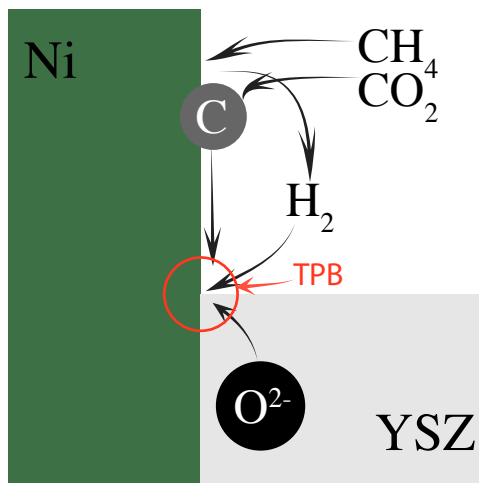


Figure 1.4: The three phases of a fuel cell anode (Ni, pore, and YSZ) during operation on CH_4

the cell. Of particular interest are the effects that contaminants, such as chlorine, sulfur, and other volatile gas phase species have on a SOFCs operating with carbon-containing fuels such as natural gas, biogas, and syn-gas. [7, 34, 35, 72–82] While the effects of contaminants on catalysts for common uses have been studied extensively, SOFCs offer unique and challenging problems to overcome given the variety of operational conditions. Traditionally, material durability studies are performed in oxidizing OR reducing environments, but a fuel cell can be subject to either at various points along the operational timeline. Sulfur, [40, 83–86] chlorine, [75, 87–90] phosphine, [77, 91, 92] and silicon [89, 93–95] have all been identified as contaminants for SOFCs. Sulfur has been studied extensively due to its persistence and steadfastness in nearly every fuel used for SOFCs. Recently, however, chlorine containing contaminants are being studied with increased frequency due to their presence in both manufactured syngas ($\text{H}_2 + \text{CO}$) and biogas ($\text{CH}_4 + \text{CO}_2$) obtained from landfill and other organic waste sites. Both biogas and syngas, when combined with SOFCs, provide an opportunity to use waste to produce electricity

efficiently. Syngas is also a byproduct for many industrial processes including ammonia production and synthetic natural gas production and can be generated from almost any carbon-containing source by way of gasification. Biogas, also called landfill gas [96,97], can be generated from human waste as well, including landfills by way of anaerobic digestion. (Equation 1.2)



Properly collected, biogas is a renewable resource derived from human activities, as it can also be generated from livestock manure, organic materials left over from crop harvesting, food waste, and more. [96–100] Biogas often contains a vast variety of contaminants in extremely varied concentrations due to the source diversity. A simple yet powerful way to monitor the effect of these contaminants on cell performance is by measuring cell potential and other electrochemical data over time. Electrochemical techniques are employed in order to study the effects these contaminants have on SOFC performance. [7,34]

Electrochemical Derivation and Characterization

Most literature studies described in this dissertation primarily use two electrochemical techniques to quantify SOFC performance: linear scan voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). (Figure 1.5) [75,84,92,101] LSV (Figure 1.5a) is a simple technique where a fuel cell is polarized in increasing increments and the current is measured until the cell bias between the cathode and anode is 0 V at which point cell is providing maximum current.

As the overpotential, the potential difference between the ideal cell voltage under open circuit conditions and actual cell voltage, increases, current increases until the

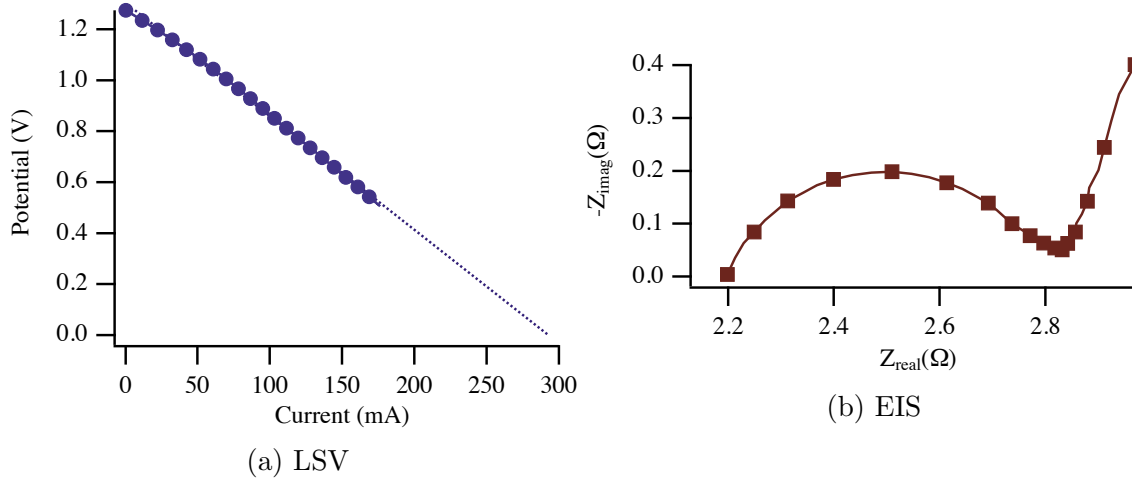


Figure 1.5: Examples of an LSV graph (a) and EIS spectra (b).

maximum current is reached. Applying Ohm's Law to LSV data provides the overall ohmic cell resistance and observing behavior at high and low overpotential can provide insight into the losses being experienced by the fuel cell.

First, however, a theoretical voltage must be calculated in order to quantify the losses. Standard state calculations for a fuel cell operating with H_2 predict a theoretical open circuit voltage (OCV) of +1.229 V from the two half reactions (equations 1.1a and 1.1b). Because fuel cells in general and SOFCs in particular do not operate under standard state conditions, one must account for changes in temperature and partial pressures to accurately predict fuel cell OCV. The equation for constant temperature Gibbs free energy (Equation 1.3a) combined with the relationship of Gibbs free energy to cell potential (in molar quantities) (Equation 1.3b) relates change

in cell potential with temperature. (Equation 1.3c)

$$dG = -SdT + Vdp \quad (1.3a)$$

$$\Delta\hat{g} = -nFE \quad (1.3b)$$

$$E_T = E^0 + \frac{\Delta\hat{s}}{nF}(T - T_0) \quad (1.3c)$$

where

S=total entropy, T=temperature, V=volume, p=pressure, $\Delta\hat{g}$ =molar Gibbs free energy, n=number of electrons transferred, F=Faraday's constant, E=cell voltage, E_T = cell voltage at temperature, E^0 = standard cell voltage, $\Delta\hat{s}$ = molar entropy, and T_0 = Initial Temperature

For a hydrogen-oxygen fuel cell operating at 700 °C, OCV resulting from this calculation is 1.07 V. Accounting for the chemical potential provides Equation 1.4a and when combined with Equation 1.4b results in Equation 1.4c, the Nernst equation, accounting for temperature and concentrations of reactant and products and their effect on cell voltage.

$$E_T = -\frac{\Delta\hat{g}^0}{nF} - \frac{RT}{nF} \ln Q \quad (1.4a)$$

$$E^0 = -\frac{\Delta\hat{g}^0}{nF} \quad (1.4b)$$

$$E_T = E^0 - \frac{RT}{nF} \ln Q \quad (1.4c)$$

where

R=ideal gas constant, and Q=reaction quotient

Using this equation the final OCV for a hydrogen-oxygen fuel cell operating at

700 °C is calculated to be 1.06 V. This theoretical voltage is what the cell would operate at given ideal conditions and materials while no current is being drawn. However, there are a variety of losses associated with operating a real life fuel cell including activation, ohmic, and mass transfer resistances. At low overpotential (left side of LSV trace)(Figure 1.6) the losses are associated with overcoming the activation energy of molecular oxygen dissociation/reduction at the cathode and can be modeled using the Tafel equation (Equation 1.5a). [102,103] For low temperature fuel cells this loss is significant, represented by a steep slope in LSV data at low overpotential. [104–106] (Figure 1.6 top left section) For high temperature fuel cells the losses are smaller or nonexistent allowing the fuel cell to provide current in the ohmic regime as soon as an overpotential is applied.(Figure 1.5a) “Ohmic” losses arising from oxide transport through the SOFC electrolyte, are referred to as the “ohmic” losses simply because they obeys Ohm’s law (Equation 1.5b). The voltage drop caused by charge transport can be calculated using Equation 1.5c, given the number of electrons transferred, bulk concentration of the reactant, thickness of the diffusion layer, and effective reactant diffusivity within the catalyst layer Electrolytes are made as thin as possible in an attempt to lower this value.

[107–109]

$$\eta_{act} = a + b \log i \quad (1.5a)$$

$$V = IR \quad (1.5b)$$

$$V = j \frac{L}{A\sigma} \quad (1.5c)$$

where

a=Tafel slope, b=Tafel constant, i = exchange current density, V=voltage, I=current, R=resistance, j=charge flux, L = length of the conductor, A=area of the conductor,

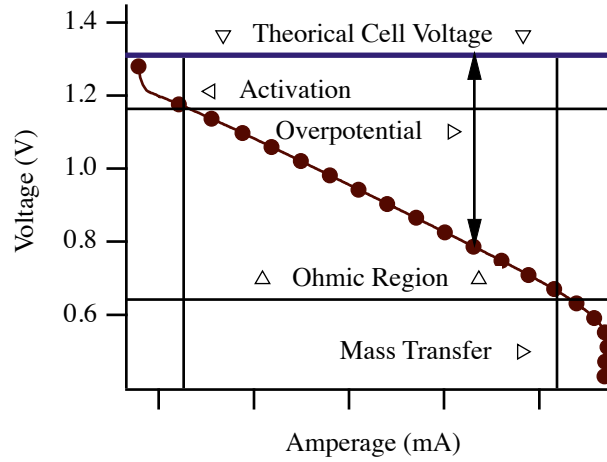


Figure 1.6: Schematic of an LSV trace with regions associated with specific losses.

σ =conductivity of the conductor

Finally, mass transport losses arise due to diffusion limitations in both the anode and cathode. Under strong polarization, diffusion cannot provide reactants and remove products fast enough to adequately fuel an ohmic limited current so the effective cell resistance increases. Fick's law (Equation 1.6a) can be modified to calculate the effective binary diffusivity of two gas species given the binary diffusivity of both gas species and the porosity and tortuosity of the porous media. [102,110–112] More importantly, the limiting current density can be calculated using Equation 1.6b, setting an upper limit on the current density due to mass flow restrictions. Large concentration resistances are incurred when heavily polarizing a SOFC with a porous anode microstructure obstructed with coke formed from methane decomposition, for example. This effect manifests itself as a very sharp increase in slope in the LSV trace. [110, 113] (Figure 1.6 bottom right section) In this way, LSV data provide much more information than simply the maximum current the cell can produce. Absent in LSV data, however, is any mechanistic information about why overall cell

resistances changes. EIS is much better suited to discern mechanistic changes within an operational SOFC.

$$D_{ij}^{\text{eff}} = \frac{\varphi}{\tau} D_{ij} \quad (1.6a)$$

$$j_L = nFD^{\text{eff}} \frac{C_R^0}{\delta} \quad (1.6b)$$

where

D_{ij}^{eff} =effective diffusivity, τ =tortuosity, j_L =limiting current density, C_R^0 =bulk reactant concentration, and δ =diffusion layer thickness

Electrochemical Impedance Spectroscopy (EIS)

EIS is a sophisticated technique in which a low voltage amplitude AC wave is passed through the fuel cell and the resulting current is measured. Unlike DC current that is strictly governed by resistance in accordance with Ohms law (Equation 1.5b), AC current is governed by impedance (Equation 1.7a), a complex quantity comprised of real and imaginary components associated with resistance and capacitance/inductance respectively. Voltage and current can be expressed as Equations 1.7b and 1.7c and combined to form the complex representation of impedance, Equation 1.7d.

$$Z = \frac{V(t)}{i(t)} \quad (1.7a)$$

$$V(t) = V_0 \cos(\omega T) \quad (1.7b)$$

$$i(t) = i_0 \cos(\omega T - \varphi) \quad (1.7c)$$

$$Z = Z_0 \cos\varphi + jZ_0 \sin\varphi \quad (1.7d)$$

where

Z =impedance, V =voltage, i =current, ω =radial frequency, T = time, and φ =phase

Graphing these two components along the x and y axis respectively creates a “Nyquist” (Figure 1.7) plot and provides further details on electrochemical reduction and oxidation mechanisms after assuming a model.

EIS Models

Models are developed using a combination of theoretical and empirical methods using simplified systems. Fuel cells are modeled using different circuit elements including resistors (R), capacitors (C), constant phase elements (Q), inductors (I), and warburg elements (W). When these elements are arranged in series-parallel configurations, often with resistor-capacitor (RC) parallel circuits, each combination of elements, called “equivalent circuit elements,” represents a different process within the fuel cell structure. As the AC wave passes through the fuel cell components, various processes impede the movement of charged species (electrons, oxides). The ohmic impedance, associated with the oxide flux through the electrolyte, diminishes the amplitude of the time dependent current with a 0° phase shift. (Figure 1.8a) Capacitive effects within the fuel cell also reduce current flow by way of frequency

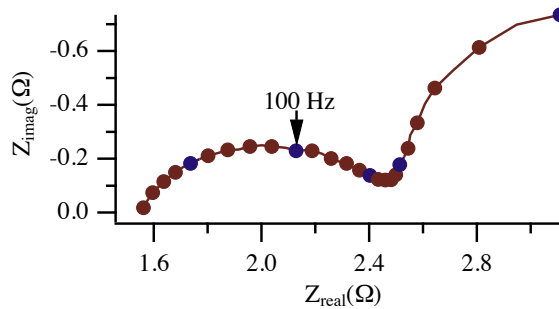


Figure 1.7: Typical Nyquist Plot

dependent capacitive resistance (Equation 1.8a), in the process inducing a phase shift between voltage and current by -90° . Similarly, inductive reactance has a frequency dependent resistive element (Equation 1.8b) caused by the resistance to the change in current within the inductor. An inductor, however, shifts the current by $+90^\circ$. (Figure 1.8b) Using Equation 1.8c, the equation for a parallel RC circuit can be derived. (Equation 1.8d)

$$Z_c = -\frac{1}{j\omega C} \quad (1.8a)$$

$$Z_i = j\omega L \quad (1.8b)$$

$$\frac{1}{Z_{\text{parallel}}} = \frac{1}{Z_1} + \frac{1}{Z_2} \quad (1.8c)$$

$$Z_{RC} = \frac{1}{\frac{1}{R_f} + j\omega C} \quad (1.8d)$$

where

$j=\sqrt{-1}$, C =capacitance, L =inductance

A potentiostat can measure these changes in the AC wave and plot results as a function of frequency to which a model is applied. SOFCs typically show 1-3 arcs in EIS spectra (Figure 1.7) corresponding to anodic impedance, cathodic impedance, and mass transfer impedance, but more arcs can be modeled if more complicated chemistry is expected. [41, 103, 110, 111, 114–117] Capacitance in fuel cells results largely from a phenomenon as “double layer capacitance.” Because fuel cells have separate conductors for the negatively charged electrons, negatively charged oxides, and oxidized fuel, adjacent phases within the electrode will be charged differently, like the plates of a capacitor, causing a capacitive effect. [110, 118, 119](Figure 1.9) By monitoring changes in individual arcs or number of arcs, one can identify how

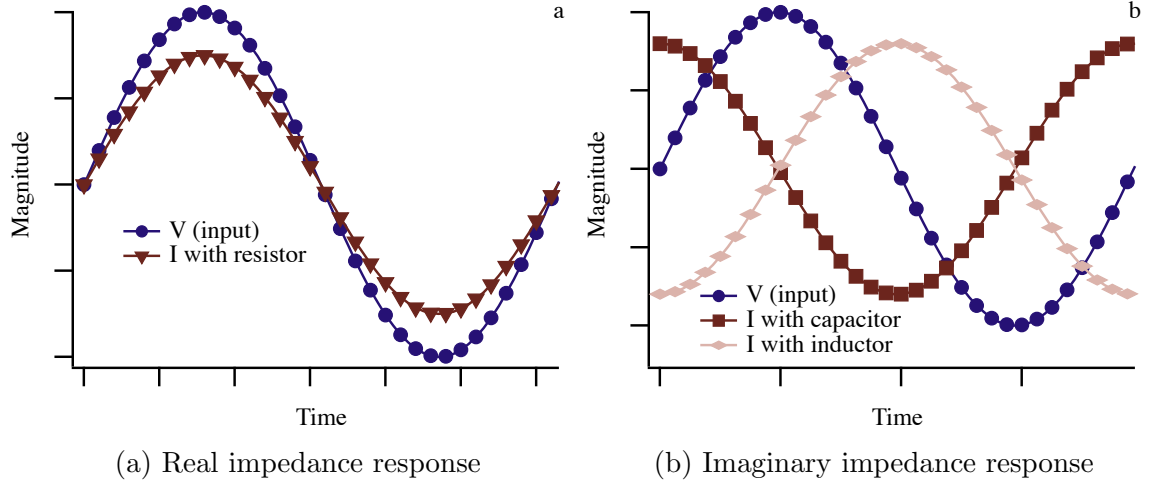


Figure 1.8: A sinusoidal voltage perturbation with resulting real (a) and imaginary (b) current response.

different charge transfer and transport processes change during a cell's operation, allowing for prediction of SOFC mechanisms.

One final technique for monitoring fuel cell performance is also the most simple and widely used. Polarizing the cell galvanostatically (constant current) provides a useful indicator of fuel cell performance when observing the potential over time. As the fuel cell performance drops, the overpotential required to produce a certain current will increase, resulting in a drop in observed potential while polarized. Polarizing

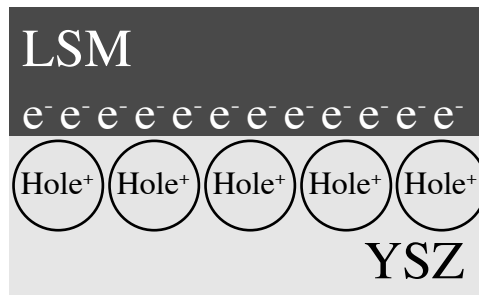


Figure 1.9: Schematic representation of the double layer capacitance in a SOFC with a LSM cathode and YSZ electrolyte.

the cell potentiostatically (constant potential) and measuring the current provides analogous information. These measurements can quantify rates of degradation allowing possible mechanisms to be inferred. Very often in the literature, contaminant degradation is studied using only the above techniques, occasionally with *ex-situ* supplementary measurements performed before and after the fuel cell has operated. [75,84,92,101] While these reports do identify longevity of certain types of fuel cells in specific situations, they do not provide direct insight into the mechanism of why the cell failed. Molecularly specific, *operando* measurements are required in order to test and validate, if appropriate, proposed reaction mechanisms. *Operando* optical spectroscopy has proven a useful development to answer these questions.

Raman Spectroscopy

Raman spectroscopy provides real time, molecularly specific information that can be directly correlated to SOFC reactions. [43, 113, 120–122] In a Raman experiment monochromatic light is used to irradiate the anode, scattering off of atoms on the surface to a virtual energy state, ultimately relaxing to either a higher vibrational energy state as the Stokes shift, or a lower energy state as the anti-Stokes shift. (Figure 1.10)

SOFC operational temperatures require the use of a relatively short incident wavelengths in order to avoid blackbody radiation. (Figure 1.11) While the blackbody radiation can be modeled using Planck’s Law to predict surface temperature (Figure 1.11), the high background reduces signal to noise and hides signals with large Raman shifts. Raman measurements with UV lasers are hampered by expensive and inefficient optics; therefore 488 nm is a good compromise. High temperature Raman spectroscopy is also difficult because many species decompose or pyrolyze, reducing the number of Raman active species available. SOFCs operating with H₂ show little

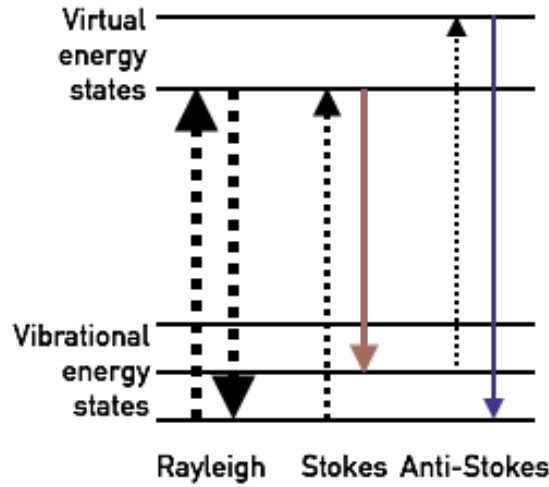


Figure 1.10: Schematic representation of Rayleigh, stokes and anti-Stokes shift for Raman spectroscopy.

observable Raman spectroscopic information save for nickel oxide being formed if the cell is aggressively polarized, particularly under lean fuel conditions.

However, when SOFCs operate with carbon-containing fuels, Raman spectroscopy can be used to measure the methane catalytic activity of the fuel cell

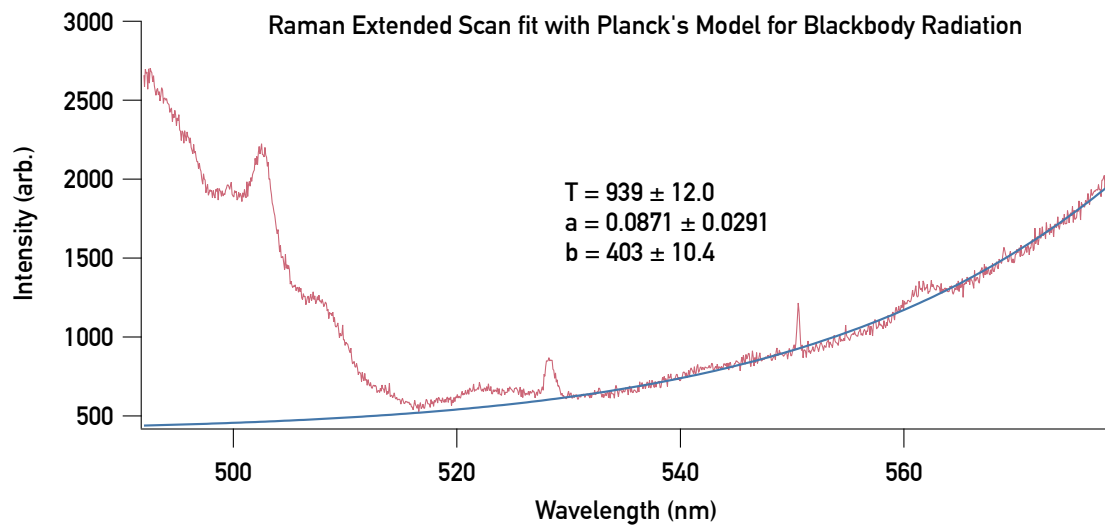
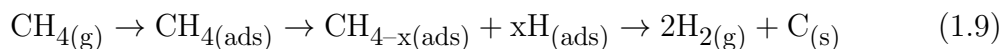


Figure 1.11: Raman extended scan of an SOFC Ni-YSZ anode taken at 675 °C fitted to Planck's model for Blackbody Radiation

anode by monitoring the graphite signal. Carbon (or “coke”) accumulates on a fuel cell anode by way of methane activation (Equation 1.9) producing adsorbed and/or gaseous hydrogens and solid carbon. Figure 1.12 shows an *operando* spectrum of carbon on the surface of a fuel cell. [43,72,87,88,113,120–125]



Four features are prominent in the chlorine free *operando* spectrum of accumulated carbon on a Ni-YSZ cermet anode. The first peak at 595 cm^{-1} results from the $\text{F}_{2\text{g}}$ mode in cubic zirconia. [126–128] The remaining peaks result from carbon on the anode surface, starting with the ‘D’ peak at 1360 cm^{-1} resulting from point defects and/or grain boundaries in graphite, commonly referred to as “disordered” carbon. “Ordered” carbon, that is defect-free sp^2 hybridized carbon, produces the peak at 1560 cm^{-1} , due to the in-plane optically active vibration

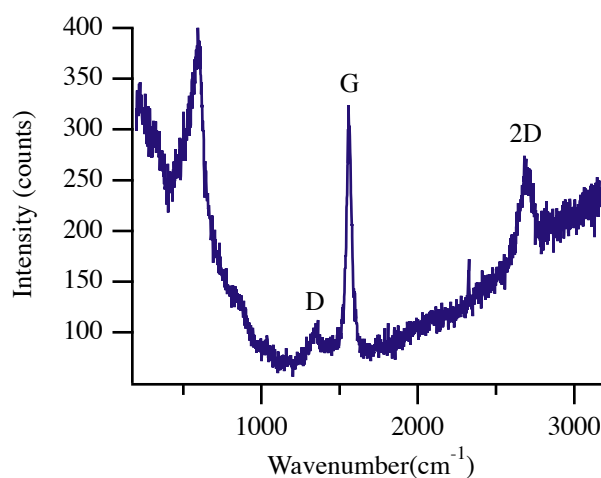


Figure 1.12: *Operando* Raman extended scan of coke on the surface of a SOFC anode operating on methane at $700 \text{ }^{\circ}\text{C}$

(E_{2g} mode). Finally, the peak at 2700 cm^{-1} is typically assigned to the electron-phonon coupling of the second order zone boundary phonons in graphite that are disallowed in the first order spectra. [129–134] The most common carbon observed on fuel cell anodes during methane activation is ordered, graphitic carbon with increasing amounts of disordered carbon as the molecular weight of the fuel is increased. The carbon ‘G’ peak intensity plotted vs. time (Figure 1.13b) shows the kinetics of carbon formation and the overall temporal stability of that carbon on the surface of the anode. This approach allows for real time assessment of the anode’s catalytic activity toward the methane cracking reaction, an important property when studying SOFC longevity while operating with contaminated carbon-containing fuels. Furthermore, monitoring the ‘G’ peak intensity allows for insight into the type of degradation caused by contaminants. Electrochemical measurements demonstrate that the cell is failing, but Raman measurements more clearly detail why degradation is occurring at all.

Other optical spectroscopic methods such as near infrared thermal imaging

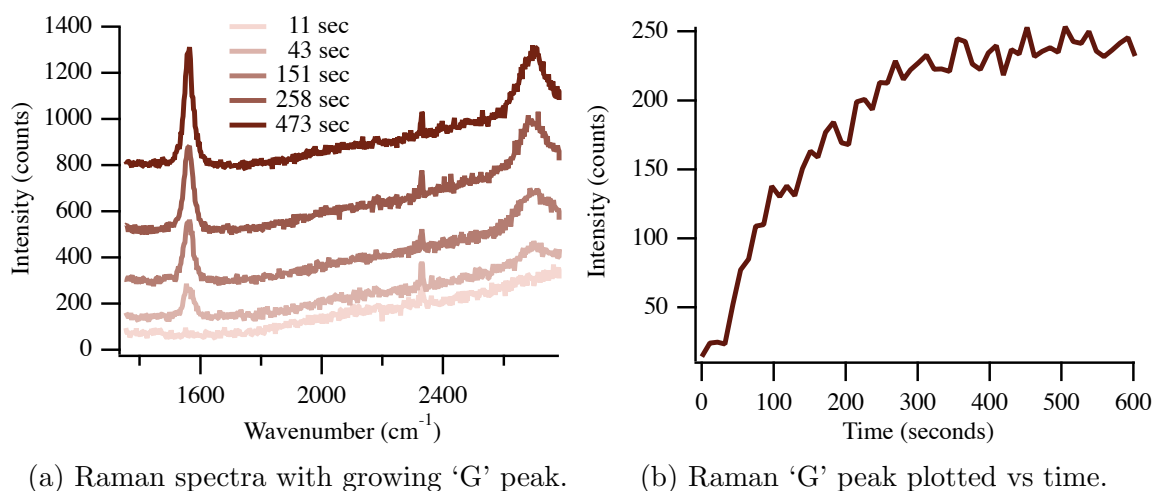


Figure 1.13: Raman ‘G’ peak kinetics

(NIRTI) [135–137] and Fourier transform infrared emission spectroscopy (FTIRES) [122, 123, 136, 138] offer complementary data that, when combined with electrochemical and Raman measurements, provide a more complete mechanistic picture of a fuel cell operating on contaminated carbon-containing fuels. NIRTI provides insight into the thermodynamics of the reactions occurring on the surface and spatial distributions of localized heating or cooling. FTIRES identifies gas phase species above the anode adding to the molecularly specific information gained from Raman spectroscopy.

Most studies reporting on SOFC failure have focused on contaminant degradation when a SOFC is operated with H_2 or H_2 containing fuels such as syngas. [73, 75–77, 79, 139] In order for degradation mechanisms of SOFCs operating with carbon-containing fuels to be accurate, general (non electrochemical) degradation mechanisms of normal high temperature catalysts must be taken into account. The initial experiments propose a two-step degradation method of a SOFC poisoned by chlorine while operating on H_2 . The first occurs quickly when the cell is initially exposed to chlorine (in the form of HCl or CH_3Cl). Chlorine atoms dissociatively chemisorb to the nickel catalyst surface, blocking some surface sites for H_2 chemisorption resulting in some small, reversible performance loss. (Figure 1.14a) The second step of degradation depends on temperature, but can result in irreversible degradation over the course of hundreds of hours. Adsorbed chlorine reacts with the nickel forming nickel chloride compounds impeding electron flow throughout the anode. (Figure 1.14b) At higher temperatures ($> 700\text{ }^\circ\text{C}$) nickel chloride has a non-zero partial pressure and will evaporate, temporarily exposing fresh nickel material to the oncoming fuel stream, but causing irreversible loss of anode material in the process. [75, 89, 90] These mechanisms are still present, but are not the main failure mechanism when operating on carbon-containing fuels. *Ex-situ* FE-SEM images clearly show the differences in degradation for a fuel cell exposed to chlorine-

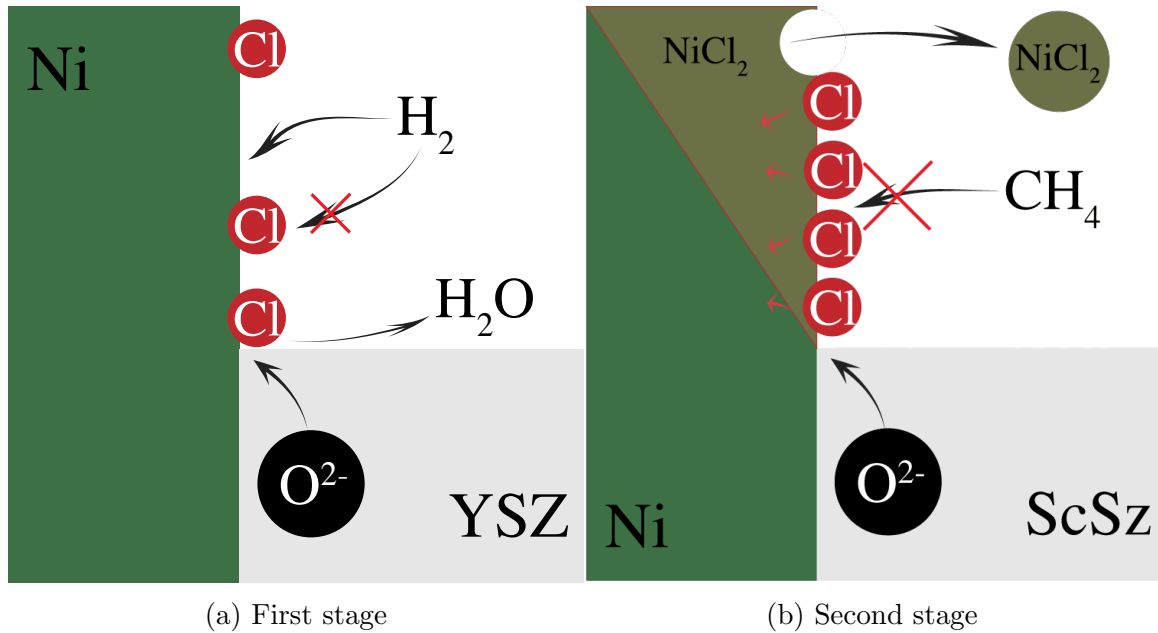


Figure 1.14: Schematic representation of the two stages of degradation when a SOFC is operated with chlorine containing H_2

contaminated methane operating at $650\text{ }^\circ\text{C}$ (Figure 1.15a) and $700\text{ }^\circ\text{C}$. (Figure 1.15b) The image taken of a SOFC operated at $650\text{ }^\circ\text{C}$ shows smooth nickel particles and even some grain boundaries. At $700\text{ }^\circ\text{C}$ however, the nickel particles are corroded and pitted, corresponding with the evaporation of parts of the particle itself. The degradation ultimately responsible for device failure, fuel starvation, does not appear in the images at all.

While these observations fall directly in line with mechanisms predicted from H_2 experiments, they do not explain the catastrophic failures and significant time difference before failure experienced by SOFCs operating on carbon-containing fuels when compared to SOFCs operating on H_2 . Experiments using chlorine-contaminated H_2 last for many hundreds of hours and often result in only single digit percentage point losses in performance. Operation with carbon-containing fuels shows SOFCs failing catastrophically after 10s of hours, an order of magnitude less than with H_2

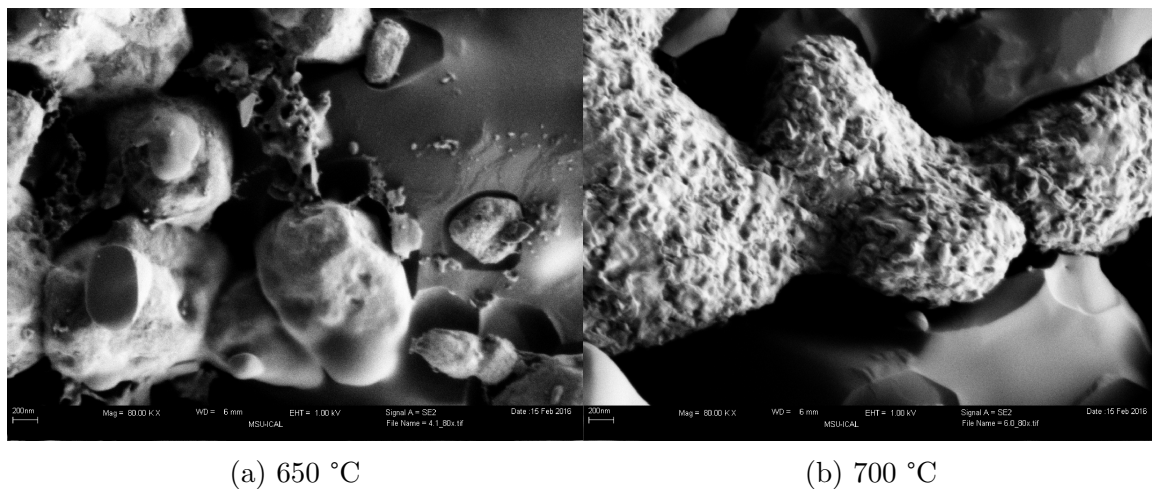


Figure 1.15: FE-SEM images of chlorine degradation of a SOFC operating on methane at 650 °C (a) and 700 °C (b)

alone. It is clear that in order to pursue SOFC technology as a viable alternative to traditional power plants, degradation when operating on carbon-containing fuels must be fully understood outside of the confines of H_2 to prevent premature failure in the field.

Work presented in this dissertation chlorine-induced SOFC anode degradation mechanisms change when a carbon-containing fuel is used. The degradation mechanisms relevant to H_2 operation are still present, but not predominant. Chlorine more effectively blocks active sites for CH_4 activation compared than H_2 , causing fuel starvation and anode cannibalization under galvanostatic conditions. Moreover, the presence of any excess H_2 present in the fuel stream actively hides degradation as the packing efficiency of chlorine on the nickel surface is not sufficient to block all available H_2 active sites. The chapters below discuss a number of publications that delve deep into this problem attempting to explicate the degradation mechanisms of a SOFC operating on chlorine-contaminated methane and other carbon-containing fuels, and what role H_2 plays in that degradation.

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CHAPTER TWO

IN OPERANDO VIBRATIONAL RAMAN STUDIES OF CHLORINE CONTAMINATION IN SOLID OXIDE FUEL CELLS

Contribution of Authors and Co-Authors

Manuscript: In Operando Vibrational Raman Studies of Chlorine Contamination in Solid Oxide Fuel Cells

Author: Kyle W. Reeping

Contributions: Collected and analyzed all data. Wrote and edited manuscript.

Co-Author: Robert A. Walker

Contributions: Assisted with data interpretation manuscript editing.

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THE EFFECTS OF CH₃Cl ON A FUEL CELL OPERATING ON METHANE AT
650 °C

Introduction

Solid oxide fuel cells are electricity-generating devices capable of fuel-to-electricity conversion efficiencies of more than 80% when combined with heating applications. [140–142] These efficiencies far outpace even the most modern fossil fuel fired power plants. In addition, the high operating temperatures of solid oxide fuel cells (SOFCs) allow operation with many different fuels including biogas, syngas, natural gas, gasoline and even some alcohols. [143–146] However, this versatility comes at the cost of having to develop SOFC materials capable of withstanding impurities intrinsic to each fuel type. These impurities include, but are not limited to, carbon, sulfur, chlorine, silicon, phosphorus, and mercury. Each can cause premature degradation of SOFC materials. [144, 147–153] Many, if not all, of the impurities have been studied extensively using electrochemical methods. Techniques such as electrochemical impedance spectroscopy and voltammetry consistently show how exposure to these individual contaminants lead to performance degradation with differing levels of severity and reversibility. However, while the electrochemical results quantify overall cell degradation, direct, in-situ evidence of the mechanisms responsible for diminished performance remain speculative. Coupling electrochemical methods with in-situ optical spectroscopy, such as Raman spectroscopy or XPS, advances understanding of the reactions that occur on the SOFC electrode surfaces as well as how those reactions affect performance. Raman spectroscopy has already shown to be a promising technique for high temperature in-situ characterization of molecules on the surface of an SOFC operating on hydrocarbon fuels. [154–156]

Optical spectroscopy has been used extensively to study degradation in SOFCs caused by carbon accumulation. [151,157–159] These studies have shown that when carbon deposits form, anode degradation can occur via several mechanisms including metal dusting, loss of porosity, and elimination of electrical connectivity throughout the anode. Carbon accumulation or “coking” represents one of the primary challenges facing commercial development of SOFCs that use carbon containing fuels. This problem is not limited simply to hydrocarbon fuels. CO in syngas can form carbon deposits through Boudouard chemistry and alcohols such as methanol and ethanol are capable of forming large carbon deposits in SOFC anodes as is biogas (a mixture of CH_4 and CO_2) at relatively low temperatures (700 °C). [143] However, the effects of contaminants on carbon accumulation with cells running with even the simplest carbon-containing fuels are unknown. Some reports suggest that contaminants have positive coordinated effects on fuel cell performance by mitigating poisoning effects of other contaminants present in the fuel stream. Methyl chloride, for example, has been shown to counter phosphine poisoning effects on Ni/YSZ based SOFCs operating at 750 °C. [160] Many other contaminant combinations remain uncharacterized simply because the primary methods used to produce alternative fuels from coal or landfill mass do not remove the contaminants present in the original materials. Alternative fuels derived from renewable resources also contain many different contaminants. [150,161]

Syngas, a popular fuel for electricity production, is primarily produced by a process called coal gasification. The process involves partially oxidizing pulverized coal by heating it and flowing a mixture of oxygen and water through the powder. However, since some coal contains high levels of sodium chloride, ranging from 0.01% to 0.5%, the resulting syngas can contain chlorine contaminants. [162,163] Water scrubbing can only partially mitigate chloride contamination, with up to one

third of the original Cl concentration remaining in the fuel stream. [164] Even at concentrations as low as 20 ppm, chlorine is responsible for significant degradation of SOFC anodes. [162] However, completely removing chlorine contaminants from the fuel stream of an SOFC is both costly and complicated. [163, 165]

Understanding how chlorine affects SOFC performance with carbon containing fuels and the material properties of electrocatalytic anodes will help better assess tolerable upper limits on chlorine concentration in SOFC fuel streams.

In the studies described below, vibrational Raman spectroscopy is used to examine how a Cl-containing contaminant, methyl chloride (CH_3Cl), affects carbon accumulation on Ni-YSZ cermet anodes in operando. Complementing the Raman experiments are electrochemical measurements that monitor cell performance and the condition of cell components. Data show that chlorine poisoning coupled with metal dusting due to carbon accumulation degrades the anode at an accelerated pace when compared to either contaminant alone. The degradation is partially reversible with the cell recovering to 70% of its original performance.

Experimental

25.4 mm diameter membrane electrode assemblies (MEAs) with a 250 – 300 μm thick electrolyte were purchased from Fuel Cell Materials. (www.fuelcellmaterials.com) The electrolyte was composed of Fuel Cell Material's Hionic, zirconia based, substrate. The electrodes consisted of a 50 μm Ni-YSZ cermet with a thin (5 μm) Ni-GDC interlayer and a 50 μm LSM with an LSM-GDC interlayer on opposite sides of the MEA. Small 3x3 mm silver and platinum current collectors were placed on the Ni-YSZ and LSM electrodes and held in place with gold and platinum paste respectively. Electrochemical results were collected using a Princeton Applied Research Versastat 3. The MEAs were

assembled in a compression sealed assembly dubbed SAwCER (SOFC Assembly with Concurrent Electrochemistry and Raman). Raman spectra were collected using a Renishaw inVia Raman Microscope and a 25 mW, 488 nm Ar-Ion laser with 10 second exposures. Cells were heated to 650 °C at 3.5 °C per minute under argon on the anode and air on the cathode. Once at operational temperatures, final gas flows were adjusted to 55 sccm argon on the anode and 85 sccm air on the cathode. The anode was then reduced using an 18 sccm flow of H₂ until the potential stabilized. The hydrogen flow was then increased to 100 sccm for the final reduction. Benchmark electrochemical impedance spectroscopy (EIS) and linear scan voltammetry (LSV) measurements were run to test for a functional cell upon electrochemical stabilization. Once cell performance was confirmed, methane exposures commenced. After benchmarks were run under 100 sccm H₂, hydrogen flow was reduced to 18 sccm to conform to previous experimental conditions. Following stabilization at 18 sccm H₂, the fuel was switched to 20 sccm CH₄ and polarized to the desired potential. After a 10 minute exposure to CH₄, EIS and LSV measurements were made. Then, any accumulated carbon was removed electrochemically by polarizing the cell and removing the CH₄ from the fuel source. The cell was then reduced again under 100 sccm H₂ and the process repeated until the cell performance dropped to ~40% of the original benchmarks. After the benchmarks and setup were completed, 110 ppm CH₃Cl was introduced into the fuel stream for the remainder of the experiment. Following all experimental steps, the cell was cooled under argon on both anode and cathode for ex-situ analysis.

Results

The Fuel Cell Materials MEAs provided a consistent substrate on which to perform experiments. Representative EIS and LSV data of an MEA operating on

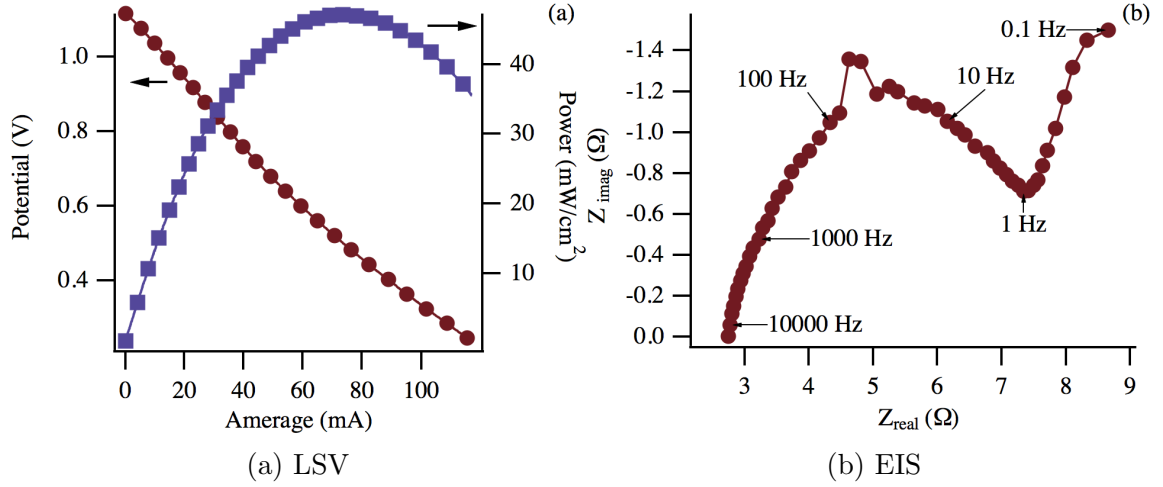


Figure 2.1: (a) LSV (red circle) and power (blue square) curves for typical Fuel Cell Materials MEAs operating at 650 °C. (b) EIS curve for typical Fuel Cell Materials MEAs operating at 650 °C. The two extraneous points at 70 and 60 Hz are due to interference from the resistively powered furnaces.

hydrogen at 650 °C are shown in Figure 2.1. The sloped LSV (Figure 2.1a) shows no indication of high activation barriers or mass transport limitations that would be evidenced by more negative slopes at the low current and high current limits, respectively. [166] The EIS data (Figure 2.1b) show a low bulk resistance (R_{Bulk}) of 2.75 Ω . This resistance is slightly higher than typical experiments that are run at temperatures between 675 °C and 800 °C. [159] Immediately obvious are the two points offset from the trace at about 60 Hz. These extraneous points are due to the experimental setup, specifically interference from the resistively powered furnaces surrounding the cell. We chose to model the EIS spectra using the 4-element RC circuit shown in Figure 2.2. [167–169] The first element, R_{Bulk} , corresponds to the ohmic resistance of the electrolyte. The remaining elements are RC circuits, all of which contribute to the overall polarization resistance R_{Pol} . The second and third circuit elements (RC1 and RC2) represent cathode and anode processes respectively. Finally, the last element (RC3) correlates to mass transfer limitations. [170,171]

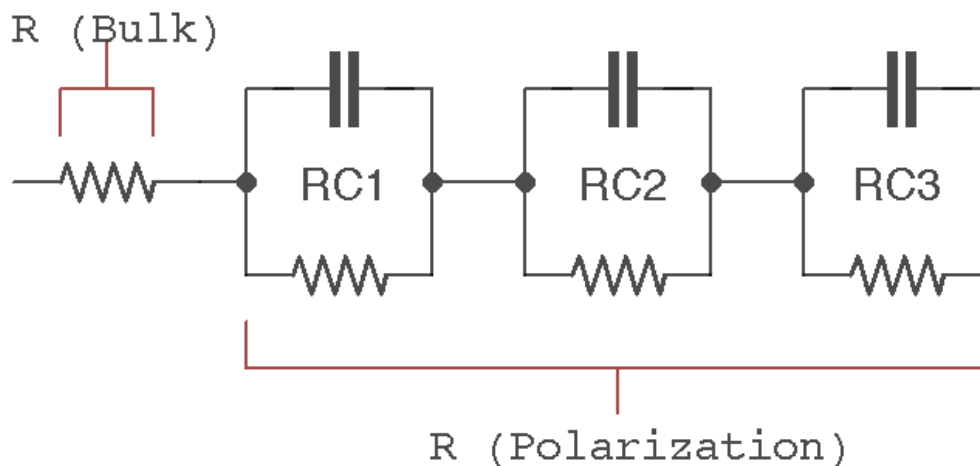


Figure 2.2: Schematic of the DC circuit used for EIS analysis.

Often the electrode activation process elements overlap and are difficult to differentiate, which is why only two arcs are visible in the EIS spectrum (Figure 2.1b). Only part of the mass transfer arc is visible, starting at ~ 1 Hz.

Raman Spectroscopy

Chlorine has no thermodynamically stable, spectroscopically visible products that form at 650 °C, but chlorine's effects on Ni-based anodes operating with CH_4 are readily apparent in the carbon accumulation data. Figure 2.3a shows a Raman spectrum of typical carbon accumulation on the anode of an SOFC. Three peaks are discernible: The 'G' peak at 1560 cm^{-1} represents ordered graphite sheets, the 'D' peak at 1350 cm^{-1} represents defects or edges in the graphite sheet, and the '2D' peak at 2650 cm^{-1} arises due to electron phonon coupling. [172, 173] Carbon formation kinetics were measured by plotting the 'G' peak intensity versus time (Figure 2.3b). These traces were acquired at a polarization of 50% I_{max} as chlorine poisons the cell. Given its low concentration, we assume that carbon accumulation from the CH_3Cl is negligible. Before CH_3Cl is added to the fuel stream, Ni anodes

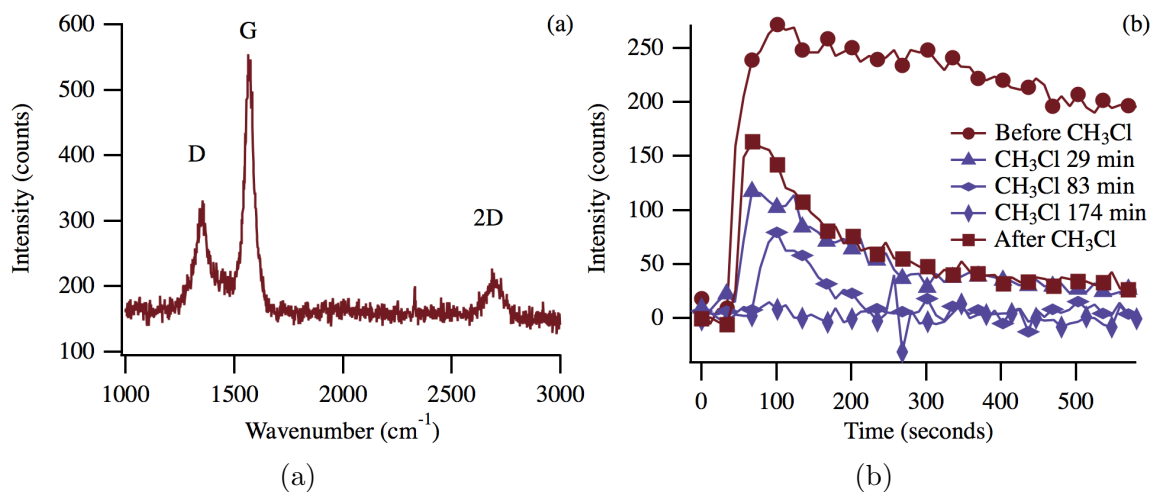


Figure 2.3: (a) Raman spectrum acquired in operando on the surface of an SOFC anode. (b) G peak intensity monitored over time showing carbon signal disappearance after exposure to CH_3Cl for different amounts of time. The red circle and square traces were acquired before and after CH_3Cl exposure, respectively.

exposed to CH_4 show rapid carbon accumulation (red circles). With the introduction of CH_3Cl to the fuel stream, accumulated carbon becomes much less stable. At only 29 minutes of exposure to CH_3Cl , the maximum carbon signal intensity from CH_4 drops to less than half of its early-time, maximum signal. (blue upward triangles) The carbon signal intensity continues to drop as the chlorine exposure is prolonged, and eventually (after 174 minutes of CH_3Cl exposure) exposure to methane results in no observable carbon accumulation. (blue vertical diamond) This phenomenon was accompanied by a measurable electrochemical performance drop as measured by LSV (Figure 2.4a). Halting the CH_3Cl exposure and allowing the cell to stabilize under hydrogen led to partial recovery of performance. The first exposure to CH_4 after the CH_3Cl had been removed resulted in observable carbon accumulation with absolute intensity at approximately half of that observed prior to CH_3Cl exposure (Figure 2.3a).

Electrochemistry

Signs of cell degradation are observed in both LSV (Figure 2.4a) and EIS (Figure 2.4b). LSV traces from MEAs operating with CH_4 in the presence of CH_3Cl show increasingly steeper slopes (and lower maximum currents), a phenomenon that mirrors the continued loss of observable carbon accumulation in the Raman spectra. All LSV traces show low resistance at low currents indicating facile catalytic oxidation at the anode and surprisingly, little to no loss of catalytic activity. Like the intensity in the Raman spectra monitoring carbon accumulation, the LSV traces recovered to about half of the original performance once the contaminant was removed and the cell recovered under hydrogen. However, the shape of the recovered LSV differed from the LSV trace acquired prior to CH_3Cl exposure. The activation resistances at low current look similar, as does the resistance corresponding to mass transport at high current. The difference in shape and increase in resistance occurs at an intermediate current that is generally associated with ohmic losses. In the EIS data, both R_{Pol} and R_{Bulk} increased steadily during exposure to CH_3Cl (Figure 2.4b). When the CH_3Cl was removed, R_{Bulk} returned to its pre-exposure limit ($2.75\ \Omega$) but R_{Pol} remained large, indicating that the MEA retained good connectivity between the electrolyte and the anode, but the anode microstructure suffered partial irreversible damage during exposure.

Unlike the results above for CH_4 , benchmark LSV and EIS results run under hydrogen showed very little degradation during the entire duration of exposure to CH_3Cl (Figure 2.5). Figure 2.6 shows the potential vs. time traces of the cell under galvanostatic polarization. Prior to CH_3Cl exposure, cell potential remained constant when polarized. However, stabilization does not occur while the polarized cell is exposed to CH_3Cl . During the early stages of CH_3Cl exposure, the potential rose very gradually but with longer exposures, cell potential rose more rapidly until

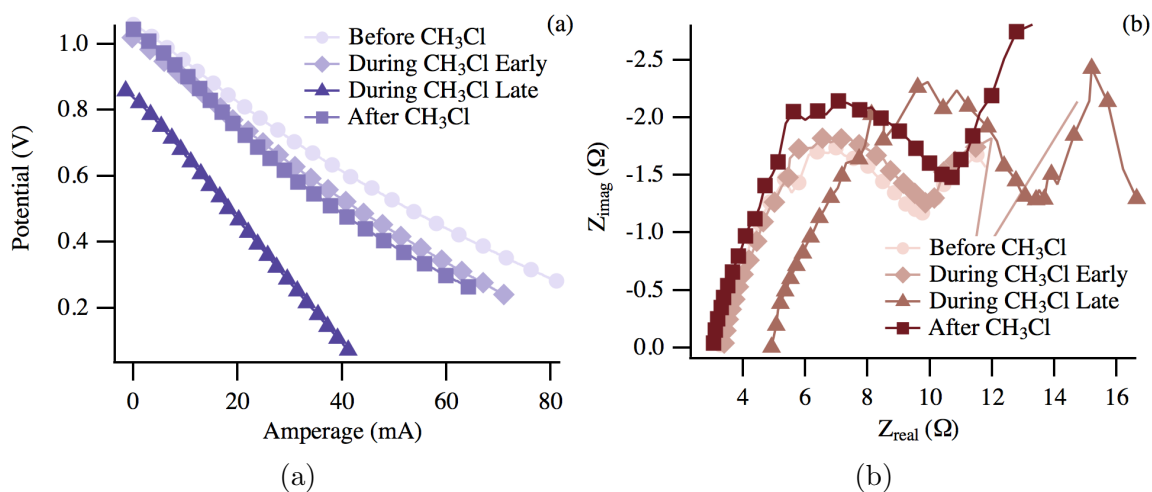


Figure 2.4: (a) LSV curves performed using CH₄ fuel before CH₃Cl exposure (circles), during exposure early (diamonds), during exposure late (triangles) and finally after recovery in H₂ (squares.) (b) EIS curves before CH₃Cl exposure (circles), during exposure early (diamonds), during exposure late (triangles), and finally after recovery in H₂ (squares.)

it passed through 0.0 V indicating that electrochemical oxidation of CH₄ was no longer thermodynamically favored. [169] Like the electrochemical behavior and carbon accumulation kinetics, this behavior reverses following removal of the CH₃Cl and reconditioning the anode with H₂. The irreversible anode degradation can be seen in the post CH₃Cl potential under polarization that is constant but smaller in magnitude than the potential prior to CH₃Cl exposure.

Discussion

Published reports describing chlorine contamination of SOFC anodes have proposed that, like sulfur [174–176], chlorine poisoning occurs in two stages. First, chlorine reversibly adsorbs to the nickel surface, blocking active sites. The second, irreversible poisoning mechanism is proposed to be the formation of nickel chloride compounds. [177, 178] However, since nickel chloride species are volatile at

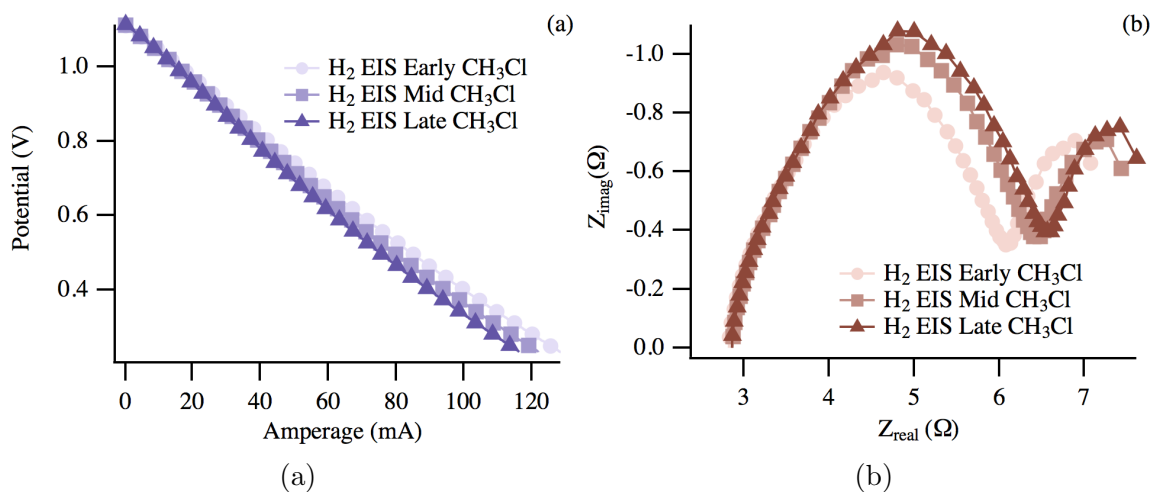


Figure 2.5: (a) LSV and (b) EIS curves performed using H₂ fuel during CH₃Cl exposure early (circles), mid (squares) and late (triangles.)

operational temperatures, any species that do form will likely sublime, removing part of the anode in a process commonly referred to as metal dusting. Previous electrochemical studies of Cl induced degradation in SOFCs, using hydrogen as a fuel, reported degradation rates of 1.7% per 100 hours of exposure. [177]

The experiments described above suggest much more aggressive degradation (extrapolated to ~15% per hour) when Cl is present with SOFCs operating with CH₄. Even allowing for differences in exposure conditions, such extreme degradation in so short a time raises the prospect that these effects arose from a cooperative degradation mechanism involving both carbon and chlorine simultaneously. This hypothesis is supported by both the potential vs. time plots (Figure 2.6a) and the LSV plots (Figure 2.4a). Both experiments show a rapid decrease in performance when the cell is exposed to carbon (in the form of CH₄) and CH₃Cl simultaneously, but not when exposed to hydrogen and CH₃Cl simultaneously (Figure 2.4 and 2.5). Despite the fact that the hydrogen exposures were completed after the methane performance had dropped to very low levels, the

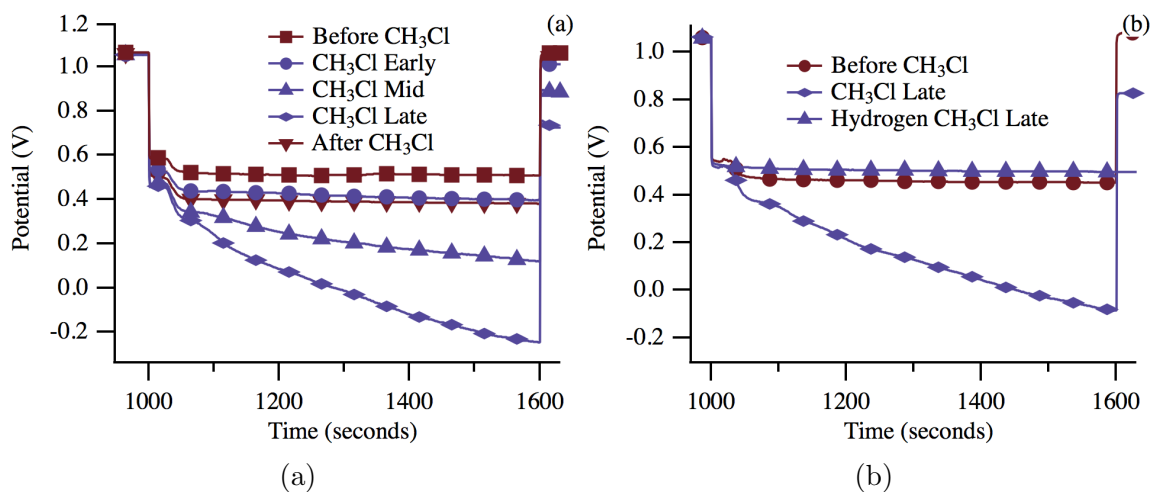


Figure 2.6: Cell potential plotted against time during polarization at 50% $I_{\max}$ with CH₄ as fuel. Red traces were acquired before (squares) and after (inverted triangles) CH₃Cl exposure. Blue traces show different amounts of CH₃Cl exposure early (circles), mid (triangles), and late (horizontal diamonds). (b) Cell potential plotted against time during polarization at 50% $I_{\max}$ with CH₄ as fuel (red circles and blue horizontal triangles) and H₂ as fuel (triangles). Hydrogen potential (triangles) shows no slope (and subsequently degradation) unlike the CH₄ trace run immediately previous to it (horizontal diamonds.)

cell appeared to be operating normally under hydrogen with little to no performance loss (Figure 2.6b). The LSV traces showed similar results, with only small amounts of degradation associated with normal operation being apparent (Figure 2.5). Metal dusting is a degradation mechanism not only associated with chlorine, but also with direct graphitization on the nickel particles of an SOFC anode. [179,180] Given that metal dusting with carbon occurs on the order single hours and metal dusting with chlorine (and H₂) occurs on the timescale of days, we presume that the observed accelerated degradation mechanisms when both CH₄ and CH₃Cl are present results from chlorine assisted metal dusting due to carbon formation. Carbon induced metal dusting of a cermet anode can occur when the formation of carbon within the pores of the cermet overcomes the mechanical

strength of the cermet itself, causing it to break apart. With the chlorine occupying available active sites of the exposed nickel particles one must consider that carbon deposits will preferentially form on the surfaces of the Ni within the porous microstructure of the cermet, closer to the electrolyte, thereby accelerating electrochemical performance loss. EIS results support this hypothesis. Figure 2.4b shows that the both R_{Bulk} and R_{Pol} increased over time. However, upon CH_3Cl removal and subsequent recovery using hydrogen, R_{Bulk} returns to its pre-poisoned state. R_{Pol} , on the other hand, increased by 37% during CH_3Cl exposure but only recovered 20% of that increase. Typical methane degradation with this setup shows an increase in R_{Bulk} but not R_{Pol} . Consequently, the increase in polarization resistance appears to result from chlorine exposure, and this increase in R_{Pol} indicates a loss of catalytic activity, a result consistent with metal dusting.

The data presented above provide an internally consistent and compelling explanation of how irreversible damage occurs to SOFC anodes operating with methane and exposed to chlorine. Previous studies have proposed that chlorine adsorbing to active sites on nickel particles accounted for the reversible performance loss. Electrochemical data coupled with direct, in operando spectroscopic measurements presented above support that hypothesis by showing the disappearance of observable carbon correlates with EIS data that imply an increase in mass transport resistance. LSV traces show reduced performance with increasing CH_3Cl exposure time, a result that is consistent with the loss of active nickel. Previous studies that varied the amount of metal in an SOFC cermet anode have shown similar performance loss with decreasing metal content. [181] The EIS Nyquist plots presented in Figure 2.4b show an overall increase in both RC1 and RC2 , even after the CH_3Cl is removed from the fuel stream. R_{Bulk} , showed a marked increase during exposure to CH_3Cl . As indicated earlier, R_{Bulk} represents

the ohmic resistance of the electrolyte, the contact resistance of the assembly, and other resistances not involved directly with charge transfer redox reaction. Additional insight into changes observed in Figure 2.4b is found by viewing the same imaginary impedance data as a function of frequency in a Bode plot. Figure 2.7 shows the frequency dependent impedance for a cell operating with CH_4 during the early stages of CH_3Cl exposure, after prolonged (~ 4 hours) CH_3Cl exposure and after CH_3Cl has been removed as a contaminant. All data have been background corrected relative to a virgin cell operating with CH_4 prior to any CH_3Cl exposure. Several features of these spectra stand out. First, differences between the early and late exposure data are most apparent in the high frequency limit where, following long term exposure, cell impedance rises broadly. Models describing SOFC impedance data generally assign changes in this frequency region to increased impedance to charge transfer reactions as well as ion transport through the bulk electrolyte. Second, removing CH_3Cl from the fuel feed leads to quantitative recovery of the original, high frequency impedance, implying that chlorine blocking catalytic sites had been removed. Third, at frequencies below 40 Hz, prolonged exposure to CH_3Cl leads to an irreversible increase in cell impedance. Again, impedance models attribute changes of impedance at these lower frequencies to changes in an electrode's microstructure. At the lowest frequencies (~ 0.2 Hz), the long-term and post- CH_3Cl exposed cells impedance values are again larger in magnitude than those of the cell at early exposure. These low frequency regimes are associated with mass transfer of fuel and products through the anode and will be adversely impacted by changes in anode microstructure.

The chemical mechanism(s) responsible for these changes remain unidentified, but correlations between the spectroscopic and electro- chemical data provide suggestive clues. Chlorine is not known to interact with the electrolyte material,

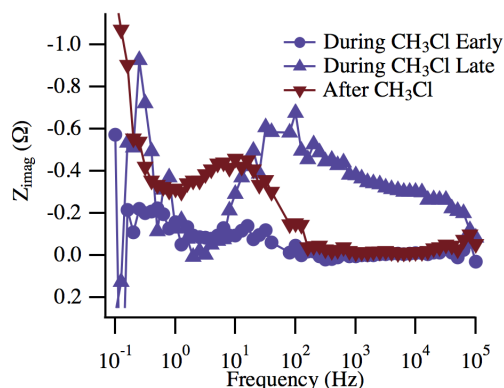


Figure 2.7: Imaginary impedance data plotted against frequency with virgin cell data subtracted from subsequent data to highlight differences in spectra during exposure to CH_3Cl early (blue circles), during exposure late (blue upright triangles), and after recovery (red inverted triangles).

however interactions with ceria, gold, silver, and platinum have been documented. Both gold and platinum form stable chlorides at high temperature, however unlike nickel, these materials do not sublime under conditions relevant for the studies performed in this work. Chlorine also adsorbs to ceria, affecting catalytic activity and conductivity. Because none of these processes permanently affect the fuel cell, the high frequency impedance including R_{Bulk} recovered fully following removal of CH_3Cl from the incident fuel feed. The same behavior was not observed for the changes to the polarization arcs observed in the Nyquist plots (Figure 2.4b) or the frequency dependent response shown in the Body plots (Figure 2.6). The results indicate that not only were mass transport and anode activation processes affected by adsorbed chlorine, but also that these processes were most likely the precursors to the permanent degradation observed after the chlorine source had been removed. The expansion of the mass transport arc was most likely due to the carbon accumulation that constricted the cermet anode's porous structure. Even when no carbon was observed spectroscopically, the EIS data imply that carbon may still

have been forming within the cermet structure consistent with previously reported studies.

Conclusion

Raman spectroscopy coupled with electrochemical methods have been used to study the effects of CH_3Cl on a Ni/YSZ anode of an SOFC operating with H_2 and with CH_4 . In-situ Raman spectroscopic data show the loss of observable carbon throughout the exposure to CH_3Cl . Electrochemical methods were used to assess SOFC performance throughout the experiment. LSV data imply that a loss in chemically accessible nickel is occurring. The Cl poisoning is reversible at early stages of exposure, allowing some recovery once the chlorine contaminant is removed from the incident fuel. Although the CH_3Cl had a negative effect on the electrolyte, EIS data show that the irreversible poisoning occurred strictly on the anode of the fuel cell, with R_{Bulk} completely recovering once the contaminant was removed. Finally, chlorine assisted metal dusting due to carbon was proposed as the main degradation method for the SOFC anode. The main goal of this study was to determine if there were coupled effects between the chlorine and carbon poisoning mechanisms. Not only do both of the individual degradation mechanisms occur, but carbon and chlorine appear to cause extensive and accelerated damage to the fuel cell anode.

The electrochemical methods described in this paper are well supported by in-operando spectroscopic methods used to provide further insight into the reactions occurring on the surface of a SOFC anode. Using these methods, we determined that chlorine and carbon do not mitigate the detrimental effects of the other, unlike other sets of contaminants. Future work will make use of ex-situ characterization techniques to compare post mortem samples of SOFC anodes exposed to different

amounts of contaminants. Other contaminant combinations will be explored in an attempt to loosen the restrictions on acceptable contaminant concentrations of SOFC bio-fuels.

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CHAPTER THREE

CHLORINE-INDUCED DEGRADATION IN SOLID OXIDE FUEL CELLS
IDENTIFIED BY OPTICAL METHODSContribution of Authors and Co-Authors

Manuscript: Chlorine-Induced Degradation in Solid Oxide Fuel Cells Identified by Optical Methods

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Contributions: Collected and analyzed data at MSU (Raman Spectroscopy, electrochemical data, FE-SEM). Wrote and edited manuscript.

Co-Author: John D. Kirtley

Contributions: Collected and analyzed data at NRL. (NIR thermal imaging, mass spectroscopy, FTIRES, Wrote experimental section for experiments performed at NRL. Assisted in editing the manuscript.

Co-Author: Jessie M. Bohn

Contributions: Collected "long-term" Raman spectroscopy and electrochemical data.

Co-Author: Daniel A. Steinhurst

Contributions: Assisted with data collection and interpretation at NRL. Assisted in editing the manuscript.

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Contributions: Assisted with data collection and interpretation at NRL. Assisted in editing the manuscript.

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Contributions: Assisted with data interpretation manuscript editing.

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THE EFFECTS OF CH_3Cl AND HCl ON A SOFC OPERATING ON METHANE AT 700 °C

Introduction

Carbon containing fuels including natural gas, biomass, and coal are likely to remain a cornerstone of electricity production for the foreseeable future. Consequently, converting fuels such as syngas, biogas, ethanol and others into usable electrical power cleanly and efficiently is a critical requirement for reducing greenhouse gas emissions. In this context, solid oxide fuel cells (SOFCs) stand out as attractive devices for energy conversion applications. SOFCs are capable of fuel-to-energy conversion efficiencies of more than 80% when combined with heating applications [182–184] but require high operating temperatures (>650 °C) and electrocatalytic materials. Under these conditions, contaminants in fuel streams can accelerate device degradation and corrosion, compromising SOFC performance and longevity. While many mechanisms have been proposed as the origin of contaminant-induced SOFC failure, few have been validated in functioning devices.

Fuel Cells

Fuel cells, especially proton exchange membrane fuel cells, have traditionally operated with hydrogen, but the high temperatures required for SOFC operation permit these devices to use higher molecular weight fuels such as methane, propane, natural gas, alcohols, and most importantly, synthetic and biofuels such as syngas ($\text{H}_2 + \text{CO}$) and biogas ($\text{CH}_4 + \text{CO}_2$). [185–188] These diverse fuel sources inherently introduce a long list of potential contaminants in varying concentrations. Materials such as carbon (in the form of coke), [186, 189–191] sulfur, [192–194] chlorine, [195, 196] silicon, [197] and phosphorus, [198] have all been identified as

sources of SOFC degradation. Mechanisms thought to be responsible for contaminant-induced degradation include contaminant migration to the three phase boundary (TPB) where electrochemical oxidation takes place, as well as contaminant adsorption to catalytically active sites on electrodes where fuels such as H_2 or CH_4 chemisorb. Some proposed mechanisms are simply the result of contaminant chemisorption while others require that the SOFC be operational in order to promote deleterious chemical activity between contaminant and electrode. [199–208]

Fuel cell performance is easily characterized by electrochemical measurements. Despite their sensitivity to SOFC performance, however, these measurements do not provide molecularly specific information, meaning that data can be used only indirectly to evaluate proposed degradation mechanisms. Coupling electrochemical methods with operando spectroscopy, such as Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), or Fourier transform infrared emission spectroscopy (FTIRES) enables electrochemical performance to be linked directly to molecular and material changes occurring on SOFC electrodes. In particular, Raman spectroscopy and NIR thermal imaging have already shown their value as complementary techniques capable of identifying chemical processes occurring operando. [189, 196, 209] Spectroscopic observations together with electrochemical measurements such as linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) provide a direct link between the chemical and material condition of the SOFC and the device’s ability to electrochemically oxidize fuel to produce electricity and products. [187, 196, 210]

Chlorine Contamination

Of particular interest for SOFC operation are the effects of chlorine in the form of CH_3Cl and HCl on electrode stability and cell performance. The electrochemical effects have been studied in detail for SOFCs, but in most of those studies the fuel cell is operated with hydrogen, not with a carbon containing fuel. [197, 199, 204, 211] Based on voltammetry data, several degradation mechanisms have emerged, proposing that chlorine poisoning of a fuel cell operating with hydrogen occurs in two stages, similar to mechanisms proposed for sulfur poisoning. [192, 194, 195, 197, 204, 212]

The first, reversible stage of degradation occurs when chlorine containing molecules such as HCl and CH_3Cl dissociatively chemisorb on a nickel particle. Adsorbed chlorine atoms inhibit nickel's catalytic activity by reducing the open nickel surface area and number of electrocatalytic sites available for fuel activation. In this first step of chlorine degradation, eliminating chlorine from the fuel leads to almost complete recovery of SOFC performance as the adsorbed chlorine desorbs leaving the catalyst intact. A second, irreversible stage of degradation is proposed to result from the formation and subsequent sublimation of nickel chloride compounds. [192, 194, 195, 197, 204, 212] Overlooked in these models is the impact of chlorine on the performance, stability and durability of SOFC anodes operating with carbon containing fuels. Regardless of degradation mechanisms, the effects of chlorine contamination on performance and durability of SOFC anodes are clear. SOFCs operating on H_2 at $800\text{ }^\circ\text{C}$ with HCl concentrations of 100 ppm resulted in a 1.7% decrease in performance per hour of exposure. [197] Additional questions have arisen about synergistic or cooperative effects that multiple contaminants might have on SOFC anode stability, but these concerns have remained largely speculative.

In the studies described below, a suite of operando optical methods are used

to characterize the chemical changes occurring on nickel-based SOFC cermet anodes operating at 700 °C with CH₄ and 0, 100, and 300 ppm chlorine (introduced as either CH₃Cl or HCl). Vibrational Raman spectroscopy coupled with electrochemical measurements indicate that chlorine inhibits carbon accumulation and reduces cell voltage in functioning SOFC devices. FTIRES, NIR thermal-imaging (NIRTI), and exhaust mass spectrometry provide a more complete mechanistic picture by confirming that endothermic CH₄ cracking decreases as the cell ages, and the impacts of chlorine are clear. Signatures from CH₄ are monitored in operando (FTIRES) and ex situ (mass spectrometry), while NIR thermal imaging shows less anode cooling once chlorine is introduced to the fuel feed. The CO₂ oxidation product at the anode immediately decreases when chlorine is introduced, while CO production is unaffected. This last result agrees with reports from a sulfur poisoning study that indicated the WGS reaction is reversibly poisoned by chlorine, leading to less CO₂. [213]

Experimental

Raman and Electrochemical Measurements

The electrolyte supported membrane electrode assemblies were purchased from Fuel Cell Materials and measured 25.4 mm in diameter with a 250-300 μm thick electrolyte. Fuel and air electrodes were composed of a 50 μm Ni-YSZ cermet with a thin (~5 μm) Ni-GDC interlayer and a 50 μm LSM layer with a thin (~5 μm) LSM-GDC interlayer, respectively. Silver and platinum mesh current collectors (3 mm x 3 mm) and lead wires were attached to the fuel and air electrodes with gold and platinum pastes respectively. Raman spectra were collected using a Renishaw inVia Raman Microscope and a 25 mW, 488 nm Ar-ion laser. Electrochemical data were collected using a Princeton Applied Research Versastat 3.

The experimental apparatus was a stainless steel, pressure based system dubbed ‘SAwCER.’ This assembly used mica gaskets to isolate the anode and cathode environments as discussed in a previous report. [196] Relatively short delivery lines meant that incident fuel spent 0.15 seconds passing through the furnace before reaching the anode with a 2 second residence time in the anode chamber itself.

Cells were heated to 700 °C at 3 °C per minute with 55 sccm argon on the anode and 85 sccm air on the cathode. Upon reaching 700 °C, the SOFC anode was reduced using an 18 sccm flow of H₂ on the anode with 55 sccm Ar as a carrier gas. After cell open circuit voltage stabilized, H₂ flow was increased to 100 sccm for electrochemical benchmark measurements. LSV plots were acquired with a sweep rate of 0.1 V per second from OCV for 0.9 V. EIS were acquired with a 10 mV AC amplitude from 100,000 Hz to 0.1 Hz at a DC offset of 0 V. Upon electrochemical characterization of the virgin cell, methane exposure commenced. The SOFC was exposed to 20 sccm methane (with the same 55 sccm Ar carrier gas) for 10 minute intervals while the cell was polarized to 50% of the cell’s maximum current, determined from the initial methane LSV results. The initial methane exposure was completed at OCV in order to obtain opening benchmarks. Immediately following the exposure, both LSV and EIS were acquired at OCV under methane fuel. Subsequently, any carbon accumulated on the cell was removed by polarizing the cell after the methane flow was halted, effectively starving the cell of gaseous fuel. Care was taken to avoid full oxidation of the nickel anode. Finally, the cell was exposed to H₂ fuel for reduction and the cycle was repeated again, starting at the H₂ electrochemical benchmarks under 100 sccm H₂. Chlorine exposure commenced after cell performance during the 10 minute methane exposure stabilized. At that point, 100 ppm CH₃Cl or HCl was introduced into the fuel stream for the remainder of the experiment. Under chlorine, cells continued to be cycled according to the

procedure described above until they were no longer capable of producing current. Following cell failure, either cell recovery or cool down commenced. Recovery of selected cells consisted of exposing the anode to 18 sccm of H_2 for one hour. Cells not capable of recovery (catastrophic failure) were cooled down with argon on both the anode and cathode.

Infrared Measurements

The same type of commercially available, electrolyte supported SOFCs were tested using an alumina tube assembly at the Naval Research Laboratory (NRL) designed for operando infrared measurements [214,215]. Experimental details for the NIRTI and FTIRES are similar to those in the previous studies using these methods [187,214,216] including the recent modification to perform these measurements simultaneously. [215,217,218] Briefly, a calcium fluoride or sapphire window provided optical access to the anode chamber, through which infrared light emitting from the furnace and anode surface passed to a duplex Fourier Transform Infrared Spectrometer and NIR thermal imaging camera. The FTIRES data provide insight into gas composition at the anode by measuring molecularly resolved mid-infrared spectra, while temperature-calibrated NIR thermal images spatially resolve temperature changes at the anode. Fuel delivery had a 0.7 second residence time to the middle of 46 cm long furnace.

The experimental cycle described above for the Raman measurements was very similar to that used for the infrared measurements, including SOFC operation with CH_4 and H_2 fuels, and with 100 ppm CH_3Cl . Analogous experiments with 0 ppm and 300 ppm CH_3Cl were also completed. Though this work only reports electrochemical data collected in conjunction with the Raman experiments, electrochemical data were also collected alongside infrared measurements to

determine consistent electrochemical performance. Exhaust gases from the SOFC were continuously sampled by a Pfeiffer ThermoStar Quadrupole Mass Spectrometer. These ex situ measurements provided quantitative and time-dependent data regarding the SOFC exhaust composition, including CH_3Cl that could not be seen operando.

Results

The effects of chlorine on SOFCs are monitored by both LSV and EIS to quantify degradation rates and to infer relevant degradation mechanisms. Earlier reports hint that the detrimental effects of chlorine are more pronounced in SOFCs operating with carbon containing fuels than for those operating with H_2 . [195,197,204] Data presented below suggest strongly that chlorine's most important effect on SOFC anode surface chemistry is to inhibit fuel activation. While no individual technique provides definitive, direct evidence of chlorine's interactions with the nickel anode, findings from electrochemical measurements, vibrational Raman spectroscopy, NIR thermal imaging, IR emission spectroscopy, and mass spectrometric analysis of SOFC exhaust all combine to create a cohesive and internally consistent picture of chlorine's effects on fuel chemistry within the SOFC anode and the consequences of chlorine exposure on anode microstructure.

Electrochemistry

Figures 1a and 2a show LSV data from a cell operating with $\text{CH}_4/\text{CH}_3\text{Cl}$ and $\text{H}_2/\text{CH}_3\text{Cl}$, respectively. Experiments were performed using SAwCER, the assembly specifically designed for operando Raman experiments described above. Pre-chlorine exposure maximum cell currents (I_{max}) were typically ~ 220 mA (165 mA/cm²) for cells operating with H_2 at 700 °C. EIS data (Figures 1b and 2b) provide more

specific information about where the degradation is occurring within the SOFC. The EIS bulk resistance (R_{Bulk}) (high frequency x-intercept) represents the resistance contributed by any element not directly participating in the electrochemical reactions such as the lead wires, electrical connections, current collectors, oxide transport through the electrolyte, and interlayers. The polarization resistance (R_{Pol}) encompasses all of the QR elements (arcs). Three parallel QR (constant phase element/resistor) elements are used to model processes occurring within the fuel cell. A constant phase element (Q) was used to better model the non-ideal double layer capacitance present in fuel cells. The first (QR1) and second (QR2) elements represent cathode and anode processes respectively. Often these arcs overlap, complicating interpretation. The last QR element (QR3) correlates to mass transport processes. [219,220] QR3 arc is not fully resolved at low frequency. No high frequency induction arcs were observed in the data.

Initially, the slope of the CH_4 LSV plot (Figure 3.1a) decreases rapidly. However, after four cycles, degradation slows as evidenced by the decrease in the change of slope in the LSV data and the calculated I_{max} , resulting in overlapping LSV plots. The hydrogen LSV plot (Figure 3.2a) also exhibits a fast initial degradation as I_{max} decreases from 166 mA after initial exposure to chlorine to 130 mA in the first four cycles. However unlike with CH_4 , performance with H_2 stabilizes and actually rises modestly to a maximum value of 147 mA before the cell eventually fails. Similar pseudo-recovery behavior is observed in the H_2 EIS data (Figure 3.2b), indicating consistent correlation between the two methods. Methane LSV results also show a sudden large decrease of the observed maximum current between the last and second to last traces (613 and 787 minutes) correlating with the catastrophic failure of the fuel cell. The methane EIS results (Figure 3.1b) show initial growth of both the first arc and the bulk resistance, followed by a decrease in

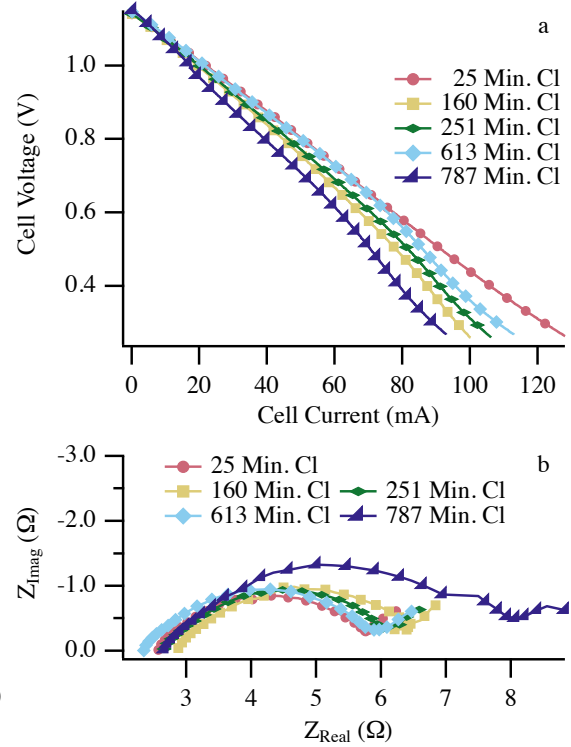
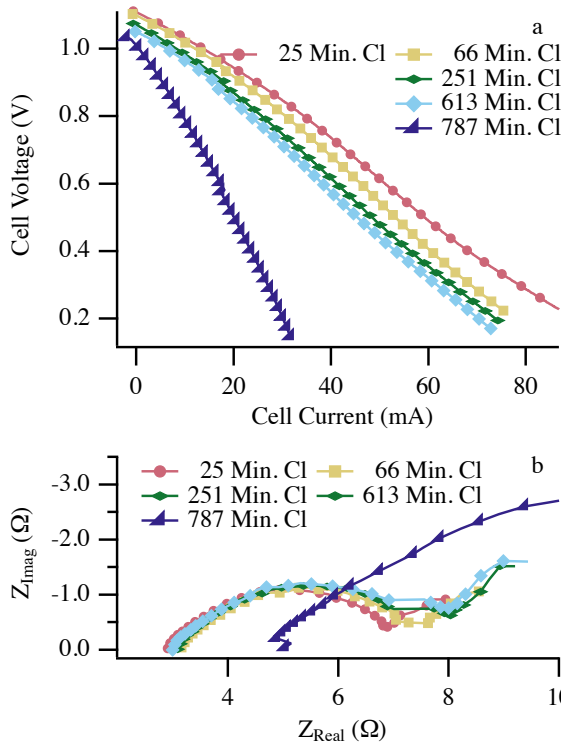


Figure 3.1: Methane LSV plot degradation (a) and EIS degradation (b) over time. Darker traces are longer chlorine exposure. Figure 3.2: Hydrogen LSV plot degradation (a) and EIS degradation (b) over time. Darker traces are longer chlorine exposure.

the bulk resistance while the first arc continues to grow. The cycle-to-cycle changes of the EIS parameters mirror the I-V degradation rates.

Figure 3.3 shows voltage traces for subsequent cycles for a SOFC when galvanostatically polarized at 50% of I_{max} determined from the CH_4 LSV results. In the absence of chlorine, the voltage stabilizes quickly and remains constant until the end of the polarization period. (Figure 3.3: blue circles) The sharp drop in voltage at the beginning of the polarization is due to switching fuels from H_2 to CH_4 20 seconds after the cell has been polarized. When chlorine is introduced, the voltage no longer remains stable during each 10-minute methane exposure, but slowly decreases. With continued chlorine exposure, the voltage decrease

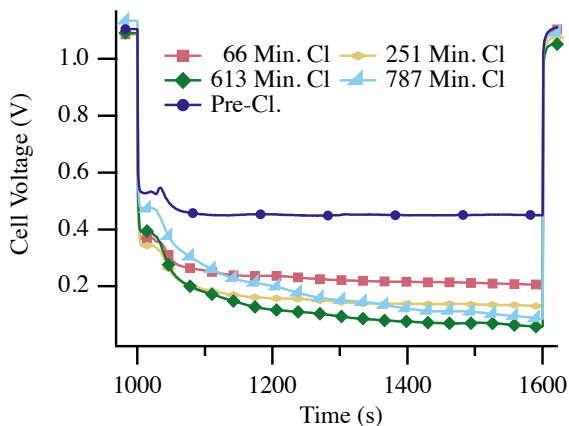


Figure 3.3: Voltage vs. Time plot showing increasing instability in the voltage over time. Darker traces are longer chlorine exposure. Red trace is pre-Chlorine.

accelerates, eventually crossing 0 V. This behavior is not observed when similar experiments are performed with clean CH_4 (no chlorine).

Both the CH_4 EIS and LSV results show evidence of partial SOFC recovery at 700 °C after chlorine is removed from the incident fuel feed; however, the effect is more pronounced in the CH_4 LSV data (Figure 3.4a). Maximum cell current under CH_4 increases from 80 mA late in the CH_3Cl exposure to 130 mA after the CH_3Cl is removed and the cell is allowed to operate with clean H_2 for 1 hour. Benchmarks performed with H_2 and exposed to chlorine, on the other hand, showed no recovery after the chlorine is removed. (Figure 3.4b) This is in stark contrast to previous results [196] at 650 °C showing much more pronounced performance recovery suggesting fundamentally different mechanisms at different temperatures.

Raman Spectroscopy

Raman active chloride-containing materials, such as NiCl_2 , are unlikely to accumulate with sufficient concentrations for operando detection due to their non-zero vapor pressure at temperature and small Raman cross sections. [208]

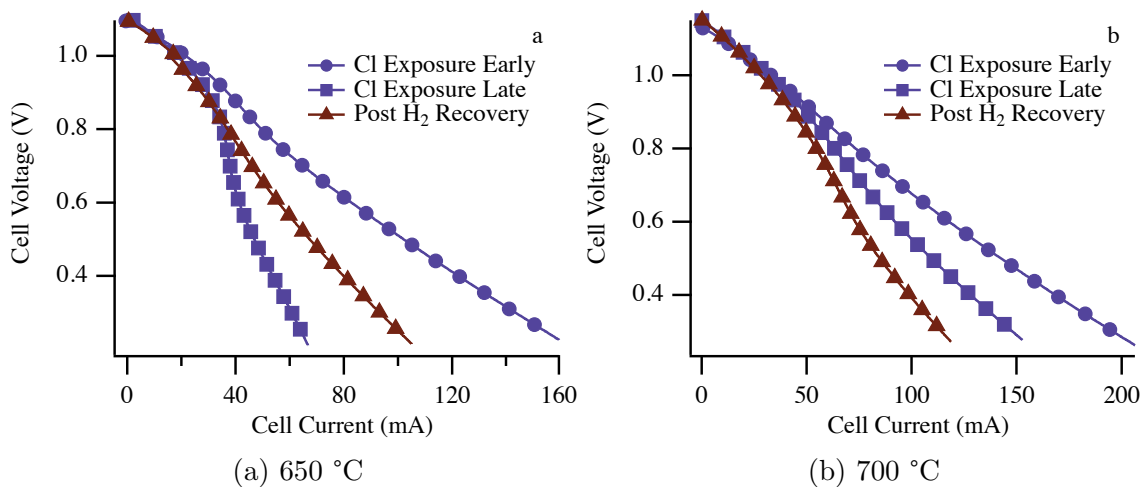


Figure 3.4: Methane LSV (a) and Hydrogen LSV (b) plots after an hour long cell recovery under 18 sccm of hydrogen, (red trace) Blue traces show previous two poisoned LSV plots.

Nevertheless, the effects of physisorbed chlorine can be inferred from a loss of anode catalytic activity. Nickel is known to activate CH bonds and promote carbon accumulation in SOFCs operating with carbon containing fuels. [191,210,221,222] Figure 3.5a shows an operando spectrum from an anode operating with CH_4 (and no CH_3Cl).

Four features are readily apparent and can be assigned. The first peak, at 595 cm^{-1} , is due to the F_{2g} mode in cubic zirconia. [223] The remaining peaks are all due to the carbon on the surface. The peak at 1356 cm^{-1} (labeled ‘D’) correlates to graphite having point defects and/or grain boundaries and is often referred to as “disordered” carbon. [224,225] The next peak, at 1556 cm^{-1} , correlates to the in-plane optically active vibration (E_{2g} mode) of defect-free graphite sheets. Finally, the peak at 2698 cm^{-1} is a second order peak often named either ‘G’ or ‘2D’. Although debated in the literature, this transition is generally assigned to electron-phonon coupling of second order zone boundary phonons that are forbidden

in the first order spectra. [224, 225] Exposing the anode to CH_4 alone promotes coking of the cell; however, introducing a 100 ppm CH_3Cl contaminant suppresses carbon accumulation. Figure 3.5b shows the behavior of G peak intensity in cells polarized to 50% I_{max} as a function of time and cumulative chlorine exposure. The data in Figure 3.5b were acquired in a single experiment with no changes in experimental setup, therefore eliminating the need for normalization. In the absence of chlorine, carbon signal intensity increases quickly then stabilizes after 100 s, indicating steady state conditions within detection limits. After chlorine is introduced, the initial jump in carbon signal from CH_4 is diminished. Subsequent trials show reduced amounts accumulated carbon and eventual carbon signal disappearance. Upon removal of chlorine from the incident fuel feed, carbon signal intensity slightly recovers, indicating that physisorbed chlorine has desorbed from the anode increasing the number of catalytic nickel sites that again promote CH_4 activation and carbon accumulation. However, this effect is less apparent at 700 °C

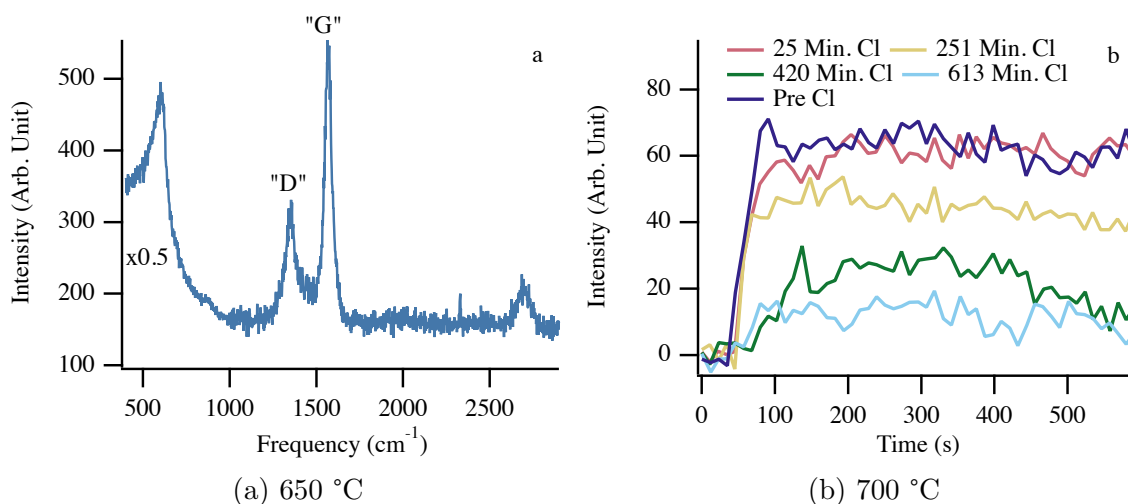


Figure 3.5: Operando Raman spectrum of carbon on the surface of a SOFC (a) and Carbon kinetics of the Raman 'G' peak over time. (b) Darker traces indicate longer chlorine exposure.

than previous results at 650 °C.

NIR Imaging

Previous studies have shown that hydrocarbon cracking and associated carbon accumulation on SOFC anodes is endothermic and spatially heterogeneous. [186, 187, 214, 226] The extent of cooling can depend on a region's proximity to the fuel flow as well as the current collector when the cell is polarized. NIR false-color thermal images of an SOFC anode operating with clean CH₄ show cooling caused, in part, by methane cracking on the surface. (Figure 3.6) Temperature changes in specific regions of interest to this study are shown in Figure 3.7. These particular regions (4-6) reflect different distances from the more electrochemically active current collector and different locations relative to the fuel inlet. (Figure 3.6) In previous experiments, more cooling is observed near the current collector and near the fuel inlet. The addition of 100 ppm chlorine results in a reduction in cooling (Figure 3.7). We note that after repeated cycling, similar losses in cooling are also eventually observed on anodes operating with clean methane. We attribute this latter effect to anode deactivation by repetitive carbon accumulation and removal.

FTIRES

The effects of chlorine on the gas composition in the anode chamber are observed using operando FTIRES. After 300 ppm CH₃Cl is added to the fuel stream, CO₂ decreases relative to the clean fuel, as the cell operates at 50% I_{max}. (Figure 3.8, green circles compared to blue squares) However, continued operation with 300ppm CH₃Cl shows that CO₂ concentrations partially recover. Additionally, during all stages of Cl degradation, CO and CH₄ concentrations increase slightly. Neither CO nor CH₄ concentrations appear to change in a systematic manner in the

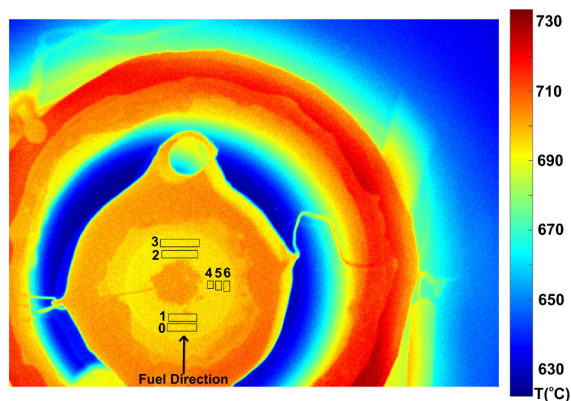


Figure 3.6: NIR image of a SOFC operated at 700 °C while poisoned by chlorine. Regions of interest 4-6 are increasingly far away from the current collector (dark spot in middle of anode.)

100 ppm case. Mass spectroscopy results for 100 ppm CH_3Cl agree with the emission results at 300 ppm showing increased CO_2 and CH_4 ; the mass spectroscopy results may exhibit these trend more clearly at lower CH_3Cl concentrations because they measure exhaust gases and do not have contributions from the reactant flow as in the headspace FTIRES data.

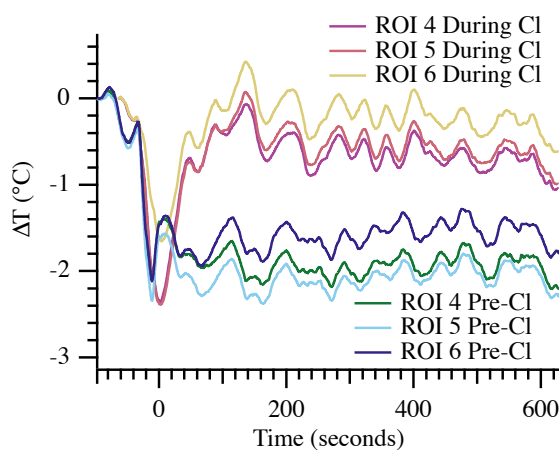


Figure 3.7: Changes in temperature of the above ROIs vs. time, showing a smaller temperature drop when chlorine is introduced into the system.

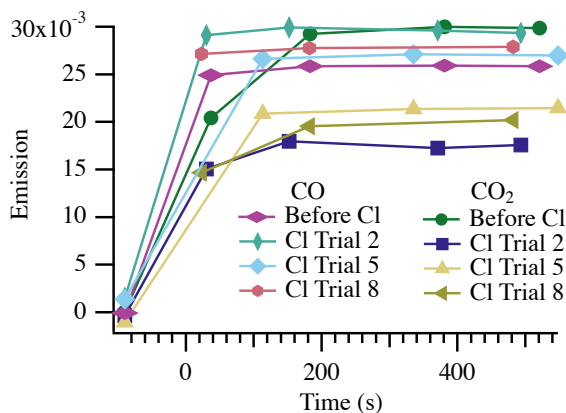


Figure 3.8: FTIRES of CO and CO₂ during methane exposure while poisoning with chlorine. CO₂ rises, and CO generally decreases, mirroring the mass spectrum data.

Discussion

A combination of electrochemistry and operando optical techniques provides new insight into chlorine's effects on nickel cermet anode degradation and decreased electrochemical activity. The electrochemical data display similar results to those seen in previous studies at higher temperatures (750 °C - 800 °C) with SOFCs using H₂ fuel when exposed to chlorine. [195, 204] A lower temperature study shows two degradation mechanisms at work. [196] These studies, in general, have proposed an initial, rapid but reversible adsorption of chlorine to the surfaces of the nickel in the anode, followed by the irreversible nickel chloride formation and subsequent sublimation. [192, 194, 195, 197, 204, 212] The data presented above support those descriptions, but also show that operation with a carbon containing fuel increases degradation rates significantly compared to operation with comparable amounts of H₂. Studies of how chlorine affects H₂ electrochemical oxidation have reported degradation rates as slow as 0.17% per hour [197] with 100 ppm HCl, markedly less than the extrapolated degradation rate of up to 10% per hour in cells operating

with CH_4 . Even after allowing for different experimental setups and conditions, this disparity is significant and suggests that data collected under H_2 fuel may not reflect the same degradation pathways that occur when chlorine contaminated SOFCs operate with carbon-containing fuels.

While Raman carbon signals without chlorine exposure are stable and reproducible, (Figure 3.5b: dark blue trace) they steadily decrease in intensity with extended chlorine exposure. This behavior was first reported at accelerated rates for cells operating with CH_4 (and exposed to chlorine) at 650°C . [196] Interestingly, the rate of carbon suppression with an equivalent CH_4/Cl mixture at 700°C is measurably slower than the rate observed at 650°C . At 700°C , carbon continues to accumulate during each ten minute CH_4 exposure window, but the intensity of the signal decreases with every cycle completed. Repeated control experiments ensured that the observed loss of signal did not result from instrumental artifacts. This slow degradation trend is also apparent in the cell voltage vs. time data. (Figure 3.3) In fact, as the number of cycles increases, the cell voltage under polarization becomes less stable and decreases consistently eventually crosses 0 V, indicating that direct electrochemical CH_4 oxidation is no longer thermodynamically favorable or that insufficient amounts of CH_4 are being activated, effectively starving the cell. This starvation mechanism is not apparent in cells operating with H_2/Cl nor with CH_4 without chlorine, suggesting that nickel activation of CH_4 is more inhibited than nickel activation of H_2 . The slow drop in potential is effectively due to the change in concentration of the accessible fuel and eventually due to different electrochemical reactions occurring altogether, specifically the oxidation of nickel to nickel oxide.

The LSV data for both H_2 and CH_4 show curious behavior. Traditional LSV plots begin with a steep section at low overpotentials reflecting a collective activation barrier to electrochemical reduction/oxidation. Once sufficient electrical

polarization has been applied to overcome this initial resistance, LSV data assume a shallower, linear relationship corresponding to the ohmic resistance of the cell. At high overpotentials (or, equivalently, high currents) LSV may again show a steeper slope that indicates a resistance due to mass transfer of material into/out of the porous anode.

Data acquired from SOFCs operating with CH_4/Cl (Figure 3.1a) begin with a relatively shallow slope and then pass through a steep section before becoming shallow again. The H_2 LSV traces (Figure 3.2a) show a slope increase toward the middle of the LSV plot, a region typically associated with the cell's ohmic resistances. The CH_4 LSV plot shows the bulk of the slope change occurring at low and intermediate overpotentials, indicative of activation and ohmic resistance changes. However, because the ohmic resistances are usually associated with the electrolyte and contact resistances, any change in the CH_4 ohmic resistance should be mirrored in the H_2 spectrum as well. The overall slope change of the CH_4 LSV can be attributed to higher polarization resistances, discussed below. The catastrophic failure between 613 minutes and 787 minutes can be attributed to fuel starvation leading to nickel oxide formation and drastically reduced performance.

Both H_2 and CH_4 EIS spectra (Figures 3.2b and 3.1b) show a slight decrease in the bulk resistance. This effect is more pronounced with H_2 . However, this effect is sometimes observed with chlorine-free CH_4 experiments and is possibly due to increased electrical connectivity in the anode due to small amounts of carbon accumulation. This relationship was not explored further in these experiments. The polarization resistance of the EIS spectra displays the most significant differences between the effects of chlorine with H_2 and CH_4 fuels. The increase in the CH_4 polarization resistance is consistent with loss of available active nickel sites, [227] whether blocked by chlorine adsorption, lost to sublimation, or electrochemically

inaccessible. Because H_2 dissociation is less effected by absorbed chlorine, the amount of degradation observed in the H_2 electrochemistry mirrors the degradation associated with only the nickel sublimation and not with chlorine adsorption, explaining the lessened performance loss in the H_2 electrochemistry. Therefore, we conclude that chlorine occupies most, if not all, of the CH_4 adsorption sites but some sites remain available for H_2 activation.

Both CH_4 and H_2 adsorption and dissociation on nickel have been well studied in the literature. [228–230] Both adsorbates preferentially dissociate over nickel sites, with H_2 dissociation having a lower activation barrier (0.10 eV) compared to CH_4 (0.18 eV). Both species require empty hollow sites next to the nickel atom for the dissociating atoms to move into. [229–231] However, chlorine atoms occupy these threefold and fourfold hollow sites when the SOFC is poisoned, preventing dissociation of CH_4 . [232, 233] The electrochemical data acquired in this work and reported by others imply that despite the presence of chlorine in these sites, hydrogen can continue to dissociate and diffuses to the triple phase boundary to be oxidized. Taken together, data from LSV, EIS and Raman measurements imply that CH_4 activation requires additional steps or has a more restricted reaction mechanism than H_2 .

The premise of chlorine blocking sites responsible for CH_4 activation is consistent with the changes observed in both the FTIRES and NIRTI results although findings from both methods showed less severe degradation than was observed in the electrochemical/Raman data. Mass spectroscopy results were used to explain differences in the severity of degradation. Previous reports show that CH_3Cl chemisorbs to alumina, [234] meaning that the walls of the IR assembly could serve as a chlorine sink and reduce the amount of chlorine delivered to the SOFC anode. Mass spectroscopy data in Figure 3.9 support this hypothesis, where

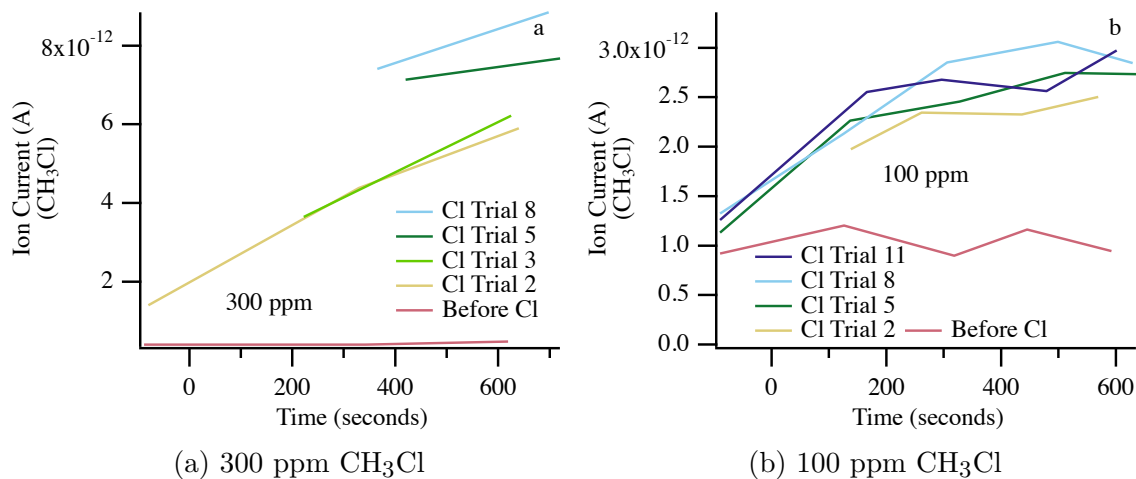


Figure 3.9: CH_3Cl signal observed in mass spectra collected from the SOFC exhaust, (a) 300 ppm CH_3Cl , (b) 100 ppm CH_3Cl .

CH_3Cl signal continues to grow with successive trials and with continued contaminant exposure, at both 100 and 300 ppm levels. While chlorine also chemisorbs to 316 stainless steel, the much shorter fuel tube and residence times in the Raman SOFC assembly (0.16 seconds vs 0.7 seconds) allow for more CH_3Cl to reach the fuel cell anode. Also, only a very short (less than 3 cm) section of the stainless steel fuel tube passes through the hot furnace, compared to ~ 20 cm of the alumina fuel tube passing through the high temperature region of the IR assembly. Careful calibration of the SOFC exhaust from the IR assembly shows a CH_3Cl concentration of ~ 20 ppm, markedly less than the 100 ppm entering the fuel tube. In the complementary 300 ppm CH_3Cl experiment, ~ 50 ppm was measured in the exhaust. (Figure 3.9) Calibration experiments show that slightly lower concentrations of CH_3Cl simply reduce the severity of degradation but do not change the overall degradation methods. Regardless of chlorine concentration, measurements from both techniques support a chlorine degradation model that addresses how carbon accumulation from methane and chlorine poisoning can

fundamentally change anode chemistry and ultimately lead to irreversible loss of performance. Available sites on the nickel are occupied and less CH_4 activation occurs, resulting in less cooling due to the endothermic nature of the CH_4 activation reaction, initially less CO_2 in the exhaust, and less spectroscopically visible carbon. The effects of chlorine are also observed in changes of CO_2 IR emission signal once chlorine is introduced. Immediately after chlorine is introduced into the cell (Trace green circles ‘Before Cl’ compared to blue squares ‘Trial 2’), the amount of CO_2 being produced by a polarized device diminishes and the amount of CH_4 rises. These observations are consistent with adsorbed chlorine blocking electrocatalytic sites. At 700 °C, the secondary degradation mechanism allows for continued small amounts of CH_4 utilization even when poisoned because nickel chloride sublimation will continually expose new nickel. Cell performance with CH_4 degrades less at 700 °C than at 650 °C, but at 700 °C degradation is irreversible. This result is supported by ex situ, post mortem FE-SEM images of fuel cells operated with $\text{CH}_4/\text{CH}_3\text{Cl}$ at 650 °C and 700 °C. (Figure 3.10) The nickel particles in the 650 °C image are relatively smooth and swollen, however at 700 °C the nickel particles are noticeably pockmarked and pitted. We propose that these differences result from sublimation of volatile nickel chloride species.

Another consequence of the increased surface area of the exposed nickel is a very slight performance increase visible in the hydrogen electrochemistry. Initially the hydrogen performance of the SOFC drops rapidly, an effect caused by chlorine occupation of some active sites. However, as the surface area of the anode is increased due to nickel chloride sublimation, the performance recovers because of the continued ability of H_2 to adsorb and move to the TPB. This is indicative of not only changes in the amount of fuel oxidation reactions occurring, but also the type, favoring H_2 over CH_4 when poisoned.

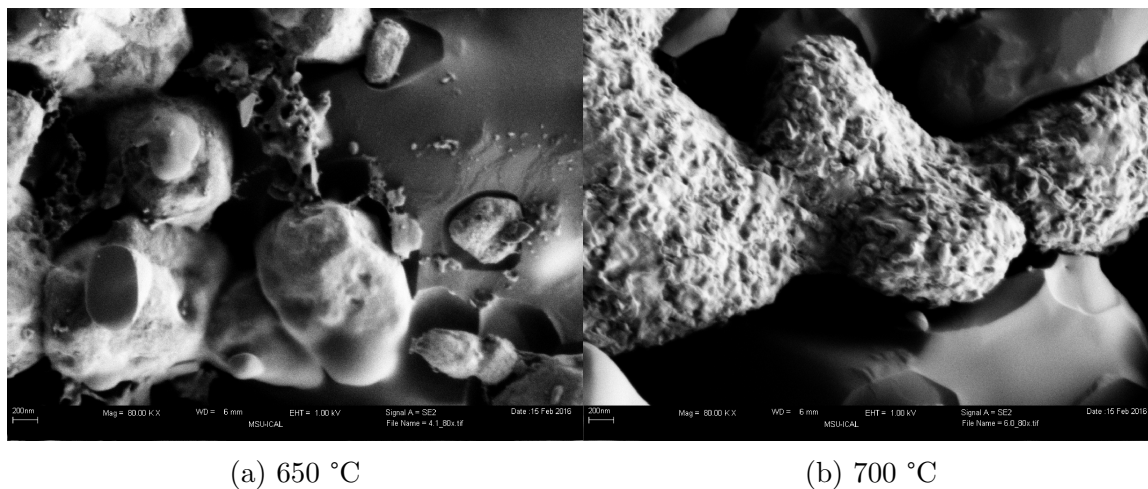


Figure 3.10: Post mortem FE-SEM image at 80,000X of a SOFC exposed to chlorine while operating on CH_4 at 650 °C (a) and 700 °C (b).

Conclusion

Chlorine significantly affects the performance of a SOFC operating on CH_4 . The degradation while operating on CH_4 is significantly faster than while operating on H_2 alone. Hydrogen electrochemical benchmarks fail to show complete degradation when oxidation of CH_4 is no longer viable. Therefore, H_2 characterization of cells poisoned by chlorine is not an effective way to assess chlorine tolerance for fuel cells intended to be used with carbon containing fuels. Despite this, the mechanisms proposed by those electrochemical publications appear to also be accurate when operating on carbon containing fuels. [195,204] Data above support the two-stage degradation theory, as well as the mechanisms behind both stages. Adsorption of chlorine onto the nickel surfaces of the anode leads to rapid and reversible degradation, followed by a slower degradation mechanism caused by sublimation of volatile nickel chloride compounds. Unlike the mechanisms responsible for degradation when operating on H_2 , operation when operating on

CH_4 has another, previously unobserved, mechanism. The inability of chlorine-covered nickel to crack CH_4 leads to fuel starvation upon cell polarization. It is this mechanism that is responsible for the accelerated degradation rate observed with CH_4 as compared the H_2 . Temperature has a non-trivial effect on the degradation as well. At higher temperatures more permanent degradation is observed due to the increased vapor pressure of the nickel chloride compounds formed. However, at lower temperatures the SOFC more quickly loses performance due to the formation, but not volatilization, of those same compounds. This allows for higher performance recoverability at lower temperatures as well. Nickel chloride does not allow for the electrical conductivity necessary for a viable SOFC, therefore performance diminishes very rapidly. In conclusion, multiple methods of operando optical spectroscopy as well as various ex situ methods were used to identify the degradation methods of a SOFC operating on CH_4 while poisoned with chlorine compounds.

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CHAPTER FOUR

CHLORINE-INDUCED DEGRADATION IN SOFCS OPERATING WITH
BIOGAS

Contribution of Authors and Co-Authors

Manuscript: Chlorine-induced degradation in SOFCs operating with biogas

Author: Kyle W. Reeping

Contributions: Collected and analyzed all data. Wrote and edited manuscript.

Co-Author: Jessie M. Bohn

Contributions: Collected "long-term" Raman spectroscopy and electrochemical data.

Co-Author: Robert A. Walker

Contributions: Assisted with data interpretation manuscript editing.

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THE EFFECTS OF CH_3Cl ON SOFCS OPERATING WITH BIOGAS AT 650 °C AND 700 °C

Introduction

Biogas is a general term that describes CH_4/CO_2 mixtures formed from anaerobic digestion of organic material. A small carbon footprint and flexible feedstocks make biogas an attractive source of renewable energy. However, raw biogas often is too lean in CH_4 to be used in conventional, natural gas powered applications, and contaminants such as H_2S and HCl can exceed levels that allow for sustained device operation. Biogas can be upgraded to biomethane using membrane purification or scrubbers, [235,236] but these processes place additional demands on gas handling equipment and require additional infrastructure. Consequently, biogas is relatively easy to produce but not as easy to use. In order for biogas to become globally viable as an electricity source, relevant technologies must be able to process, store and utilize biogas efficiently and inexpensively. Direct electrochemical conversion stands out as an appealing strategy for converting biogas directly into electricity with high efficiency and broad versatility.

Solid oxide fuel cells (SOFCs) are well suited to electrochemically oxidize biogas from a variety of sources. [237,238] Unlike low temperature devices that rely on precious metal catalysts and can operate only with H_2 , SOFCs use inexpensive electrocatalysts such as nickel [239,240] and can convert more energy dense fuels (including CH_4) into products (H_2O , CO_2 , and electricity). SOFCs operate with efficiencies as high as 85% in combined heating and power applications. [241–243] As an electrolyzer, solid oxide electrolysis cells (SOECs) use excess electricity that would otherwise go to waste from sources such as wind turbines or solar cells, to reduce CO_2 to CO and other high value products. [244–246] Both applications rely

on ion conducting solid oxide electrolytes and require operating temperatures as high as 800 °C. High temperatures improve the kinetics of the oxygen reduction reaction as well as the electrolyte's ionic conductivity, but these conditions also can accelerate processes responsible for material degradation and ultimately, device failure. [247]

Contaminants

One contaminant known to cause degradation in SOFCs is chlorine. [248–250] Chlorine present as HCl or CH₃Cl, can be found in concentrations as high as 1 g per m³ of biogas collected at landfill sites and from sources that recycle wastes such as plastic, although chlorine levels in raw biogas show large variations depending on the biogas source. [238, 241, 251, 252] In solid oxide devices, halocarbons decompose rapidly and the halogens adsorb to the electrocatalyst surface. [253] CH₃Cl decomposes to HCl quickly at SOFC operating temperatures. [254] Adsorbed halogens disrupt cell operation in a variety of ways depending on temperature. At 650 °C, adsorbed halogens reversibly occupy available active sites on the nickel [255, 256] preventing dissociation of the fuel. [257] This effect is much more pronounced for carbon containing fuels than for hydrogen. [258, 259] The loss of catalytic activity is compounded by oxidation of the nickel anode itself when SOFCs are required to produce power under the demand of constant current. [260] At these lower temperatures, removal of chlorine from the incident fuel leads to almost complete recovery of SOFC performance provided that the anode has not suffered excessive oxidative damage during chlorine exposure. [258]

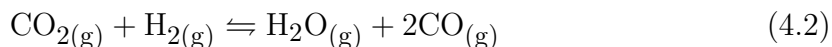
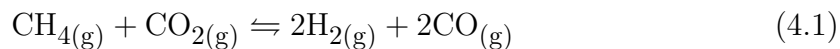
At higher temperatures (700 °C) chlorine reacts more readily with the nickel catalyst and the non-zero vapor pressure of nickel chloride results in sublimation. [259, 261] Nickel loss is an irreversible degradation mechanism that

eventually leads to total device failure. [262–266] However, in SOFCs where NiCl_x sublimation is a relevant concern, anode exposure to chlorine initially leads to improved performance with H_2 before the cell begins showing signs of chlorine induced degradation. This period of improved performance can last for several hours and has been attributed to NiCl_x sublimation creating more nickel surface area and, correspondingly, more sites for H_2 activation. [259] These effects are not observed when H_2 is replaced with higher molecular weight fuels such as CH_4 . In these instances, introducing chlorine to the SOFC anode results in a loss of cell performance that is not recoverable. [267–269] Irreversible performance loss has been attributed to chlorine more effectively blocking the larger carbon containing molecules from adsorbing, resulting in fuel starvation and nickel oxidation under galvanostatic conditions. [258, 259] Methane has a significantly higher activation barrier than hydrogen when chemisorbing on nickel, possibly accounting for chlorine’s enhanced ability to suppress the performance of SOFCs operating with methane relative to H_2 . [268–276] Regardless of the degradation mechanisms, differences between chlorine induced degradation of SOFCs operating with H_2 and with carbon containing fuels imply differences in surface chemistry and conversion efficiencies. Emerging models describing SOFC deactivation by contaminants need to account for these differences and will require experimental validation.

Biogas and Dry Reforming

SOFC surface chemistry with biogas is more complicated than with either H_2 or CH_4 . [277–279] H_2 can adsorb and either dissociate and be oxidized or recombine and desorb. CH_4 will also dissociatively adsorb on a nickel catalyst and if the SOFC is at open circuit voltage or producing only small currents, carbon that is not oxidized will accumulate in the form of graphite or ‘coke’. [260, 280] With biogas,

however, any carbon formed from CH_4 dissociation can be removed through dry reforming reactions, specifically through the direct oxidation of carbon by CO_2 . (Equation 4.3)



While favored at higher temperatures, dry reforming remains an active carbon removal mechanism [281] at temperatures as low as 650 °C. Given the sensitivity of SOFCs to chlorine surface contamination and the role played by dry reforming in keeping SOFC anode surfaces free of carbon, identifying relationships between anode stability, chlorine contamination and temperature becomes an important issue if biogas is to become a viable fuel for SOFC applications.

Studies described below examine the effects of adding 110 ppm chlorine in the form of CH_3Cl and HCl to a biogas surrogate used by electrolyte supported SOFCs operating at 650 °C and 700 °C. Operando Raman spectroscopy quantifies chlorine's ability to inhibit fuel activation and subsequent carbon accumulation on Ni-YSZ cermet anodes while electrochemical impedance spectroscopy (EIS) and voltammetry measurements monitor how SOFC performance changes as a function of exposure time and applied cell polarization. The data show interesting and surprising differences when compared with results from SOFCs operating with methane alone. Chlorine-induced degradation in SOFCs operating with CH_4 begins immediately after chlorine exposure and follows different mechanisms at 650 °C and 700 °C. SOFCs operating with chlorine containing biogas, in contrast, show only

modest degradation regardless of temperature before abruptly failing catastrophically.

The mechanism responsible for device failure appears to be electrochemically driven as passive exposure to chlorine-containing biogas does not result in irreversible cell damage on the timescale of these studies.

Methods

Electrolyte supported membrane electrode assemblies measuring 25.4 mm diameter with 250-300 mm thick Hionic electrolytes, were purchased from Fuel Cell Materials. Fuel cell anodes consisted of a 50 mm thick Ni-YSZ cermet and an approximately 5 mm thick Ni-YSZ interlayer. Cathodes included a 50 mm thick LSM layer and approximately 5 mm thick LSM-YSZ interlayer. Gold and platinum pastes attached 3x3 mm silver and platinum current collectors and lead wires to the anode and cathode, respectively. The relatively small current collectors were necessary in order to allow for optical access to the anode surface. A Renishaw in-Via Raman Microscope and a 25 mW, 488 nm Ar-Ion laser were used to collect Raman spectra and a Princeton Applied Research Versastat 3 collected electrochemical data. Mica gaskets isolated the anode and cathode atmospheres in a custom designed assembly dubbed SAwCER (SOFC Assembly with Concurrent Electrochemistry and Raman) discussed previously. [258] With 55 sccm argon on the anode and 85 sccm air on the cathode, cells were heated to a target temperature of 650 °C or 700 °C at a rate of 3 °C per minute. At the target temperature, the anode was reduced using a flow of 18 sccm H₂ in 55 sccm Ar as a carrier. When the cell reached an open circuit voltage (OCV) of 1.0 V, H₂ flow was increased to 100 sccm. After one hour of further reduction, OCV was typically 1.13 + −0.02 V relative to the O₂ reduction potential. Electrochemical benchmarks were recorded with H₂ and

Ar flows of 100 sccm and 55 sccm, respectively. LSV data were acquired with a sweep rate of 0.1 V per second and were stopped when the cell voltage reached 0.2 V in order to avoid a short circuit condition that might damage the anode. EIS data were acquired at OCV using with a 10 mV AC amplitude and frequencies ranging from 100,000 Hz to 0.1 Hz. No high frequency induction arcs were observed.

After characterizing initial cell performance, the anode was exposed to biogas. Two types of studies were performed. Cells were either subjected to multiple polarization cycles (see below) or analyzed during several hours of continuous polarization (in the presence of chlorine). In the cycling experiments the cell was first benchmarked with hydrogen and biogas without chlorine to determine the overall performance. Figure 4.1 describes the sequence of steps in a cycle for the repeated polarization experiments. After the initial H₂ reduction and characterization, the cell was exposed to synthetic biogas (50% CH₄ 50% CO₂) with 55 sccm Ar as a carrier gas at OCV. Following 10 minutes at OCV, the cell is electrochemically benchmarked under the same flow of biogas and Ar. Accumulated carbon is then electrochemically removed by polarizing the SOFC in the absence of any fuel other than the carbon on the surface. Polarization was stopped following the disappearance of carbon from the Raman spectra and well before the onset of observable nickel oxide formation. [260] Finally, cells were re-reduced using H₂ fuel and the cycle was repeated. Following the initial cycle at OCV the cell was polarized to 50% of its maximum current during the 10-minute polarization period. The maximum current was determined from extrapolating LSV data from the initial biogas LSV trace to the x intercept. Chlorine was introduced to the fuel stream in the form of 110 ppm CH₃Cl or HCl once the cell performance stabilized during the 10 minute polarization period, typically after 2-3 cycles. Cells were then cycled with a constant 110 ppm chlorine until the potential under polarization crossed 0 V.

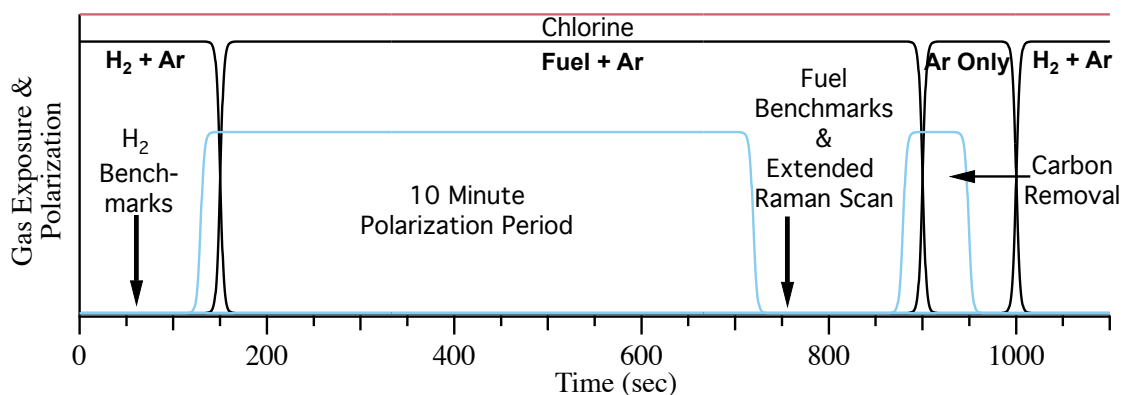


Figure 4.1: Gas flow during one typical experimental ‘galvanostatic cycle.’ Black represents fuel/carrier gas flow, red represents chlorine flow after initial stabilization, and blue represents cell polarization. Cycling experiments would continue until device failure as evidenced by a cell potential crossing 0V to provide the required current.

Following cell failure, cell recovery or cooling commenced. Recovery required exposing the anode to 18 sccm of H_2 and 55 sccm of argon for one hour. Cells were then cooled with argon on both the anode and cathode to preserve their chemical conditions for ex situ analyses.

Long Exposure Experimental

Long exposure experiments consisted of the same initial heatup and characterization as the cycling experiments. After performance stabilization during the initial cycles at OCV, the contaminant flow was turned on, the cell was polarized to 50% I_{max} and performance was monitored for 8-12 hours. Upon failure of the cell, the apparatus was cooled under argon atmospheres for both the anode and cathode.

Results and Discussion

These studies combined operando Raman spectroscopy with traditional electrochemical voltammetry and impedance measurements. Individually, both

report on different aspects of the anode's condition. Raman spectroscopy provides an operando assessment of the amount of methane activated by the nickel and deposited on the anode surface while voltammetry provides details about the overall cell performance. Together, data from the combined experiments afford unprecedented insight into how molecular and material changes in the anode correspond to electrochemical performance and oxidation mechanisms. Data from each method are described below before considering how results interrelate and suggest mechanisms responsible for chlorine-induced degradation and eventual device failure.

Raman Spectroscopy

Due to the volatility of Raman active chlorine compounds at temperatures above 600 °C, direct spectroscopic observation of chlorine containing materials is not possible with the assembly used in these experiments. [261] Instead, chlorine adsorption is inferred from a reduction in anode activity towards CH₄ activation and carbon accumulation. As more chlorine adsorbs to active sites throughout the porous anode, less carbon accumulates relative to SOFCs operating in the absence of chlorine. While carbon removal via dry reforming (Equation 4.3) is rapid at higher temperatures (e.g. 800 °C), below 700 °C, the reverse reaction becomes thermodynamically favorable (assuming standard states) so that at temperatures used in these studies - 650 °C and 700 °C - one expects to observe some carbon accumulation from biogas provided that active catalytic sites remain available. [279] Figure 4.2 shows an operando spectrum of carbon on the anode surface following ten minutes of exposure to biogas at 650 °C while the cell was held at OCV.

Moving from low to high frequency, the first peak in this spectrum occurs at 595 cm⁻¹ and results from the F_{2g} mode in cubic zirconia. [282] The remaining

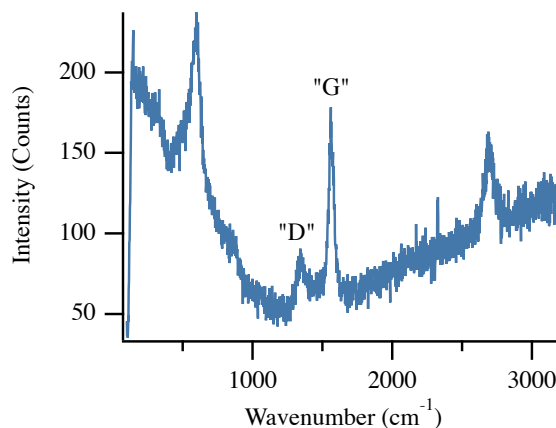


Figure 4.2: Operando spectrum of accumulated carbon on the surface of a SOFC operating with biogas at 650 °C and held at OCV.

peaks indicate carbon on the anode surface. The peak at 1356 cm^{-1} (labeled ‘D’) correlates to graphite containing point defects and/or grain boundaries and is often referred to as ‘disordered’ carbon. The next peak, (labeled ‘G’) at 1556 cm^{-1} , correlates to the in-plane optically-active vibration (E_{2g} mode) of defect-free graphite sheets. [283,284] Finally, the peak at 2698 cm^{-1} is a second order peak often named either G’ or 2D. Although the origin of this feature remains debated in the literature, this transition is typically assigned to electron-phonon coupling of second order zone boundary phonons that are disallowed in the first order spectra. [283,284]

Exposing the anode to 110 ppm CH₃Cl or HCl suppresses carbon accumulation when operating with biogas much more quickly than with CH₄ alone. Figure 4.3 shows the kinetics of G peak intensity growth in cells operating at 50% I_{max} as a function of time and cumulative chlorine exposure at both 650 °C and 700 °C. In the absence of chlorine, carbon signal intensity increases rapidly before stabilizing. (Figure 4.3, red traces) Carbon “G” peak intensity when operating on biogas is lower than typically observed with methane experiments, indicating steady

state conditions. The first cycle following the start of chlorine exposure (27 minutes) shows no carbon accumulation during the 10-minute polarization period at both temperatures. In contrast, when exposed to chlorine-containing methane without any carbon dioxide present, carbon accumulation is suppressed more slowly at 650 °C and never completely suppressed at 700 °C. [258,259] The reduction in signal with methane was attributed to chlorine adsorption to the nickel surface, with adsorbed chlorine blocking active catalytic sites and preventing CH bond activation. Carbon still continued to accumulate over the first ~3 cycles at 650 °C and ~14 cycles at 700 °C with methane. The abrupt reduction in signal with chlorine-containing biogas implies that although dry reforming is not favorable enough to keep carbon from forming in the absence of chlorine (Figure 4.2), by reducing the total amount of carbon that can accumulate (and reducing the number of active sites through chlorine adsorption), dry reforming at 650 °C and 700 °C is efficient enough to keep anodes ‘carbon free’ (within detection limits) when chlorine is present. Carbon signal intensity returns upon removal of chlorine from the incident fuel feed (discussed above), indicating that physisorbed chlorine has desorbed from the anode, restoring catalytic sites.

Electrochemistry

Figures 4.4 and 4.5 show LSV and EIS results at 650 °C operating with H₂/CH₃Cl and CH₄:CO₂/CH₃Cl respectively. The H₂/CH₃Cl data shown here are very similar to results reported previously and are included for comparative purposes. [258,259] (Biogas and H₂ data acquired at 700 °C appear very similar to 650 °C data.) A small decrease in the maximum cell current throughout the experimental cycling is shown in the H₂ LSV plot (Figure 4.4a), as evidenced by a slight increase in the V-I slope throughout the ohmic region. (Similar effects with

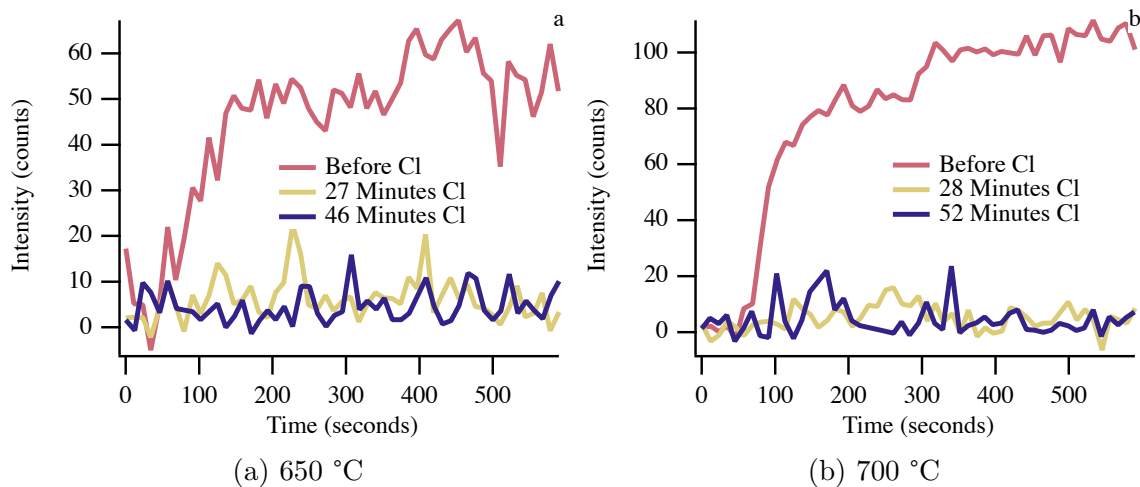


Figure 4.3: Carbon “G” peak kinetics at 650 °C (a) and 700 °C (b).

H₂ were also observed with no chlorine present.)

Complementary behavior is observed in H₂ EIS data with a modest increase in the polarization resistance while the series resistance remains unchanged. A slight recovery between the penultimate and ultimate cycles can be attributed to a longer than normal dormant period between exposures, allowing for the release of some adsorbed chlorine resulting slightly higher performance than expected. Biogas EIS data (Figure 4.5) behave similarly to the H₂ results, with the most pronounced change being a larger increase in the polarization resistance, most prominently in the low frequency arc, traditionally attributed to mass transport throughout the anode. [285,286] When operating with carbon containing fuels, an increase in this arc signifies carbon accumulation within the anode’s porous microstructure of the anode. In the current studies, any carbon that does form must be far enough into the anode so that it is not observed in Raman spectra that sample only the top-most anode surface. [260] Despite CH₄ being one of the two principle components of biogas, significant differences distinguish the electrochemical

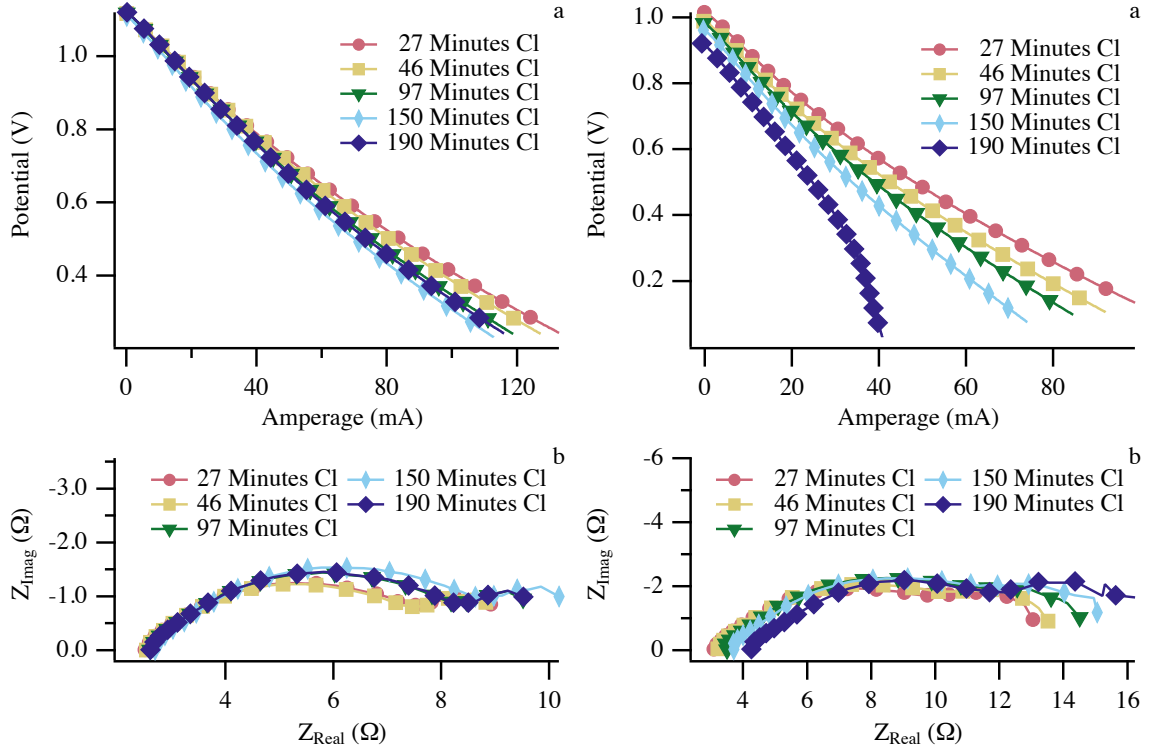


Figure 4.4: Hydrogen LSV (a) and EIS (b) at 650 °C acquired at the ‘H₂ Benchmarks’ arrow in Figure 4.1

Figure 4.5: Biogas LSV (a) and EIS (b) at 650 °C acquired at the ‘Biogas Benchmarks’ arrow in Figure 4.1.

behavior of SOFCs operating with chlorine containing biogas from those operating with chlorine containing methane.

The biggest difference between the biogas and CH₄ experiments is that at some time after chlorine exposure begins, the cell operating with biogas fails catastrophically as evidenced by a steep decline in the biogas voltammetry data. (Figure 4.5a: blue diamonds) Identical catastrophic failures were observed across multiple experiments at both 650 °C and 700 °C using chlorine-containing biogas as a fuel, but never when CH₄ (with chlorine) was used by itself. [258, 259] Unlike previous reports that demonstrated different degradation methods and significantly longer operation until failure with CH₄ at 700 °C compared to 650 °C, data from

the biogas experiments resulted in identical failure mechanisms occurring on similar time scales at both temperatures.

Potential vs. Time Neither Raman experiments nor electrochemical measurements provide direct, material specific information about the origin of the failure observed in Figure 4.5. However, failure mechanisms can be inferred by considering degradation rates. Galvanostatically polarizing the cell to 50% $I_{\max}$ resulted in catastrophic failures during cycling in both the 650 °C (Figure 4.6) and 700 °C (Figure 4.7) experiments. The mechanism at both temperatures resulted in rapidly falling potential under polarization (dark blue diamonds on both figures). Unlike results with chlorine contaminated methane, little degradation occurred before the catastrophic failure, as is particularly evident in Figure 4.7. Generally, catastrophic failures such as those observed in Figures 6 and 7 (blue diamond traces) would be attributed to some sort of structural breakdown that compromised separation between anode and cathode atmospheres or large-scale material changes such as those that result from redox cycling or formation of insulating phases. [260,287,288] However, the SOFC remained intact and gas separation was never compromised, as evidenced by recovery data and ex-situ cell analysis. The failures observed in these chlorine containing biogas studies occur only when the cell is polarized and never when the cell is at OCV indicating that active electrochemical oxidation plays a role in promoting the sudden and dramatic degradation.

Proposed Mechanism

Previous work concluded that chlorine-induced degradation in cells operating with methane resulted from fuel starvation due to chlorine occupation of nickel's catalytically active sites and forced electrode oxidation due to the galvanostatic polarization. [258,259] Methane dissociates on a pristine Ni-YSZ anode producing

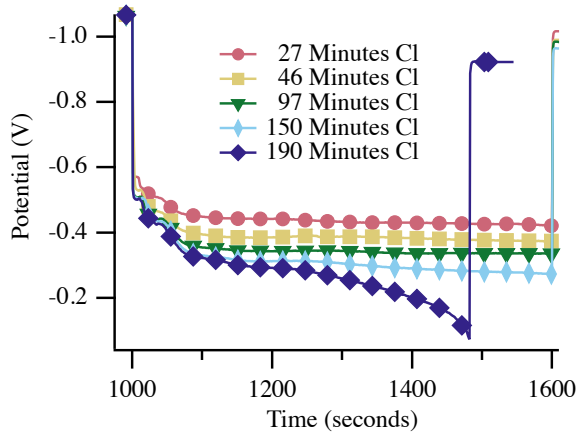


Figure 4.6: Potential vs time at 650 °C during the 10 minute polarization period while the SOFC was polarized to 50% $I_{\max}$ and operating with biogas.

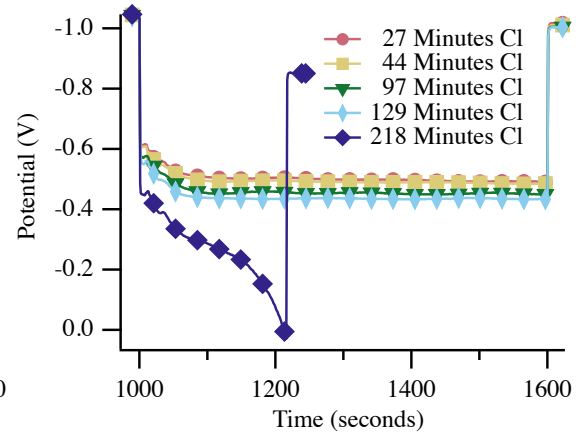


Figure 4.7: Potential vs time at 700 °C during the 10 minute polarization period while the SOFC was polarized to 50% $I_{\max}$ and operating with biogas.

adsorbed hydrogen and carbon, [272] and both species can be electrochemically oxidized. Adsorbed chlorine slowly, over the course of 5-6 hours, limits CH_4 chemisorption by adsorbing to catalytically active nickel sites. Chlorine blocks CH_4 adsorption and decomposition; eventually starving the SOFC of oxidizable fuel (coke and hydrogen), leading to cell cannibalization via nickel oxidization under galvanostatic conditions. At 700 °C, fuel starvation is slightly mitigated, likely by the formation of NiCl_x compounds that sublime, constantly exposing fresh nickel surface. [261] Cell failure occurs eventually due to both the anode's diminished nickel content and chlorine occupying sites on the remaining nickel particles. The same mechanisms will occur with biogas, but with increased chemical complexity on the anode surface.

One explanation for the differences observed between biogas and methane assumes that the biogas degradation results from a cascade of heterogeneous surface reactions that compromise cell performance and ultimately destroy the nickel anode when the cell operates galvanostatically. CO_2 can remove built up carbon via dry

reforming. (Equation 4.3) This process will adversely affect anode performance by removing oxidizable fuel, assuming that the newly formed CO desorbs and is not electrochemically oxidized. Less fuel forces the cell to oxidize nickel to provide current when chlorine blocks methane adsorption. Furthermore, CO₂ itself is a weak oxidizing agent and can further oxidize the nickel anode to NiO. [289] In the absence of chlorine, carbon removal through dry reforming will simply reopen active nickel sites for further dissociative CH₄ chemisorption. Chlorine, however, can adsorb to the newly unoccupied nickel site further limiting anode electrocatalytic activity. The minor, adverse changes in electrochemical behavior of cells operating with biogas resemble those observed with SOFCs operating with hydrogen and imply that the cell is operating with hydrogen and not carbon. This scheme is illustrated in Figure 4.8.

The critical step in this mechanism is the formation of NiO (Figure 4.9) and the irreversible loss of anode conductivity, either through electrochemical oxidation or through heterogeneous surface reactions with CO₂. In addition to the anode's electrical conductivity being compromised by NiO formation, it is further reduced at 650 °C by the formation of electronically insulating nickel chloride compounds. (Figure 4.8d) At 700 °C, these compounds volatilize, removing nickel from the anode network and reducing biogas performance over time, but the data suggest that degradation caused by the nickel oxidation far outpaces any degradation due to NiCl_x sublimation. Post failure, the cell's OCV does not return to the pre-failure value indicating that cell failure has resulted in material change fundamentally altering the electrochemical reactions that can occur.

Fuel Cell Temperature with Raman

Raman data provide some evidence of physical changes that occur within the cell during a failure event such as the ones shown in Figures 6 and 7. As the cell nears failure, the vibrational feature at 595 cm^{-1} , assigned to an F_{2g} mode of YSZ, shifts temporarily to lower frequency. Shifts in cubic zirconia's F_{2g} vibrational frequency can arise from several sources. High temperature aging over hundreds of hours is known to slowly change the material's local yttria content and induce a slow phase transition from a cubic to tetragonal lattice structure. [282,290] With its different symmetry and phonon structure, however, the dominant feature in a tetragonal YSZ vibrational spectrum shifts to higher frequency, not lower.

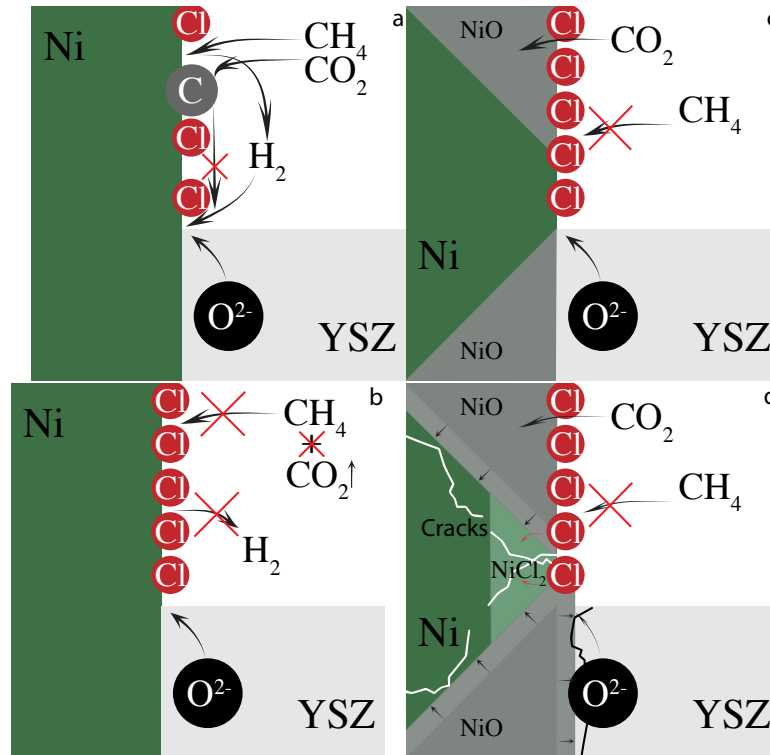


Figure 4.8: Schematic representation of degradation caused by biogas containing chlorine. (a) biogas operation with small amounts of adsorbed Cl, (b) biogas operation with full Cl coverage, (c) NiO formation from oxide flux and CO_2 (d) anode destruction from NiO expansion and $NiCl_x$ formation

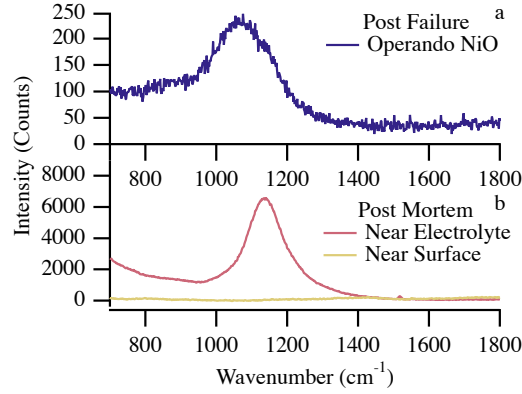


Figure 4.9: a) Operando Raman spectrum of NiO after catastrophic failure. b) Cross-section Raman spectra at room temperature near the anode/electrolyte interface (red) and near the anode surface (yellow).

Furthermore, given the relatively short duration of the experiments described in this work, such large-scale changes in material composition seem unlikely. The F_{2g} vibrational frequency also depends on temperature with a well-defined temperature dependence: [291]

$$\omega = -0.0338 \cdot T + 618.5 \text{ cm}^{-1} \quad (4.4)$$

where ω is the vibrational frequency in cm^{-1} and T is the YSZ temperature in degrees Celsius. [291] Figure 4.10 shows spectra with the F_{2g} peak for two trials. The first trial (blue trace with yellow fit) corresponds to the start of a cycling experiment while the second spectrum (green trace with red fit) was measured immediately after catastrophic cell failure. Differences between the spectra are subtle but reproducible. The spectrum acquired immediately after failure repeatedly shifted $\sim 5\text{-}7 \text{ cm}^{-1}$ to lower frequency and broadened repeatedly. Each scan was acquired immediately following the 10-minute polarization cycle while the cell was still exposed to biogas. If this frequency change is thermally induced, the

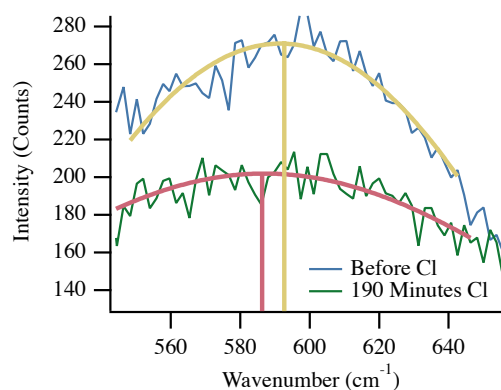


Figure 4.10: Expanded view of YSZ F2g peak position with respect to chlorine trial number (and subsequently chlorine exposure time.) Vertical lines indicate center of fit.

anode temperature would need to rise temporarily by ~ 180 °C. Such extreme and relatively rapid fluctuations would lead to severe structural strain and weakening of cohesion between the anode and electrolyte as well as anode and leads.

Effect of Redox Cycling on Aging Kinetics

Redox cycling of a fuel cell anode causes irreversible degradation and diminished performance over time [286,288] likely due to irreversible change within the SOFC anode's microstructure. [287,292,293] In order to eliminate the redox cycling itself as a source of the final catastrophic failure, long term experiments with no cycling were also performed. These experiments show the same type of degradation as in the cycling experiments, although the degradation requires a longer exposure, implying that the cycling experiments introduce a small degree of accelerated aging. Observed degradation with biogas is still much quicker than with chlorine-contaminated H_2 or CH_4 , however. Figure 4.11 shows a potential vs. time plot while the cell was polarized to 50% I_{max} for ~ 6 hours while operating with biogas. The plot shows the slow degradation associated with chlorine

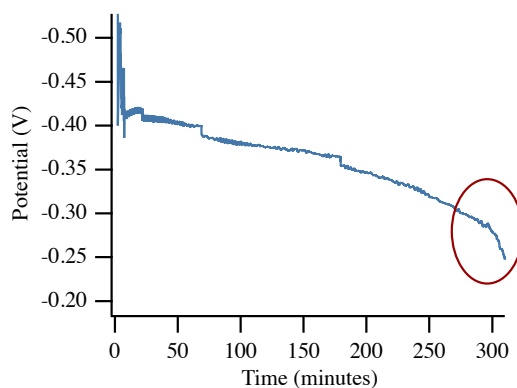


Figure 4.11: Potential vs. Time trace for non-cycling experiment showing a significant and sudden voltage drop of an SOFC operated on biogas at 650 °C.

contamination. Toward the end of the experiment the slope becomes significantly steeper indicating the onset of device failure (red circle), even in the absence of redox cycling. Control experiments with the more harsh cycling procedure showed virtually no change in slope during polarization, even after many hours.

Conclusion

Degradation induced by chlorine in a SOFC operating with biogas is different than the mechanism proposed by electrochemical studies using either hydrogen or methane as a fuel. Cell degradation rates with biogas are faster than with either hydrogen or methane alone. The data above do support the initial two-stage mechanism consistent with proposed degradation in SOFCs operating with both chlorine containing H_2 and CH_4 , but operation with biogas also shows new mechanisms not considered previously. Chlorine adsorption reduces methane cracking by nickel and what solid carbon is formed is removed by CO_2 , reducing fuel available to the SOFC and causing rapid degradation. Continued chlorine exposure eventually impedes methane cracking and dry reforming reactions

completely, heating the fuel cell due to the loss of the endothermic dry reforming reaction. The loss of oxidizable fuel causes anode cannibalization due to the galvanostatic polarization conditions, forming NiO and destroying anode interconnected microstructure, causing the potential to rise and the fuel cell to fail catastrophically at both 650 °C and 700 °C. These mechanisms occur much more rapidly than nickel chloride sublimation thought to be responsible for the long-term degradation in SOFCs operating with hydrogen and chlorine. Raman spectroscopy was used to monitor the effect the chlorine had on nickel's catalytic activity towards methane. Additionally, Raman data showed evidence of large but transient thermal stress that accompanied device failure. In conclusion, multiple electrochemical techniques combined with operando Raman spectroscopy provide a mechanistic picture of the degradation occurring on the anode of a fuel cell when operating on biogas and exposed to chlorine contaminants.

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CHAPTER FIVE

THE PALLIATIVE EFFECT OF H₂ ON SOFCS OPERATING ON
CONTAMINATED CARBON CONTAINING FUELSContribution of Authors and Co-Authors

Manuscript: The palliative effect of H₂ on SOFCs operating on contaminated carbon containing fuels

Author: Kyle W. Reeping

Contributions: Collected and analyzed all data. Wrote and edited manuscript.

Co-Author: Jessie M. Bohn

Contributions: Collected "long-term" Raman spectroscopy and electrochemical data.

Co-Author: Robert A. Walker

Contributions: Assisted with data interpretation manuscript editing.

Manuscript Information Page

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THE PALLIATIVE EFFECT OF H_2 ON SOFCS OPERATING ON CONTAMINATED CARBON CONTAINING FUELS

Introduction

Despite over a century of development, fuel cells have only recently begun to draw attention as a means of producing cleaner, more efficient electricity compared to traditional internal combustion sources. [294–296] Fuel cells can operate exclusively on hydrogen, producing only water as a product, but hydrogen is energetically expensive to produce and store. High temperature fuel cells such as solid oxide fuel cells (SOFCs) are capable of operation using hydrogen or more readily available and easier to produce carbon-containing fuels. Consequently, these devices are attractive for producing electricity from traditional and emerging fuels including natural gas, syngas ($H_2 + CO$), and biogas ($CH_4 + CO_2$). [297–300] Carbon-containing fuels contain their own contaminants, however, and fuel delivery systems must often be equipped with the means to remove species such as sulfur, chlorine and chromium in order to keep SOFC electrodes from suffering material degradation and performance loss. [299,300] Biogas, for example, can be produced from existing industrial processes or from the collection of gasses off of landfills and other organic waste sites. Because of biogas's diverse sources, contaminant identity and concentration can vary (0-1000 ppm) meaning that contaminant removal strategies must be similarly sophisticated. [294,298,301,302]

Most studies of contaminant-induced degradation in SOFCs have relied on electrochemical measurements performed as the device operates with H_2 or H_2 containing fuels (such as syngas) with varying amounts of added contaminants. [303–306] Electrochemical experiments such as voltammetry or impedance spectroscopy have provided valuable, real-time data that monitor cell

performance but these results do not contain the direct, materials specific information necessary to formulate validated, predictive mechanisms describing SOFC degradation. Furthermore, in instances when SOFCs are operating with mixed-composition fuels such as syngas or biogas or more complex hydrocarbon mixtures, electrochemical data cannot be used to isolate the role of each species in SOFC performance. [302, 307–310]

Recent studies of SOFC performance have shown unequivocally that Ni-YSZ cermet anode degradation in the presence of chlorine proceeds via qualitatively different pathways depending on fuel type and temperature. Specifically, chlorine only minimally impacts SOFC operation with H_2 , but operando optical spectroscopy shows that chlorine poisons Ni’s catalytic activity towards CH_4 activation leading to a loss of performance and eventual destruction of the electrolyte supported membrane electrode assembly. These effects were more severe when CO_2 was present with similar amounts of CH_4 simulating a typical biogas mixture.

Reconciling these results with proposed degradation models is difficult. Contaminant induced degradation of a SOFC operating on H_2 is thought to proceed through a two-stage process. The first, reversible stage of degradation occurs when Cl adsorbs to active sites on the nickel, reducing available active sites for fuel activation. [311, 312] Then, adsorbed Cl forms compounds with the nickel that either sublime or form insulating compounds depending on temperature. [313–318] While these mechanisms are still present in SOFCs operating with a chlorine contaminated, carbon containing fuel, the loss of catalytic activity dramatically accelerates cell degradation and device failure. With no way of producing oxidizable fuel (through C-H bond activation), the SOFC anode cannibalizes itself to produce current and nickel oxide. The differences in degradation methods between H_2 and carbon containing fuels imply differences in fuel activation, surface chemistry, and

conversion efficiencies as well as bring up questions regarding preferential fuel activation and catalyst deactivation by contaminants.

Studies described in this work explore the effects on SOFC performance of adding small amounts of excess H_2 to either methane or a simulated biogas surrogate containing chlorine. Of particular interest is whether or not H_2 limits chlorine-induced degradation of SOFC anodes operating with carbon containing fuels. Electrochemical measurements such as linear scan voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) provide direct performance evaluation and indirect mechanistic assessment. Raman spectroscopy affords direct, molecularly specific, time-resolved insight into the reactions occurring on the surface of the fuel cell anode. Results show that while the device will continue to show stable operation under galvanostatic conditions so long as H_2 is present, removing the small amount of H_2 from the incident fuel leads to rapid and irreversible failure, implying that the H_2 served only to mask the degradation known to occur when SOFCs are forced to operate with chlorine and CH_4 .

Methods

Membrane electrode assemblies measuring 25.4 mm in diameter were purchased from Fuel Cell Materials (www.fuelcellmaterials.com). Electrodes consisted of a 50 μm thick Ni-YSZ cermet and an approximately 5 μm thick Ni-GDC functional anode layer and a 50 μm thick LSM layer with an approximately 5 μm thick LSM-GDC interlayer cathode. The electrolyte consisted of 250-300 μm thick "Hionic" material. 3x3 mm silver and platinum meshes were attached to the anode and cathode using gold and platinum paste, respectively. The current collectors were smaller than the full anode area in order to facilitate optical access to the anode surface. A 50 mw Coherent Sapphire SF 488 nm laser was used in

conjunction with a Renishaw in-Via Raman microscope to collect Raman spectra and a Princeton Applied Research Versastat 3 collected electrochemical data. A pressure based, dual atmosphere, custom designed assembly dubbed SAwCER (SOFC Assembly with Concurrent Electrochemistry and Raman) [319] was used to heat the SOFC and provide ports to the anode and cathode chambers for gas flow. Cells were heated to a target temperature of 650 °C or 700 °C at a rate of 3 °C per minute with 55 sccm Ar on the anode and 85 sccm air on the cathode. At temperature, cells were reduced with 18 sccm H₂ until the cell open circuit voltage reached -1.0 V, at which time the H₂ flow was increased to 100 sccm for one hour. OCV was typically -1.12 ± 0.02 V after full reduction. Electrochemical benchmarks were performed with H₂ and Ar flow of 100 sccm and 55 sccm respectively. EIS data were collected at OCV using a 10 mV AC amplitude with frequencies ranging from 100,000 Hz to 0.1 Hz. No high frequency induction arcs were observed below the real axis on a Nyquist plot. LSV data were acquired with a sweep rate of 0.1 V/s and were stopped at -0.2 V to avoid any damage to the cell that might result from short circuit (0.0V) conditions. The maximum current was calculated by linearly extrapolating the ohmic region of the LSV data to 0.0 V. Experiments described below polarized the cell to 50% of the maximum current either cyclically for 10-minute intervals or for several hours consecutively.

Polarization timing, gas flows, and benchmark periods are outlined in Figure 4.1. After initial electrochemical characterization using H₂ as the fuel, H₂ flow was reduced to 18 sccm. After the potential stabilized, a 10-minute polarization period (at 50% I_{max}) commenced, followed 10 seconds later by a switch to the fuel being tested. For these experiments, that fuel (whether biogas or CH₄) was supplemented with 5% H₂. Ar flow throughout the experiment was a constant 55 sccm. The first “polarization period” was completed at OCV without

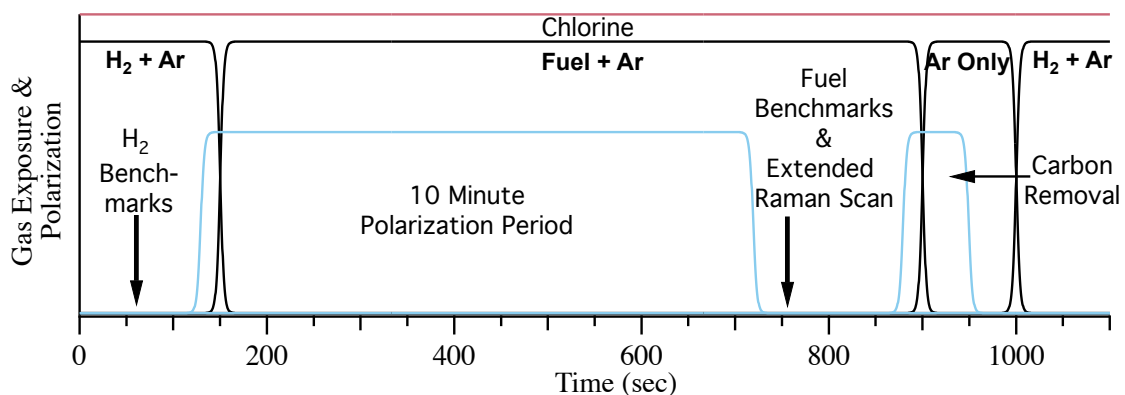


Figure 5.1: Gas flow during one typical experimental ‘galvanostatic cycle.’ Black represents fuel/carrier gas flow, red represents chlorine flow after initial stabilization, and blue represents cell polarization. Cycling experiments would continue until device failure as evidenced by a cell potential crossing 0V to provide the required current.

contaminant in order to ascertain the maximum current while operating on the fuel being tested and not H₂. Subsequent polarization periods were operated at 50% of that maximum current.

After the initial cycle at OCV, 2-3 cycles were completed at 50% $I_{\max}$ without contaminant until the electrochemical benchmarks stabilized, then 110 ppm CH₃Cl was introduced into the anode chamber for the remainder of the experiment.

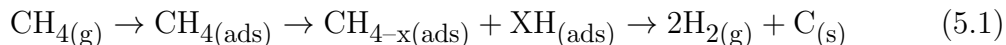
Following polarization, electrochemical benchmarks were completed while operating under the fuel being tested, in this case biogas or CH₄ with 5% H₂. Polarizing the cell while ceasing fuel delivery until the carbon “G” peak disappeared in the Raman spectra then removed any accumulated carbon. The cell was then re-reduced using H₂ and the cycle was repeated. Cycling experiments with H₂ were repeated for a duration that extended more than two times the period expected for device failure were H₂ not present. After 20-30 cycles, H₂ was removed from the fuel stream during the polarization period allowing the cell to operate solely on chlorine contaminated biogas or CH₄, depending on the experiment.

Long exposure experiments consisted of the same initial startup procedure as the cycling experiments, except instead of cycling the cell with CH_3Cl , the cell was polarized once after initial benchmarks and performance stabilization for 6-12 hours, at which point the H_2 flow was removed. Upon cell failure, the apparatus was cooled with argon atmospheres on both the anode and cathode.

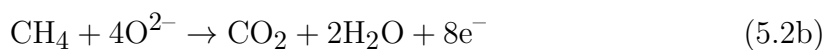
Results and Discussion

Raman Spectroscopy

Neither hydrogen nor chlorine reacts with anode materials to produce compounds whose vibrations have Raman cross sections large enough to be spectroscopically visible in operational fuel cells. However Raman spectroscopy can be used to observe the accumulation of carbon or “coke” on the surface of the anode due to the methane cracking reaction (Equation 5.1).



The amount of coke that accumulates is related directly to Ni’s catalytic activity. Once CH_4 dissociatively chemisorbs on the SOFC’s Ni anode surface, both carbon and hydrogen can be electrochemically oxidized to produce CO_2 and H_2O , respectively. (Equation 5.2)



Chlorine adsorbs to active catalytic sites, deactivating Ni and preventing C-H bond activation. This action effectively starves the anode of oxidizable fuel. Reduced catalytic activity produces two noticeable effects in the time-dependent vibrational Raman spectra. First, observable carbon accumulation decreases as more chlorine adsorbs to the active sites responsible for methane cracking. If the SOFC is operating under galvanostatic conditions in the presence of chlorine, Raman spectra eventually show evidence of Ni oxidation (in the form of NiO) as the anode cannibalizes itself to continue providing current. Recent studies have reported that CO₂ in a biogas surrogate exacerbates both symptoms, accelerating the removal of any carbon already on the surface and oxidizing nickel. [319,320] An operando spectrum of accumulated carbon formed on Ni anodes operating on biogas and methane (and no chlorine) appears in Figure 5.2. Four features are prominent. Starting at low wavenumbers, the first peak at 595 cm⁻¹ results from the F2g mode in cubic zirconia. [321] The two peaks at 1356 cm⁻¹ and 1556 cm⁻¹ result from the first order peaks of carbon on the anode surface. The peak at 1356 cm⁻¹ is assigned to graphite containing point defects and/or grain boundaries and is commonly referred to as “disordered” carbon. “Ordered” carbon composed of defect-free graphite results in the peak at 1556 cm⁻¹ due to the in-plane optically active vibration (E2g mode). [322,323] The final peak at 2698 cm⁻¹ is typically assigned to the electron-phonon coupling of the second order zone boundary phonons in graphite that are disallowed in the first order spectra. [322,323]

Plotting the “G” peak intensity as a function of time monitors the kinetics of carbon accumulation on the anode surface, as seen in Figure 5.3. Carbon accumulates quickly on Ni SOFC anodes operating with methane and 5% H₂ while polarized to 50% of the maximum current at both 650 °C (Figure 5.3b) and 700 °C (Figure 5.3c) and then stabilizes at a level that stays relatively constant throughout

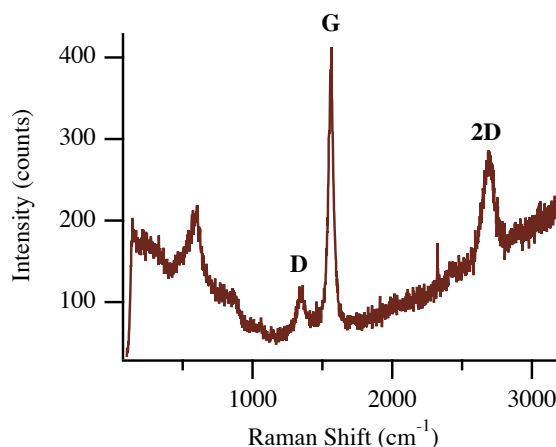


Figure 5.2: Operando spectrum of carbon on the surface of a SOFC operating on biogas at 650 °C. Carbon accumulation is observed on SOFCs operating with biogas and 5% H₂ at both 650 °C and 700 °C under 50% polarization when no chlorine is present.

the rest of the 10 minute polarization period. Carbon signal remains present for the remainder experiment without CH₃Cl present. When CH₃Cl is added to the fuel without excess H₂ however, the stable “G” peak registers increasingly weaker intensities until no carbon is observed spectroscopically. Interestingly, carbon accumulation is suppressed more effectively at lower temperatures (650 °C) than at higher temperatures (700 °C). [320] This result has been attributed to NiCl_x formation and subsequent volatilization. NiCl_x sublimation will be more pronounced at the higher temperature and will result in a renewed anode surface with clean, nickel that can continue to activate CH₄ and promote carbon formation. When H₂ is added to the CH₄/CH₃Cl mixture “G” peak kinetics more closely resemble the kinetics of clean CH₄ with no CH₃Cl present. The complete loss in signal typically observed with poisoned CH₄ does not occur, and the carbon Raman signal stays relatively consistent until H₂ is removed from the fuel stream. (Figure 5.3b and 5.3c)

Results from SOFCs operating with chlorine containing biogas are subtly

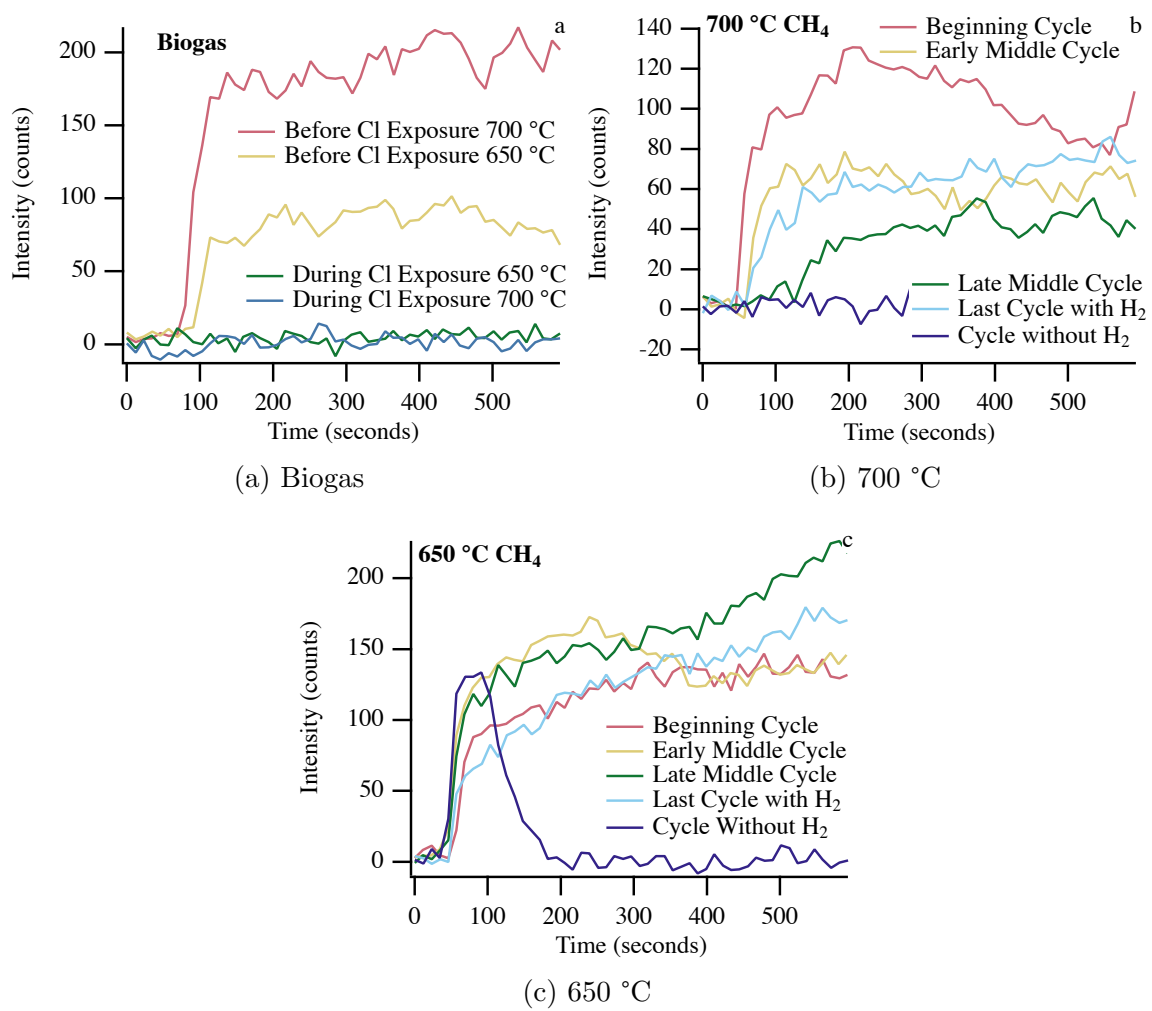


Figure 5.3: Carbon "G" peak kinetics for biogas (a) and CH₄ at 700 °C (b) and 650 °C (c). (Top = a, mid = b, bottom = c.)

different than chlorine containing CH_4 experiments. Clean biogas produces an observable carbon signal that is less stable than with CH_4 alone, but still present. (Figure 5.3a) Upon the introduction of CH_3Cl into the biogas fuel stream the observed “G” peak intensity disappears immediately (within experimental detection limits) at both 650 °C and 700 °C instead of diminishing more gradually as is the case for CH_4 . With both CH_4 (at 650 °C) and biogas, the signal reduction is due to chlorine blocking active methane cracking sites on the nickel surface, preventing adsorption and dissociation of methane. The CO_2 in biogas remains capable of actively removing or preventing carbon formation via dry reforming, therefore coke formation behavior is unchanged upon the addition hydrogen to a fuel cell fuel stream operating on CH_3Cl containing biogas at both 650 °C and 700 °C, unlike with a SOFC operating on chlorine contaminated CH_4 . (Figure 5.3a compared to 3b and 3c) No change in carbon accumulation (or lack thereof) when operating on Cl-poisoned biogas containing H_2 is observed when H_2 is removed from the fuel stream. No carbon present after H_2 is removed for both biogas and CH_4 indicates that methane cracking has ceased, however the persistence of the carbon signal when operating on chlorine containing CH_4 with H_2 indicates the presence of a mechanism for hydrogen to actively remove Cl or promote CH_4 activation. Immediately following H_2 removal, electrochemical failure of the cell is observed, indicating that Cl is once again preventing CH_4 activation.

Electrochemistry

Time-dependent potential data under polarization show that as long as small amounts of hydrogen are present, SOFC performance remains stable. As soon as H_2 is removed though, the device fails catastrophically and irreversibly. This behavior is observed clearly in SOFCs operating with Cl containing methane at both 650 °C

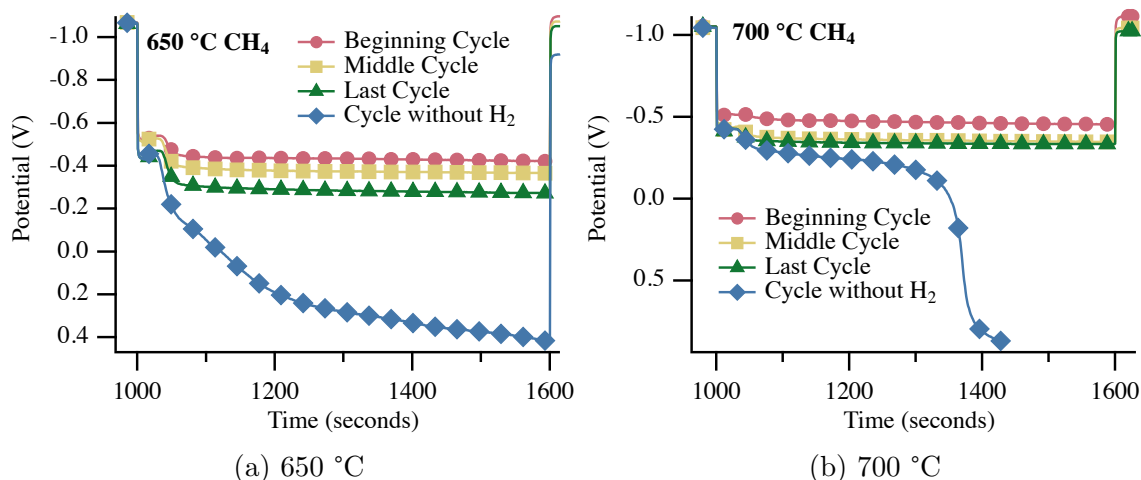


Figure 5.4: Potential vs. time traces for SOFCs operating on CH₄ at 650 °C (a) and 700 °C (b).

and 700 °C (Figure 5.4) and biogas. Under typical cycling conditions employed in these studies, SOFCs operating with Cl containing CH₄ would fail after 8-10 cycles and the degradation from cycle to cycle was readily apparent. In contrast, adding 5% excess H₂ leads to stable performance for up to 20+ cycles with no sign of cell degradation. This palliative effect vanishes abruptly when H₂ is taken out of the fuel, illustrating that H₂ masks degradation that occurs during galvanostatic operation with Cl containing CH₄ or biogas as the primary fuel source. (Figure 5.4 blue diamond traces) While excess H₂ does prevent cell failure, it does not prevent Cl-induced anode degradation. Similar results are observed during long-term experiments without cycling, discussed below. Cell failure occurs directly following the removal of H₂ from the fuel stream. EIS and LSV data provide more information on the failure.

Figure 5.5 shows benchmark EIS and LSV of the SOFCs operating with H₂ before having completed a polarization cycle with Cl-containing CH₄ with H₂. H₂ benchmarks show little change when Cl poisons the cell reversibly; therefore

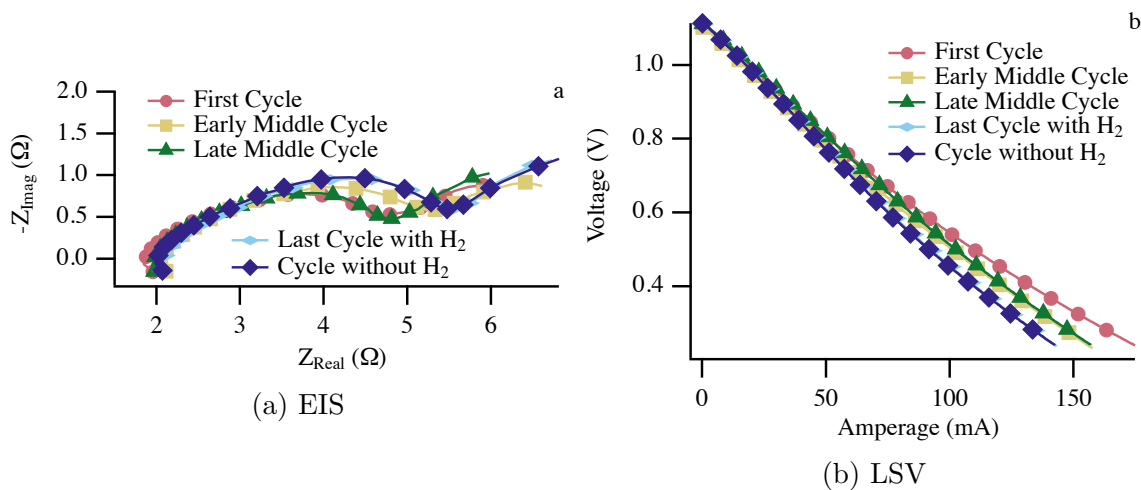


Figure 5.5: Benchmark EIS(a) and LSV(b) preformed before polarization under H₂ fuel at 650 °C.

providing only evidence of irreversible degradation to the fuel cell. Figure 5.5 shows little permanent degradation other than what would be expected due to cell aging throughout the experiment. More importantly, the LSV data show that the cell was operating normally before the final, failing polarization cycle. While H₂ was present during all but the last cycle in Figure 5.6, the subtle differences between the two sets of data show that the fuel being tested, whether CH₄ or biogas, does affect the electrochemistry even when H₂ is present.

Figure 5.6 shows equivalent data after the polarization period when operating on Cl-containing CH₄ with excess H₂. The benchmarks performed after polarization show degradation related to fuel activation and better represent the performance losses of a cell operating with non-idealized fuels such as natural gas. In these experiments, both sets of benchmark electrochemical data are very similar because H₂ is present. The LSV data performed after polarization (Figure 5.6b) show a slow but steady decrease in performance throughout the cycles, as would be expected with a chlorine free run due to aging and redox cycling. The final cycle, however,

shows a sudden, more abrupt decrease in performance due to the removal of H_2 from the fuel stream. (Figure 6b) These results are consistent across experiments using chlorine contaminated methane or biogas (both with H_2) as a primary fuel. Differences between the two sets of LSV traces (before and after polarization) are apparent during the failing run. The benchmarks performed immediately before the final cycle show no indication of failure, while the benchmarks performed immediately after failure show permanent damage and much lower maximum current. EIS data show correspondingly telling results. EIS spectra for a SOFC operating on chlorine-contaminated methane (with H_2) look extremely similar in terms of shape. Both show both a high and low frequency arc but the magnitude of the impedance is different when operating on H_2 alone compared with methane containing H_2 , indicating that both H_2 and methane are being used concurrently in the latter. Despite these differences, both EIS spectra show small amounts of cycle to cycle degradation until the final cycle without H_2 . After H_2 removal from the fuel, both R_{bulk} and R_{pol} become much larger, coinciding with the loss of performance in the LSV and catastrophic rise in potential. Similar results were observed for identical experiments performed at 700 °C. In order to remove redox cycling as a cause for the final failure, continuous experiments were also performed.

Long-Term Experiments

Cycling experiments can introduce accelerated degradation to a functioning fuel cell simply due to redox cycling; therefore continuous (non cycling) experiments were also performed in order to test whether or not the cell performance sensitivity to H_2 is simply a result of experimental procedures. Figure 5.7 shows uninterrupted potential vs. time traces for experiments performed at 650 °C with CH_4 (a) and biogas (b). Unlike with chlorine contaminated methane or biogas alone, [320] the

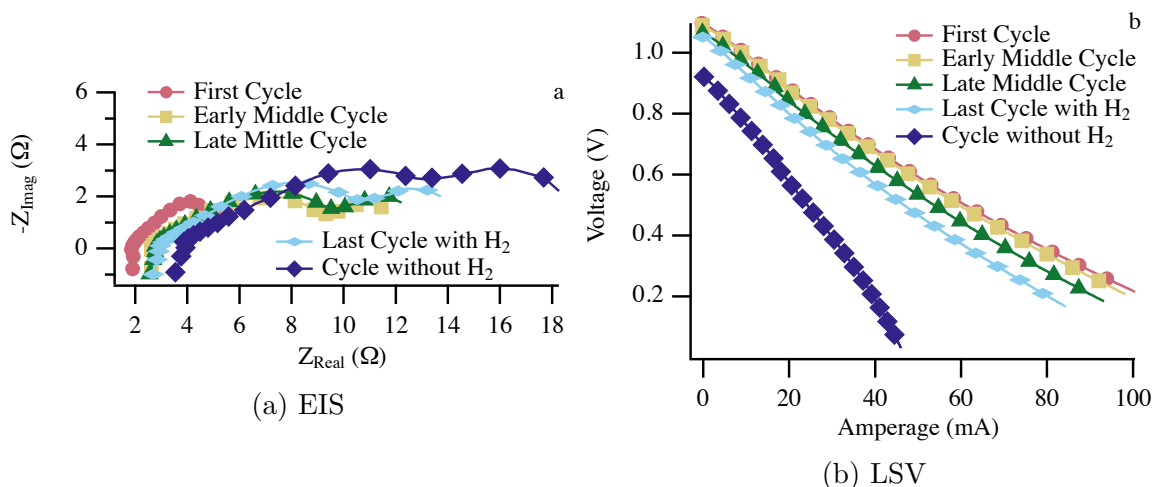


Figure 5.6: EIS (a) and LSV (b) performed after polarization under $CH_4 + H_2$ fuel at 650 °C.

potential under polarization quickly stabilizes because of the hydrogen present in the fuel stream. Cells were exposed to H_2 and CH_4 or biogas with CH_3Cl mixture for roughly 2-4x the duration necessary for a similar experiment without H_2 to fail. These extended experiments ensured that H_2 was, in fact, preventing cell failure. Once the H_2 feed was removed allowing the cell to operate solely on Cl containing CH_4 or biogas, depending on experiment, cells invariably failed, indicating that the cells could no longer operate on fuels other than H_2 .

Mechanism

SOFCs operating on contaminated carbon containing fuels display degradation mechanisms that are fundamentally different than when operating with hydrogen containing fuels. Furthermore, hydrogen appears to temporarily “hide” but not prevent degradation caused by operation on carbon containing fuels. The mechanism behind this behavior is of yet unknown. The discussion below compiles data from a number of experiments to propose a mechanism responsible for both

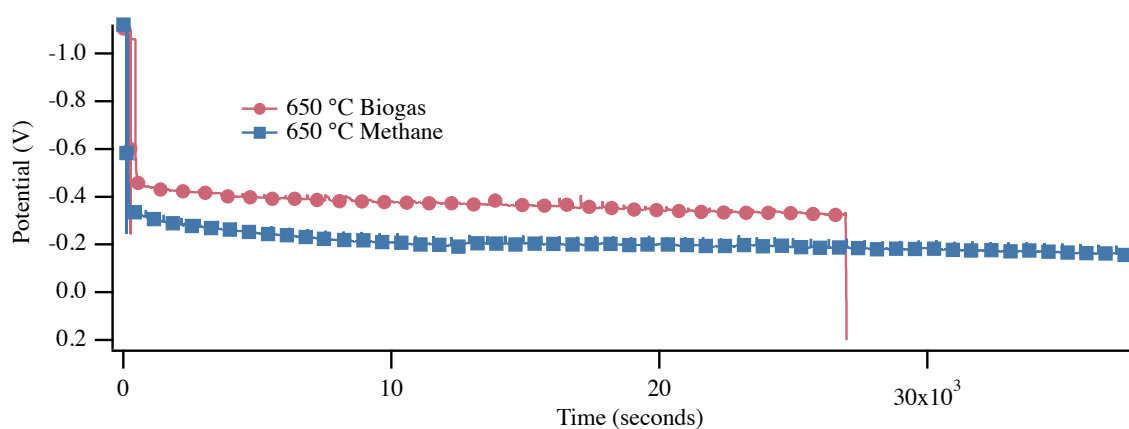
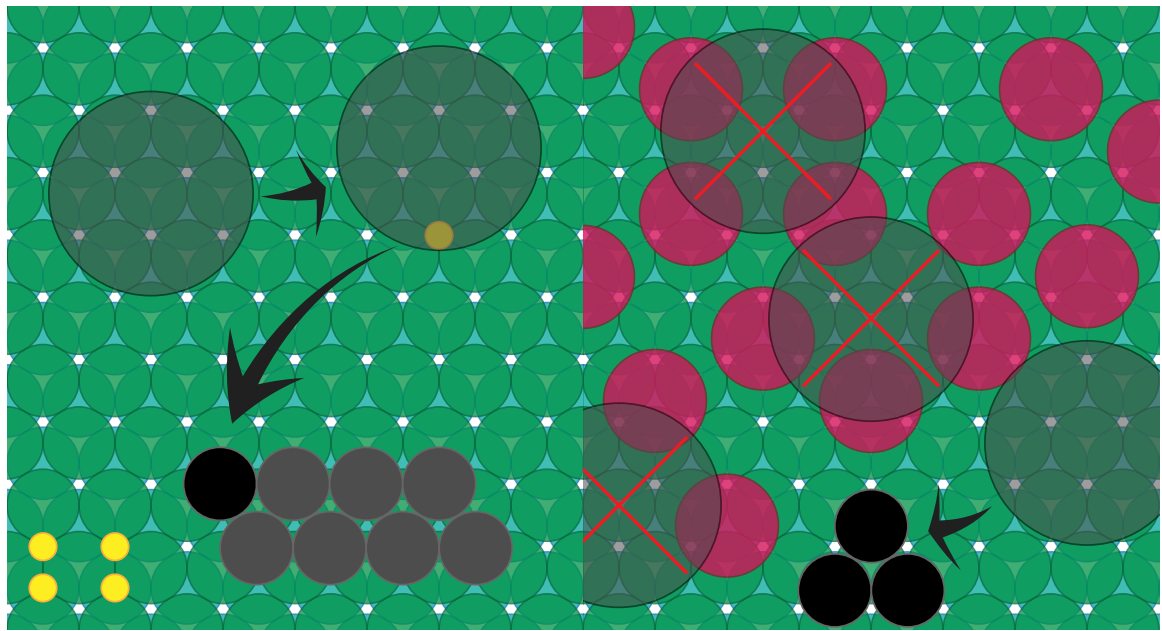


Figure 5.7: Long experiment potential vs. time data showing failure immediately when H_2 was removed from a long biogas (red circle) and CH_4 (blue square) experiments.

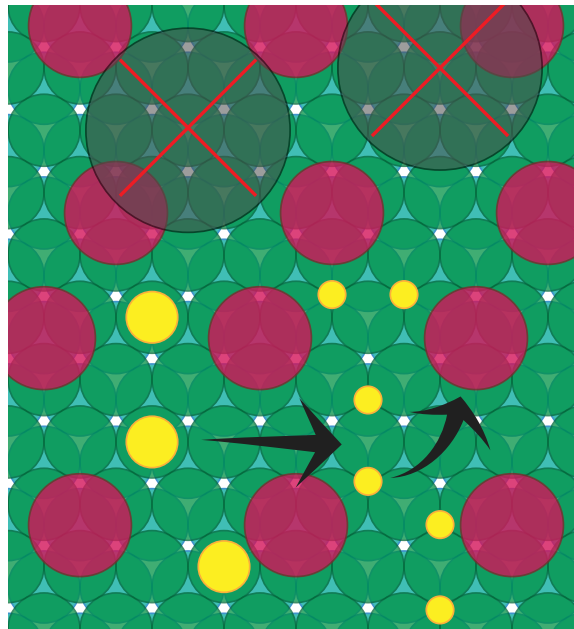
the accelerated aging when operating with contaminated carbon containing fuels as well as the palliative effect of hydrogen on that aging process. Chlorine deactivates nickel catalysts outside of fuel cell constraints; therefore it is likely that reactions relevant to these mechanisms occur on that surface. the surface of the cell, reducing the overall fuel available as chlorine poisons the cell, and also oxidizes Ni to NiO.

Figure 5.8a shows normal SOFC operation with methane. Methane (large transparent grey circles) dissociatively chemisorbs onto the nickel surface (green circles, two layers) over top of a nickel atom producing a hydrogen (small yellow circle) and methyl group bound at opposite hcp and fcc hollow sites. CH bond activation continues eventually producing 4 individual hydrogen atoms and a carbon atom (black circle), likely in a graphite lattice (grey circles.) When exposed to chlorine (red circle), a SOFC using a Ni-YSZ anode immediately loses some performance due to chlorine adsorbing to the most accessible active sites on the Ni particles. (Figure 5.8b) Carbon can continue to form at this stage of degradation. At temperatures lower than 700 °C, chloride accumulates on the surface, blocking an



(a) Normal operation on methane

(b) Operation on methane when poisoned



(c) Hydrogen is not affected by Cl poisoning

Figure 5.8: Mechanism for chlorine poisoning on a Ni-YSZ cermet anode. Atoms and molecules are to scale as much as possible. A: Normal methane operation, B: Operation on methane while partially poisoned. C: Hydrogen operation while poisoned by chlorine. Methane: Large grey transparent circle. Chlorine: Red circles bound at hcp sites. Carbon: Black circle (grey circles for graphite lattice). Diatomic hydrogen: Larger yellow circles on top of nickel atom. Hydrogen atoms: small yellow circles at hcp and fcc hollow sites.

increasing number of active sites for fuel activation. The adsorbed chlorine can form nickel chloride compounds that reduce electronic conductivity throughout the anode. When operated under galvanostatic conditions the reduced electronic conductivity and lowered catalytic efficiency of the anode results in fuel starvation, causing fast oxidation of the Ni to form NiO, resulting in a metal decomposition and overall reduced structural integrity due to the increase in the size of the Ni particles upon oxidation (and subsequent reduction in size upon reduction.) Temperatures of 700 °C or above also result in the formation of nickel chloride compounds, but those compounds will volatilize resulting in physical nickel removal from the cell. Removing Ni from the cell anode slowly degrades cell performance and is often the degradation mechanism cited when operating on H₂ alone. However, the removal of Ni from the cell has a side effect of allowing the cell to continue operating on CH₄ for longer periods of time due to the constant supply of fresh (non-poisoned) Ni following nickel chloride sublimation. This extended life comes at the cost of permanent degradation, whereas adsorption of chlorine and formation of nickel chloride compounds at low temperatures is reversible. Removing chlorine from the fuel stream leads to substantial recovery of the device's original performance.

Biogas has similar degradation mechanisms to CH₄ above, albeit at an increased rate as CO₂ amplifies the mechanisms responsible for anode oxidation. CO₂ removes any carbon on cells operating with biogas fail about 30% more quickly than ones operating with CH₄ when exposed to chlorine. All of these degradation mechanisms appear present, yet hidden, when H₂ is added to the fuel stream. H₂ does not prevent degradation: it prevents catastrophic failure. Figure 5.8c shows that much less than a full monolayer of chlorine atoms can effectively block all methane adsorption sites, yet molecular hydrogen (larger yellow circles) can still dissociate into hydrogen atoms (smaller yellow circles) and move freely between

chlorine atoms, even with tightly packed Cl covering the surface. Furthermore, hydrogen is soluble in nickel, allowing for subsurface transport of hydrogen atoms, completely bypassing chlorine poisoning. Unlike methane, hydrogen dissociation on Ni faces a very small, effectively barrierless activation. [324,325] Methane must overcome a 0.54 eV activation energy to simply chemisorb, followed by increasingly higher activation energies to be converted to adsorbed carbon and hydrogen. [326] Given the steric hindrance of CH_4 and lower activation energy for hydrogen adsorption; it is much more likely for hydrogen to be activated on the nickel surface than carbon, even at low Cl coverage. At high coverage, methane cannot be activated at all, resulting in SOFC starvation when H_2 is not present. However, as mentioned previously, carbon Raman signal is still present on the surface of the anode, even after many hours of Cl poisoning in the presence of 5% H_2 . Therefore hydrogen must be reacting with and removing some fraction of the adsorbed chlorine (Figure 5.8c, bottom) allowing for increased clean Ni surface area, resulting in carbon accumulation. These results illustrate clearly that H_2 delays, but does not prevent permanent degradation due to chlorine poisoning of an SOFC.

Conclusion

The primary method of degradation induced by chlorine in an SOFC operating on a carbon containing fuel is fundamentally different than in an SOFC operating with H_2 . The degradation associated with H_2 alone provides the lower limit for chlorine contamination severity. Performance loss is orders of magnitude more severe when using carbon-containing fuels like CH_4 and biogas due to chlorine more effectively poisoning the C-H bond activation mechanism. In the absence of H_2 , chlorine packs efficiently enough to block large carbon containing fuels from adsorbing, but not to prevent H_2 from adsorbing and moving freely on the surface.

Raman spectroscopy was used to monitor carbon accumulation in these experiments in order to assess the catalytic activity of the nickel within the anode and electrochemical measurements were used to monitor performance losses of the fuel cell. In conclusion, multiple electrochemical techniques as well as operando Raman spectroscopy provide a more complete mechanistic picture of the degradation occurring on the anode of a fuel cell operating with chlorine contaminated biogas or CH_4 with 5% H_2 .

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CONCLUSION

Energy conversion technologies are constantly being improved to match the increased demands for electrical power. These technologies, however, can require years or even decades and pass through many stages of development before being integrated into a multi-dimensional, power production portfolio. SOFCs stand out as an example of one such technology. SOFCs can produce electrical power from both legacy and emerging fuel sources, and are also capable of operating in the context of a H₂-based economy or with fuels produced by carbon-free processes. Studies presented in this dissertation characterize SOFCs performance and durability when influenced by chlorine contaminants. Data show that Cl-induced degradation depends on a number of variables including operational temperature, cell polarization and fuel feed composition. These findings are important because previous models to describe device degradation and eventual failure were based on findings from studies using only H₂ or fuel mixtures where H₂ was a significant component. Findings presented in Chapters 2-5 show that degradation and failure mechanisms change with temperature and device failure can be rather rapid when the incident fuel consists only of carbon containing species without H₂. None of the above experiments described in this dissertation would have been possible without the use of a custom designed optically accessible SOFC rig capable of interfacing to existing Raman microscope instrumentation, SAwCER. The devices also provided an important reference to benchmark studies performed in the original SOFC rig, Rocket. Working with contaminants in general is difficult as they adsorb to most materials, including those used to construct scientific instrumentation. Minimizing the amount of time the fuel (and contaminant) spent at operational temperature before reaching the fuel cell increased the concentration of contaminant that reached

the anode. Results performed at the Naval Research Laboratory in Washington D.C. showed that in order to replicate the results of SAwCER in a Rocket like setup with a much longer path at temperature to the anode, the concentration of contaminant had to increased 3-fold. The shorter residence time in SAwCER reduced that problem and also significantly reduced contaminant “sink” effects where adsorbed contaminants on the rig would be released over time, even on “clean” experiments. Details about SAwCER design and fabrication are reported in Appendix 2.

Using SAwCER, chlorine contamination of SOFCs was studied in a variety of conditions with several different fuels. Results from operation with CH_4 at $650\text{ }^\circ\text{C}$ showed discrepancies when compared to previous electrochemical experiments using H_2 alone. Degradation with Cl-contaminated CH_4 was fast, orders of magnitude faster than with contaminated H_2 . After eliminating all other possibilities for the increased rate of degradation we began developing new mechanisms to explain this increased degradation rate. We concluded that Cl was very effective at blocking catalytically active sites on Ni, effectively turning off the catalyst’s ability to activate the C-H bond of methane and preventing subsequent dissociative chemisorption and eventual electrochemical oxidation. In contrast H_2 activation on the Ni anode remained unaffected by the presence of Cl, implying different mechanisms at the start of the electrocatalysis process. The slow degradation observed with Cl-containing H_2 relied on formation or evaporation of very low vapor pressure nickel chloride materials as the main source of performance loss, where as when the SOFC operated with Cl-containing CH_4 , reaction sites simply had to be blocked, and performance loss resulted quickly. Results with CH_4 at $700\text{ }^\circ\text{C}$ corroborated this mechanism. Interestingly, when parts of the nickel anode volatilized, clean patches of nickel were left behind, allowing for continued C-H bond activation until those areas were poisoned as well. The difference between Cl

contamination at 650 °C and 700 °C was that loss of anode material through sublimation at high temperatures resulted in continued operation (with lower efficiencies) but irreversible degradation. At the lower temperature, removing the Cl from the fuel feed led to significant recovery of anode performance. The next question this research addressed was “How would the addition of CO₂ affect this mechanism?” Adding CO₂ to CH₄ creates a mixture commonly referred to as “simulated biogas.” Experiments similar to those performed with CH₄ were also carried out with biogas to ascertain whether the addition of CO₂ would change the fundamental mechanism of anode degradation and potential recovery. CO₂ did change the observed outcomes, but not the overall proposed mechanism of electrode degradation and eventual failure. While the cell is in the early stages of chlorine poisoning, C-H bond activation is still possible due to incomplete Cl coverage on the nickel surface. While operating on biogas, however, any carbon that is formed on the nickel surface is removed through dry reforming, reducing the amount of oxidizable fuel available to the SOFC. Therefore, SOFCs operating on biogas failed about 30% faster than with CH₄ alone. CO₂ also partially oxidized the nickel, resulting in an increased degradation rate even at higher temperatures where anode sublimation might be expected to maintain fresh Ni surfaces. The CH₄ and biogas studies leads one to conclude that chlorine poisoning of SOFCs operating on carbon containing fuels affects primarily the C-H bond activation pathway. All of the above experiments showed little degradation for H₂ benchmarks, leading to the final query of “Can H₂ be used to suppress or prevent chlorine degradation?”

SOFC performance with H₂ consistently showed less degradation than similar studies performed with carbon containing fuels. Therefore hydrogen must have a different activation pathway relative to CH₄. In order to test this hypothesis, experiments were performed with a small (5%) amount of H₂ in fuels consisting of

Cl-contaminated CH_4 and biogas. Expectations were for the cells to show little to no degradation when H_2 was present, but when removed after a significant exposure to Cl, performance would fail immediately with mirrored degradation mechanisms to the H_2 free experiments. Experiments showed that was indeed how the mechanism proceeded leading to the complete mechanistic description in Chapter 5. While this result seems immaterial, it is, in fact, the most important result from this dissertation. Molecular hydrogen is small enough to dissociatively chemisorb even when the nickel anode is poisoned by adsorbed chlorine. A near perfect monolayer of chlorine on the nickel (111) surface still does not effectively block all active sites for H_2 activation. The conclusion from this chapter is that hydrogen masks, but does not prevent degradation of Cl-poisoned SOFC Ni anodes. The consequences of this finding are important, because any mechanism of anode degradation based on SOFC performance with fuel mixtures containing H_2 will not capture the systemic damage that occurs but is hidden by the readily oxidized H_2 . Finally, continuous experiments were performed consider the effects of cycling. Data from continuous operation experiments resulted in slightly slower (20%) degradation but identical methods of failure for all combinations of temperatures, fuels, and contaminants. The results discussed above make clear that studying SOFC contamination using hydrogen does not provide sufficient information to predict degradation mechanisms in commercially relevant applications where carbon-containing fuels are employed. Furthermore, electrochemical results alone only provide evidence of cell performance and not direct measures of the processes responsible for cell degradation. This limitation necessitates molecularly specific techniques capable of providing real-time data about material changes that accompany changes in performance.

While the studies presented in this dissertation do not replicate perfectly the conditions experienced by commercially deployed SOFCs, the mechanistic insight

from combined electrochemical and optical spectroscopy studies provide a more complete and comprehensive perspective into electrochemical oxidation and materials degradation in high temperature SOFCs.

In order to mimic even more closely the conditions sampled by commercial SOFCs, several different types of studies could be performed. Chlorine is not the only contaminant present in true to life SOFC fuel streams, and interactions between degradation mechanisms on the SOFC surface are likely to cause many unforeseen problems for SOFC durability. Furthermore, the experiments described in this dissertation used only a single chlorine concentration (110 ppm). Electrochemical studies have sampled lower and higher concentrations but never with fuels free of H_2 and rarely with the mechanistic insight provided by optical spectroscopy. Other limitations of the work presented in this dissertation are the result of the rig, itself. While commercial rigs are often made from inexpensive stainless steel, commercialized SOFCs are utilized in stacks with interconnects between large cells rather than individual cells, resulting in decreased headspace above the anode and cathode of the cell. Subtle differences between the two assemblies in our laboratory, Rocket and SAwCER, suggested that differences in headspace volume and flow geometry might affect conversion efficiency and degradation rates. Other experimental limitations arise due to the methods used. Raman spectroscopy is a powerful tool for observing carbon and other molecular and material species having large Raman cross sections but not all molecules and materials have Raman active vibrations. While carbon is a direct product of the reactions occurring on the surface, specifically C-H activation, it is not a direct product of the poisoning mechanisms. Using carbon to infer mechanisms is one step removed from the mechanistic products themselves. For direct observation of reaction products, a technique like mass spectroscopy or FTIRES would have to be

employed. A single study performed by the Liu group at Georgia Tech showed the formation of nickel sulfide presence using Raman spectroscopy and a similar rig to SAwCER, but rig limitations and phase transitions required that experiments be performed at temperatures less than 600 °C. Ideally, a product directly resulting from the poisoning mechanism could be observed operando but the high temperatures required for SOFC operation and difficulty of high temperature Raman spectroscopy continue to pose challenges. Future experiments along the lines of those performed in this dissertation would follow two paths. The first and most obvious is changing contaminant concentration and identity while looking for the appearance of new materials that explicitly include the added contaminant. A second line of inquiry could explore further the interaction of hydrogen with contaminated fuel cells and whether or not H_2 can be used as a ‘cleaning’ agent. An experiment not discussed above involves humidifying the fuel stream, as is typical for commercial SOFCs. Very preliminary data show no degradation, leading to the hypothesis that water (or water’s dissociated fragments on a Ni surface) removed the chlorine contaminant from the fuel stream. However, in light of the experiments described in Chapter 5, an alternative hypothesis is that the hydrogen produced by water dissociation simply hid any degradation.

The experiments described in this work along with the subsequent analysis and discussion strongly suggest that previous SOFC studies of chlorine contamination were poorly informed. The assumption that degradation under simple fuels such as H_2 would form the basis of the major degradation pathways using more complicated carbon contained fuels is mainly false. More severe mechanisms come into fruition and make previous mechanisms inconsequential. SOFCs are capable of providing power at much higher efficiencies than what is observed today. The experiments above lay the foundation for characterizing SOFC

performance degradation due to contaminants using molecularly specific techniques combined with ex-situ methods and electrochemical techniques.

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APPENDICES

APPENDIX A

IN SITU OPTICAL AND ELECTROCHEMICAL STUDIES OF SOFC CARBON
TOLERANCEContribution of Authors and Co-Authors

Manuscript: In situ optical and electrochemical studies of SOFC carbon tolerance

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Contributions: Assisted in data collection.

Co-Author: Robert A. Walker

Contributions: Assisted with data interpretation manuscript editing.

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APPENDIX A

IN SITU OPTICAL AND ELECTROCHEMICAL STUDIES OF SOFC CARBON
TOLERANCE

Introduction

Solid oxide fuel cells (SOFCs) are energy conversion devices that can electrochemically oxidize a wide variety of fuels using relatively inexpensive materials. Capable of reaching efficiencies of 70% in combined heating and power applications, SOFCs readily surpass the energy efficiency of combustion-based sources of electrical power [1–3]. However, high cost to power ratio as well as durability concerns have prevented fuel cells from being integrated into national energy infrastructures [4,5]. However, because of a large activation energy associated with oxide ion conduction through ceramic materials, SOFCs are required to run at elevated temperatures anywhere from 650 °C to 1000 °C. These conditions accelerate corrosion and material degradation, meaning that cell and interconnect materials must be capable of withstanding these environments. Such materials are expensive and hard to manufacture [6]. Since studies have shown that both the electrolyte and electrodes degrade relatively quickly at these temperatures, compared to conventional power plants, establishing and maintaining a fuel cell power plant is a sizeable endeavor [7–11]. Furthermore, repairs for individual cells are almost nonexistent, normally requiring the replacement of the defective cell. Given the difficulties associated with operating SOFCs at high temperatures, significant research has focused on developing materials that would allow these devices to function in more easily attainable environments [1,12,13]. New electrode materials have improved catalytic performance and new electrolyte materials have shown high ionic conductivity at temperatures as low as 550 °C [2]. One of these electrolyte materials, Scandia-stabilized Zirconia (ScSZ), stands out for its superior electronic conductivity and higher mechanical strength [13–18]. Relevant properties of ScSZ and YSZ are summarized in Table A.1.

- Materials -	Conductivity at 1073 K S/cm	Thermal Expansion Coefficient	- Observed Phase	Mechanical Strength MPa
11 ScSZ	0.11	$10.5 \times 10^{-6}/\text{K}$	Cubic	313
7 YSZ	0.04	$10.5 \times 10^{-6}/\text{K}$	Cubic	279

Table A.1: Mechanical and Electrical Properties of ScSZ and YSZ (from References [10] and [11])

While very similar to YSZ, ScSZ is more suitable for SOFCs mainly because of its comparably higher ionic conductivity. Not only does higher conductivity improve cell efficiency, higher conductivity also allows the cell to be run at lower temperatures, mitigating adverse effects of corrosion and microstructure stability. The enhanced ionic conductivity improves overall cell performance by allowing more current to be drawn at lower cell polarizations. Higher currents increase the O₂-flux, increasing the amount of electrochemical oxidation, which, in turn, limits the amount of carbon that can accumulate on SOFCs operating with hydrocarbon fuels. Typically, conditioning of the fuel feed using reforming units mitigates carbon formation, however increasing the partial pressure of electrochemical products such as H₂O or CO₂ promotes ‘internal reforming’ within the porous anode architecture, eliminating the need for expensive precious metal catalysts. This hypothesis that a higher conductivity electrolyte will mitigate SOFC coking, however, has not been tested.

The problem of coking or carbon accumulation on the anode of an SOFC has been studied extensively using both Raman spectroscopy and FTIR [19–22]. The high catalytic activity of nickel-based anodes causes carbon containing fuels such as

methane (CH_4) and propane (C_3H_8) to form on electrode surfaces, especially at the putative triple phase boundary (TPB) where the electronically conducting anode, the ionically conducting electrolyte and gas phase fuel mixture meet [9, 22, 23]. Carbon accumulation at the TPB will block active sites, reducing cell performance. Eventually, carbon will dissolve into the Ni leading to metal dusting and irreversible damage to the cell stack. Higher molecular weight fuels like natural gas or even butane (C_4H_{10}) have been shown to deposit much more carbon onto the surface [24, 25]. Understanding the mechanisms of how carbon deposits form and identifying conditions that can remove carbon that does form are both critical to designing protocols that enhance SOFC lifetimes. These goals are especially important given that emerging fuels such as biogas and syngas are known to form carbon under conditions commonly used for SOFCs [26, 27].

Experiments described below were performed to determine if SOFCs constructed with ScSZ electrolytes were more effective than YSZ-based SOFCs at suppressing carbon accumulation using CH_4 fuel. This behavior was correlated directly with electrochemical measurements that monitored overall cell impedance as well as voltammetry data. Carbon accumulation was characterized using in situ vibrational Raman spectroscopy, a non invasive optical method capable of detecting as little as μg worth of carbon on electrocatalytic SOFC anodes. Results show that similar amounts of detectable carbon form on both ScSZ and YSZ anodes despite the markedly different electrochemical performances of the two types of cells.

Experimental

Experiments were performed on YSZ-8 and ScSZ-10 electrolyte supported cells purchased from Fuel Cell Materials (www.fuelcellmaterials.com). These membrane electrode assemblies (MEAs) consist of 25mm diameter, 250 – 300 mm thick YSZ-8

(8 mol %) or ScSZ-10 (10 mol %) electrolytes with 50 mm Ni-gadolinium doped ceria (GDC)/Ni-YSZ multi-layer anode and a 50 mm lanthanum strontium manganite (LSM)/LSM-GDC multi-layer cathode. A gold current collecting wire was attached to silver mesh and pasted onto the anode using gold paste. Another gold wire was attached to platinum mesh and passed onto the cathode using platinum mesh. The MEAs were attached to a 2.54 cm diameter alumina tube using alumina paste, and the entire apparatus was placed inside a quartz tube and heated to 675 °C. Air and fuel tubes were fed through a large silicon stopper at the bottom of the apparatus. Gas handling was performed with a manifold using Omega rotometers.

Figure A.1 is representative of the electrochemical characterizations performed with H₂. The ScSZ cells consistently performed better than the YSZ cells with maximum currents that were greater than 50% higher than those measured with standard YSZ electrolyte cells. The higher currents were also reflected in the higher power densities. Noticeable differences were also observed in the impedance measurements. ScSZ-based cells had lower bulk resistances (2.2 vs. 3.5 Ω) and polarization resistances (0.7 vs. 1.1 Ω).

Experimental Procedure

After bringing the assembly to operational temperature (675 °C), the Ni anode was reduced (with H₂ in Ar) and benchmark linear scan voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) measurements were taken with H₂ (in Ar) as the fuel. These experiments were important because data indicated whether or not the anode and cathode were environmentally separated from each other and the voltammetry data were used to establish the currents (relative to I_{max}) of subsequent experiments. Specifically, experimental sequences testing cell

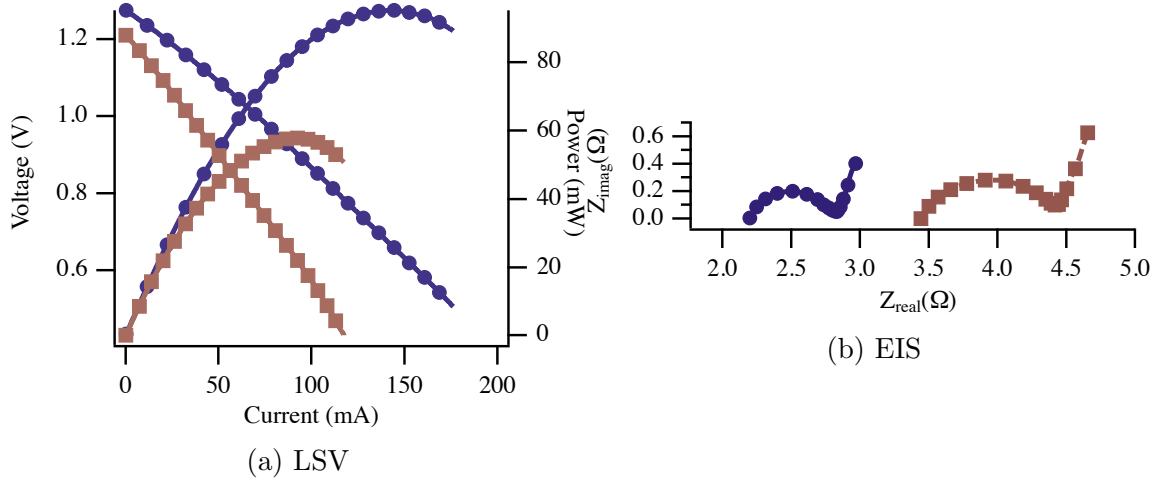


Figure A.1: LSV (left axis) and power curves (right axis) for ScSZ (blue) and YSZ (red, dashed) for a 0.75 cm^2 anode area run under benchmark conditions using H_2 (Left) and the accompanying impedance spectra (at OCV) (Right). All measurements were made at 675°C .

performance under CH_4 were made with the device polarized to draw 25%, 50% and 75% of I_{max} . Additional measurements were made at OCV. The start of an experimental sequence was marked by continuous acquisition of Raman spectra of the anode (10 sec duty cycle) with the cell held at OCV and the anode exposed to H_2 . After approximately 10 seconds, the cell was polarized to 25%, 50%, or 75% of I_{max} . After another 10 seconds, the fuel was switched from H_2 to CH_4 . Following a 10 minute exposure, the MEA was returned to OCV conditions (with CH_4 still present above the anode), and another set of LSV/EIS measurements were made while a higher resolution Raman spectrum was acquired over a larger frequency window. When the Raman scan completed, CH_4 was shut off and polarization was applied to the cell to electrochemically oxidize accumulated carbon. Exposure polarization was randomized between runs to remove the possibility of patterns having affect on the results.

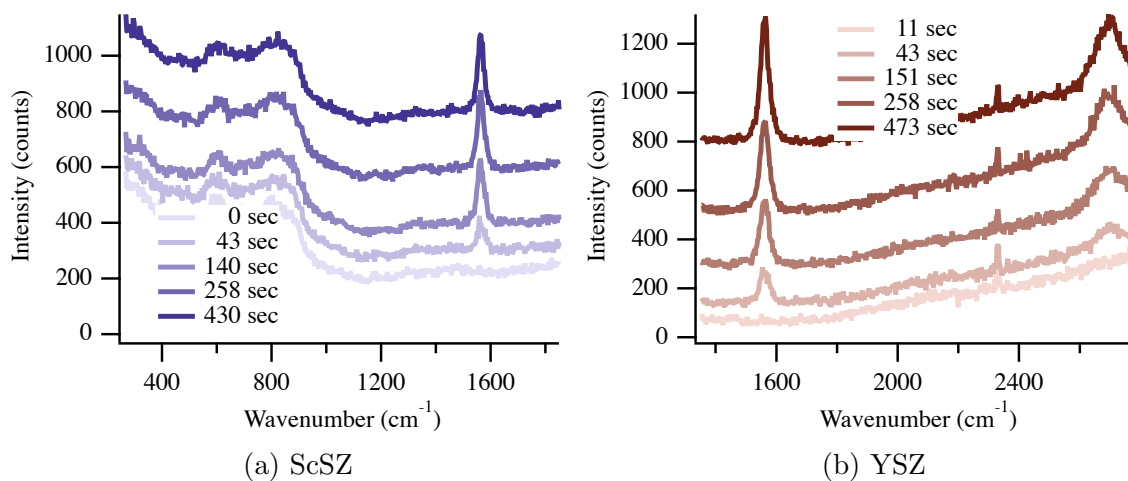


Figure A.2: Typical progression of carbon 'G' peak during a 10 minute CH₄ exposure at 25 SCCM and OCV with a ScSZ electrolyte. (a) Carbon progression with a YSZ electrolyte. (b) X-axis range shifted for clarity. Higher graphs indicate longer times.

Results and Discussion

Previous studies have shown that highly ordered graphitic carbon accumulates on Ni based SOFC anodes at temperatures above 650 °C [19–23,28]. Highly ordered graphite has a strong, distinctive vibrational signature (labeled as 'G') in Raman spectra at 1560 cm⁻¹ (at 700 °C) [29]. Disordered graphite characterized by site defects and/or grain boundaries will show evidence of a 2nd feature ('D') in its Raman spectrum at 1360 cm⁻¹. On both the ScSZ and YSZ MEAs tested in these experiments, CH₄ led to rapid accumulation of graphite on a time scale of minutes. (Figure A.2.) The data show a single, strong "G" peak around 1560 cm⁻¹ and the absence of a "D" peak around 1360 cm⁻¹.

Several observations stand out. First, neither cell type shows evidence of disordered graphite. Second, the relative terminal intensity of the G feature is very similar between the two types of cells. Normalizing the G-peak intensity to its

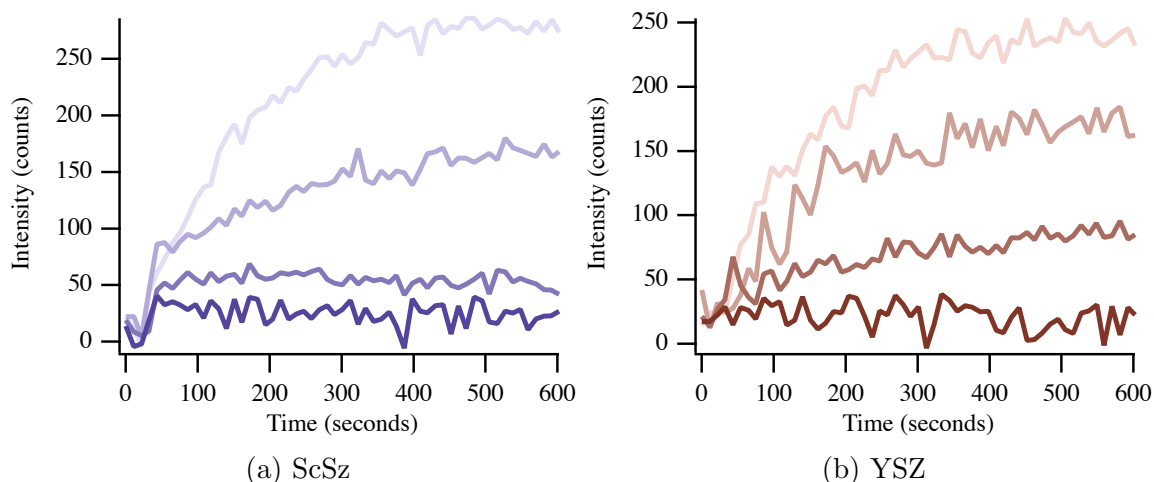


Figure A.3: 1556 cm⁻¹ intensity as a function of time for ScSZ cell (a) and YSZ cell. Light - OCV, Dark - 75% I_{max} (b) Spectrum order is as follows: (Top) OCV, (Middle-Top) 25% I_{max}, (Middle-Bottom) 50% I_{max}, (Bottom) 75% I_{max}

maximum value, timed acquisition spectra can be used to compare rates of accumulation between ScSZ and YSZ based cells. Carbon accumulates most readily on cells with no polarization, while polarizing the cell to 75% I_{max} appears to completely suppress observable carbon formation on both types of cells (Figure A.3). To our knowledge, the data in Figures 3 and 4 represent the first direct evidence of carbon accumulation on ScSZ based electrolyte supported SOFCs. Despite having a higher ionic conductivity, the rate and the amount of carbon formed is unaffected by the change of electrolyte.

Voltammetry and EIS data acquired after exposure to CH₄ showed interesting and reproducible trends. (Figure A.4) At higher cell potentials, LSV traces are very similar to the benchmark LSV data acquired with H₂. However, around 0.6 V both LSV traces reverse direction indicating a depletion of accessible fuel at a polarization of 0.5 V [30]. Exposing a carbon loaded cell to benchmarking flow of H₂ and running an LSV results in a straight LSV, much like the benchmark LSV

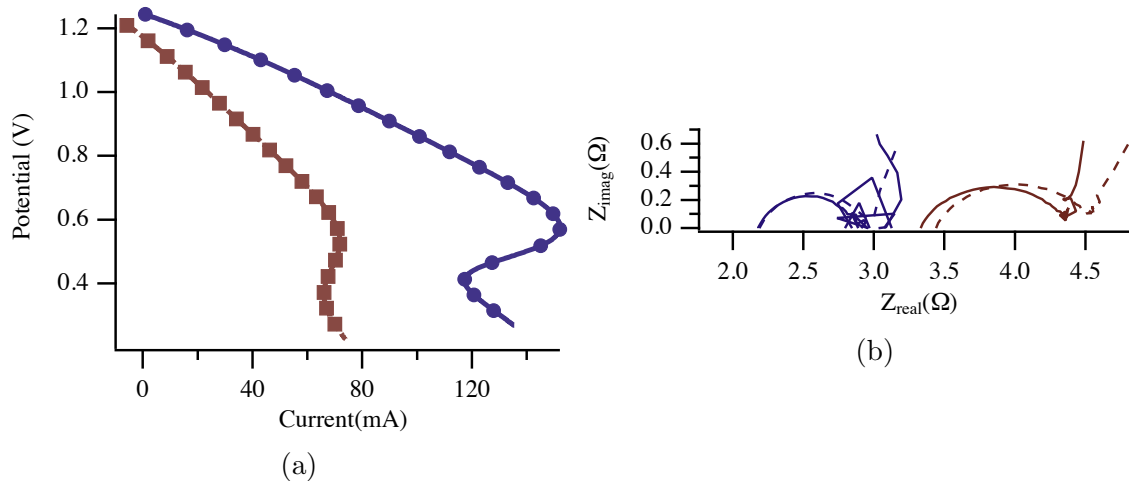


Figure A.4: Carbon on cell LSV curves for ScSZ (blue) and YSZ (red-dashed) (a) and accompanying EIS curves for ScSZ (Lower Ω) and YSZ (Higher Ω) (b). Dashed lines indicate benchmark EIS curves run under H_2 .

data seen previously in Figure A.1. These data indicate that this feature is related to the hindered mass transport of the methane fuel, or the electrochemical oxidation of the deposited carbon. Similarities in the carbon accumulation between ScSZ cells pose an interesting dilemma. We expected that the higher oxide flux in the ScSZ cells would reduce carbon accumulation. Under the conditions tested by these experiments, however, both types of cells show similar susceptibilities to carbon accumulation despite significant differences in each type of cell's electrochemical performance.

Although ScSZ electrolyte composition did show evidence of an expected reduction of R_{Bulk} and enhanced power densities, both Raman and electrochemical data show that both ScSZ and YSZ cells degrade in a similar manner. Average power for ScSZ cells was about 21 mW/cm^2 more than the YSZ cells, which was to be expected [31]. A summary of electrochemical data is reported in Table A.2. Degradation of the cell became apparent following repeated cycles of carbon

Electrolyte	$I_{\max}$ mA/cm ²	R_{bulk} (Ω)	R_{pol} (Ω)
11 ScSZ	54	3.41	0.08
7 YSZ	33	2.24	0.10

Table A.2: Electrochemical properties of ScSZ and YSZ SOFCs.

exposure and removal. The EIS traces show a slight expansion of R_{pol} indicating a loss of catalytic activity of the Ni in the anode. (Figure A.5) $I_{\max}$ decreased with each cycle and rate of degradation seemed to increase with repeated cycles of carbon exposure. Previous studies have shown that after many oxidation-reduction cycles, nickel in the anode undergoes structural changes and loses catalytic activity. [31–33].

ScSZ remains an attractive material for use in high temperature electrochemical applications. SOFCs designed with ScSZ offer higher power densities as well as more physical strength with no more disadvantages than traditional YSZ. ScSZ also has higher ionic conductivity at much lower temperatures, leading the way into intermediate temperature SOFCs. (IT-SOFC) Lowering the temperatures at which SOFCs operate has many advantages, most of which involve less expensive materials and setups, as well as increased longevity for setups and cells alike. However, the initial studies described in this work suggest that SOFCs using ScSZ-based anodes may not be any less susceptible to carbon accumulation when hydrocarbon fuels are being used. ScSZ-based cells appear to be similarly susceptible to coking and subject to similar degradation mechanisms as their less expensive YSZ counterparts.

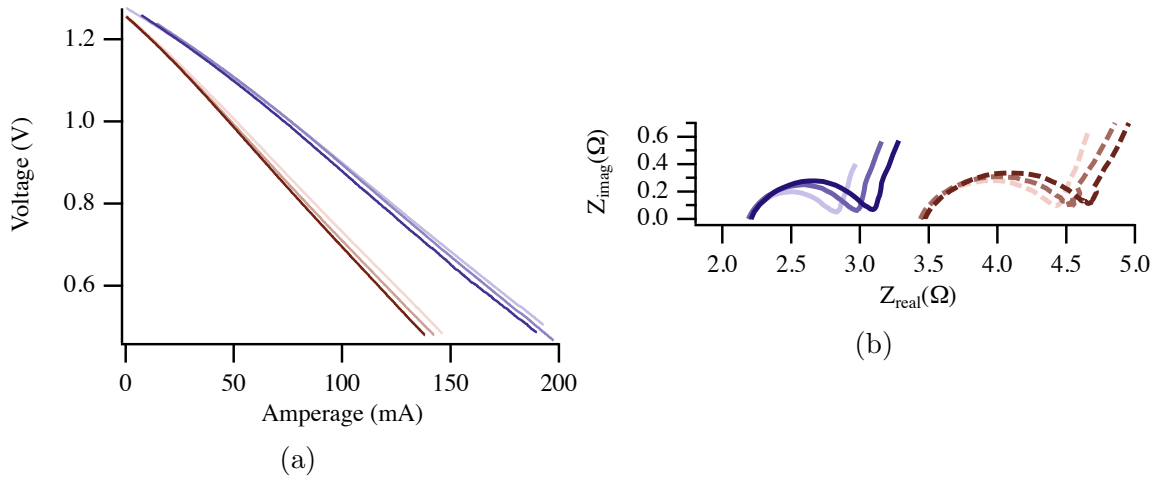


Figure A.5: LSV curve showing lower maximum current as cell degrades (Light-Top - New Cell, Dark-Bottom - Degraded Cell) for ScSZ (blue) and YSZ (red, dashed) (a). EIS curve showing the expansion of the main feature indicating a loss of catalytic activity of the nickel for ScSZ (b) and YSZ (red-dashed). Expanding curve and darkening color indicates more cell degradation. (b)

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APPENDIX B

SOFC ASSEMBLY WITH CONCURRENT ELECTROCHEMISTRY AND
RAMAN

Introduction

Using optical spectroscopy to monitor SOFC anode chemistry provides details about operational mechanisms not available when using electrochemical techniques alone. However, developing a scientific rig capable of providing optical access while heating the cell to operational temperature and keeping anode and cathode chambers gas tight is a compelling challenge. Any scientific apparatus for solid oxide fuel cell (SOFC) analysis also needs to allow for electrochemical access. Most commercial assemblies utilize clamshell furnaces that clamp around a SOFC held in place by two tubular ceramic pieces that use pressure to provide gas separation between anode and cathode. Electrochemical connections are run through ceramic tubing or are achieved by way of conductive and nonreactive meshes that press against the anode and cathode surface. Designing an optically accessible SOFC rig is considerably more complicated due to the very high temperatures involved and sensitive optical components. Optical access allows for molecularly specific information to be acquired in order to identify mechanisms responsible for SOFC operation and degradation. While degradation can be and is observed using electrochemical techniques, any mechanisms proposed from such experiments remain speculative at best. The many difficulty in designing a rig capable of optical access begin with heat management. The fuel cell can no longer be placed in the most temperature stable center, hot section of a large furnace and must be placed at the very edge necessitating hotter furnace temperatures to achieve the same cell temperature. The heat lost through the optical window radiates directly up into the objective used for optical spectroscopy, necessitating active objective cooling. Super long working distance objectives exist, but considering the temperature swings experienced in these environments, it makes practical sense to use less expensive

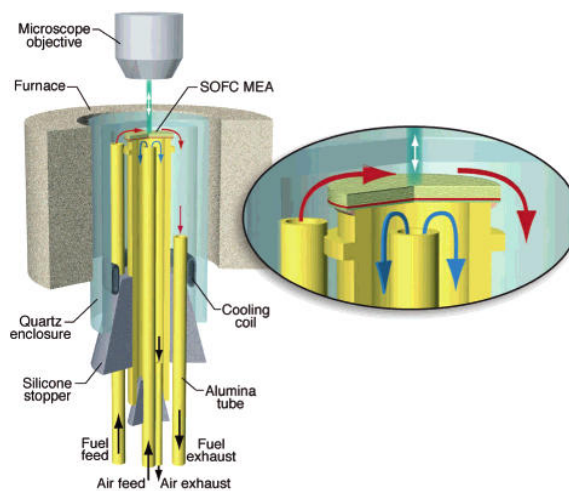


Figure B.1: Schematic for paste based optically accessible setup dubbed ‘Rocket’.

optics with shorter working distances. In order to accommodate this, the window must be placed as physically close to the fuel cell anode as possible, leaving little room for gas handling and electrical connections. The first generation assembly used for operando optical spectroscopy in SOFCs utilized a long alumina tube (25 mm diameter) inside a quartz (40 mm diameter) tube. The entire assembly is then placed inside a tube furnace. (Figure B.1) The open end of the quartz tube was sealed with a large silicon stopper with holes for electrical and fuel connections. Gold wires used for electrical connections hang down alongside the large alumina tube and out through the stopper. A smaller alumina tube was pasted alongside the main tube to direct fuel to the anode and a similar small tube was placed inside the large tube to bring air to the cathode. An optical rig above the furnace/cell holder directed the laser into an objective attached to focusing stage. The Walker Lab at the University of Maryland and later Montana State University pioneered this setup and used it to study carbon accumulation on SOFC anodes. The rig was colloquially named “Rocket” due to its appearance.

Rocket Advantages

Rocket's large furnace makes for facile temperature control of the fuel cell. The furnace has sufficient output to allow the cell to operate at temperatures as high as 900 °C. The large furnace makes the entire rig extremely stable in terms of temperature, allowing for operation for days at a time with no fear of furnace failure. The main tubes of the devices are made of non-conductive alumina, eliminating device lead shorting and subsequent damage to the potentiostat. The physical separation of the furnace from the cell fixture is also prevents shorting issues. Despite these advantages and stability of the Rocket setup, usability improvements drove the design and production of a completely different type of optically accessible SOFC rig named "SOFC Assembly with Concurrent Electrochemistry and Raman" or "SAwCER" for short.

Design

The requirements for a SOFC test rig capable of rapid heat-up and cool-down and one that placed less mechanical stress on the MEA required a new design included that accounted for new geometric, material, gas flow, and temperature restrictions.

Geometric Requirements

Operation on the stage of a Renishaw In-Via Raman microscope system was the main design goal for SAwCER. An internalized setup would not require external optics or large amounts of laser table space. Designing a 700 °C rig for operation on the stage of the microscope while protecting the microscope from thermal damage was a primary challenge. Fortunately, microscope construction consisted of cast iron or aluminum with few plastic parts near the stage area. Optimally, X-Y stage

translation would allow movement of SAwCER. The microscope set a maximum height limit for SAwCER to 10 cm, depending on the objective used.(Figure B.2 Gas handling pipes were routed around the microscope backbone and through the hole in the stage mount. Optimally, cooling the top and bottom of the device would prevent any undue heat from reaching the microscope body or objective. A modular fuel cell support design was used to allow operation using fuel cell diameters between 20 mm and 32 mm, but most commonly intended to work with cells of 25.4 mm diameter. Finally, space for a small furnace was left around the center core of SAwCER to enable fast accurate heating managed by a thermocouple.

Gas Flow Requirements

Gas connections for both the anode and cathode compartments were required for operation however; additional gas connections into the anode were used for a “sweep” gas to prevent coking of the window. Multiple fuel inlets for the anode compartment help spread out the fuel flow, reducing the “single point” effects of only having one fuel inlet.

Temperature Requirements

SOFC operational temperatures range from 650 °C to 1000 °C. Heating such a small apparatus in a localized environment surrounded by fragile optics not capable of withstanding temperatures above 100 °C to a temperature of 1000 °C is not feasible, so a lower cell temperature target of 700 °C was set. A temperature gradient of 600 °C over the small distance from apparatus to optics would still prove a challenge.



Figure B.2: SAwCER assembled and placed on the microscope stage.

Prototype

Figure B.3 shows a rendering of a cross section of SAwCER, followed by a rendering of the outside of the device. SAwCER consists of 5 interlocking 316 stainless steel pieces separated by mica gaskets that are held in compression by 8 bolts around the outside of the top and bottom pieces. The top and bottom plates of the device are water cooled to prevent heat loss to the microscope and objective. The top most of the three smaller pieces holds a gasket for the window and contains all of the gas flow tubes. Twelve tubes encircle the gas manifold with six raised as close to the window as possible for the sweep gas and six as close to the SOFC as possible for fuel delivery and exhaust. Four of the tubes are kept straight to allow electrical connections insulated by ceramic piping and for the thermocouple. Another gasket surface on the bottom of the piece seals the anode chamber around the fuel cell. Unused fuel tubes are capped to maintain anode chamber gas separation. The cell support directly under the SOFC is designed to be simple to facilitate multiple versions to support different sized cells. A gasket under the fuel cell seals the cathode chamber. Under the cell support is the cathode gas manifold with holes distributing air around the chamber and the cathode electrical connection. Finally, the bottom, water cooled piece of saucer contains the fittings for the cathode gas connections. A furnace fits around the inner section of SAwCER below the gas port tubes and inside the compression bolts.

Autopilot Design machine shop in Bozeman was contracted to machine the parts for SAwCER and future designs as well.

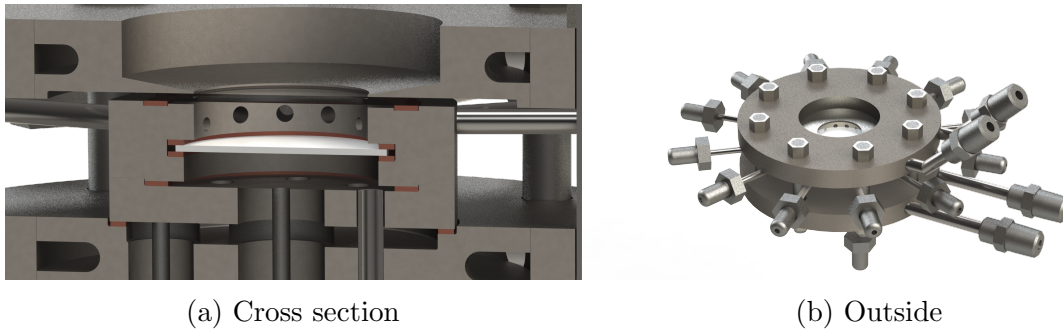


Figure B.3: Renderings of SAwCER.

Assembly and Testing

SAwCER was first assembled with a YSZ chip and tested with simple variac power sources to ascertain the maximum temperature achievable. The small furnace was built using 20-gauge Kanthal resistance wire and alumina paste to a resistance of about $7\text{-}8\ \Omega$. Upon insulating SAwCER using high temperature insulation and cooling the top and bottom shrouds using cooled water, the variac voltage was increased until the furnace current reached 5 A. The temperature stabilized at $\sim 400\ ^\circ\text{C}$ with the shrouds actively cooled and $500\ ^\circ\text{C}$ when the cooling water was removed, far below the $700\ ^\circ\text{C}$ benchmark. Often the wire inside the furnace would melt emphasizing the need for a larger additional furnace to provide increased heating capability. This additional furnace was built to fit around the large upper and lower pieces of SAwCER, with cutouts for the gas flow tubes to fit through the furnace. Figures B.4 and B.5 show SAwCER assembled with inner and outer furnace.

Temperature Issues

Despite the addition of another furnace to the assembly, the highest temperatures achieved with this original design maxed out at $\sim 600\ ^\circ\text{C}$ with

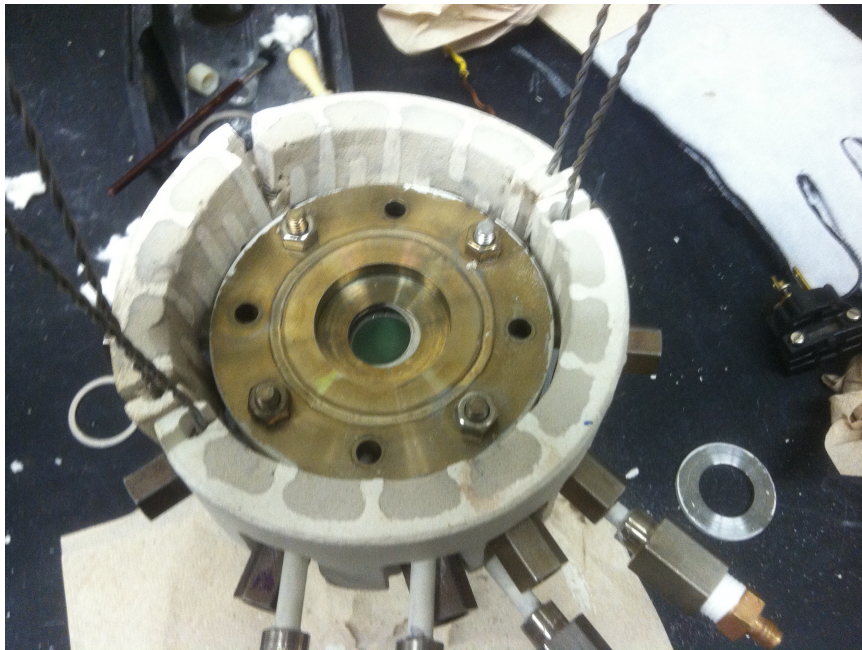


Figure B.4: SAWCER assembled with an inner and outer furnace. Top view.



Figure B.5: SAWCER assembled with an inner and outer furnace. Side view.

maximum current through both furnaces and water chilling the top and bottom of the assembly. There simply was not enough heating power in both furnaces to bring the entire assembly up to temperature while the top and bottom were actively cooled. Removing the cooling allowed for operation of up to 725 °C however, the objective was then in danger being damaged due to the large thermal stress. The objective temperature was manageable below 400 °C cell temperature however, anything above required active cooling. The first attempt at objective cooling consisted of a coil of copper tubing with holes drilled along the inside for airflow. While it did keep the objective cool, it also significantly cooled the cell temperature because of the minimal amount of insulation above the cell itself. Therefore another objective cooling solution was required. Eventually a water cooling shroud for the objective was machined. (Figure B.6) The shroud seals against the smooth outer cylinder of the objective by way of silicon gaskets and water flows directly adjacent on the objective itself. (Figure B.7) This water cooling shroud keeps the objective well below 100 °C when water is flowing through it. Given the small water channels through the shroud, it is imperative to keep the cooling water absolutely clear of insulation particles and other particulates that could cause blockages. If blockages do occur, the experiment is immediately stopped as it is impractical to attempt to remove the objective from the setup at temperature. With the objective water cooled, temperatures of 725 °C were once again achievable.

Other issues

The second main issue with operation of SAwCER was electrical shorts of the furnaces to the metal body of SAwCER. Both furnaces for SAwCER were homemade or modified in the lab, introducing problems one wouldn't expect with professionally constructed furnaces. The shorting issue was partially mitigated by



Figure B.6: Objective cooler mounted to the objective.



Figure B.7: Objective cooler showing seals.

using non-conductive (ceramic) paint on the inner and outer surfaces of SAwCER and the coils of the furnaces. The same paint was used to prevent electrical shorts of the leads around the anode and cathode chambers. The cause of the problem was proximity. Even when properly setup, the coils of the furnace were millimeters away from the gas pipes of SAwCER, eventually spurring a redesign of the gas handling system to allow for stock commercial furnaces to be used for heating. The modular design of SAwCER allowed for a single piece to be replaced instead of the entirety of the rig. The remaining problem with SAwCER operation arose from the AC voltage used for the outer furnace and steel body of SAwCER. SAwCER effectively acts like a secondary winding or the iron core of a transformer and will cause the leads of the cell to have a measurable AC voltage at 60 Hz. This effect was readily observed in electrochemical LSV and EIS data. Proper grounding of SAwCER eliminates this problem completely.

Operational differences between Rocket and SAwCER

There are a few operational differences between Rocket and SAwCER that make both setups useful for different types of experiments. The most obvious is that SAwCER is portable, capable of operation on any stage of similar construction. Because SAwCER sits on the stage of the microscope, all of the microscope optics can be used in the normal manner, so brightfield images can be acquired using the camera on the microscope. This has more than one advantage however, because the laser focus can also be observed using the microscope camera, focusing the laser for Raman acquisitions using SAwCER is a simple manner, compared to the external optics used for Rocket. Cell setup and heat up for SAwCER is much quicker, taking only two hours to prepare a cell for an experiment. Experiments using SAwCER can occur the same day one decides to run an experiment. Instead of relying on

pastes that need to be cured in air and in a drying oven, the pressure seals used in SAwCER require no preparation, providing additional advantages other than setup time. The use of a pressure seal eliminates problems caused by different coefficients of thermal expansion for the paste and cell. Paste based setups must be heated and cooled very slowly to prevent cell fractures due to slightly differing coefficients of thermal expansion while SAwCER can be heated and cooled as fast as the furnaces will allow, resulting in a 2.5 hour heat up compared to 12-14 hours for paste based setups, allowing faster turnover and less down time in the case of a failed experiment. Finally, SOFCs removed from SAwCER are fully intact, allowing for easier ex situ analysis. Technical drawings of SAwCER's pieces are included at the end of this appendix for reproduction purposes. (Figures B.11- B.16)

Conclusion

SAwCER is a fully featured, easy to use, optically accessible SOFC test rig that works extraordinarily well for acquiring Raman spectra and electrochemical data from SOFCs operando. (Figures B.8 and B.9) SAwCER offers some advantages over paste based setups in terms of ease of use and experiment throughput. While it cannot reach as high of temperatures as Rocket and is not as stable, it excels at short experiments with fuel cells or materials in at and below 700 °C. (Figure B.10)

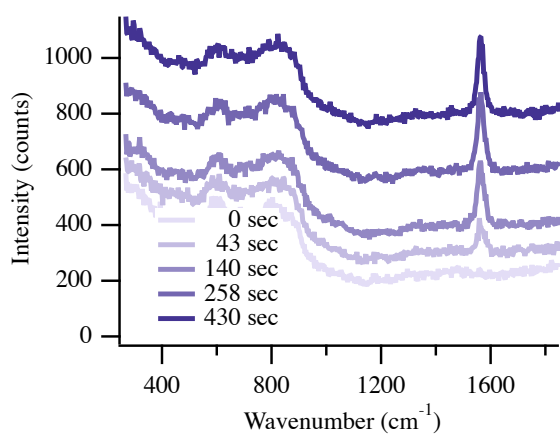


Figure B.8: Operando Raman spectroscopy using SAwCER.

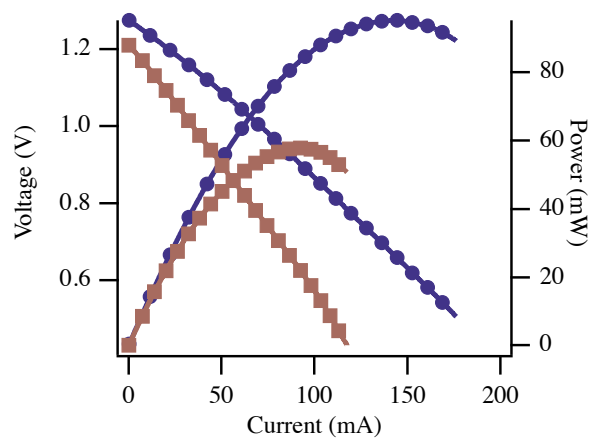


Figure B.9: Linear scan voltammetry acquired with a fuel cell operating inside of SAwCER.

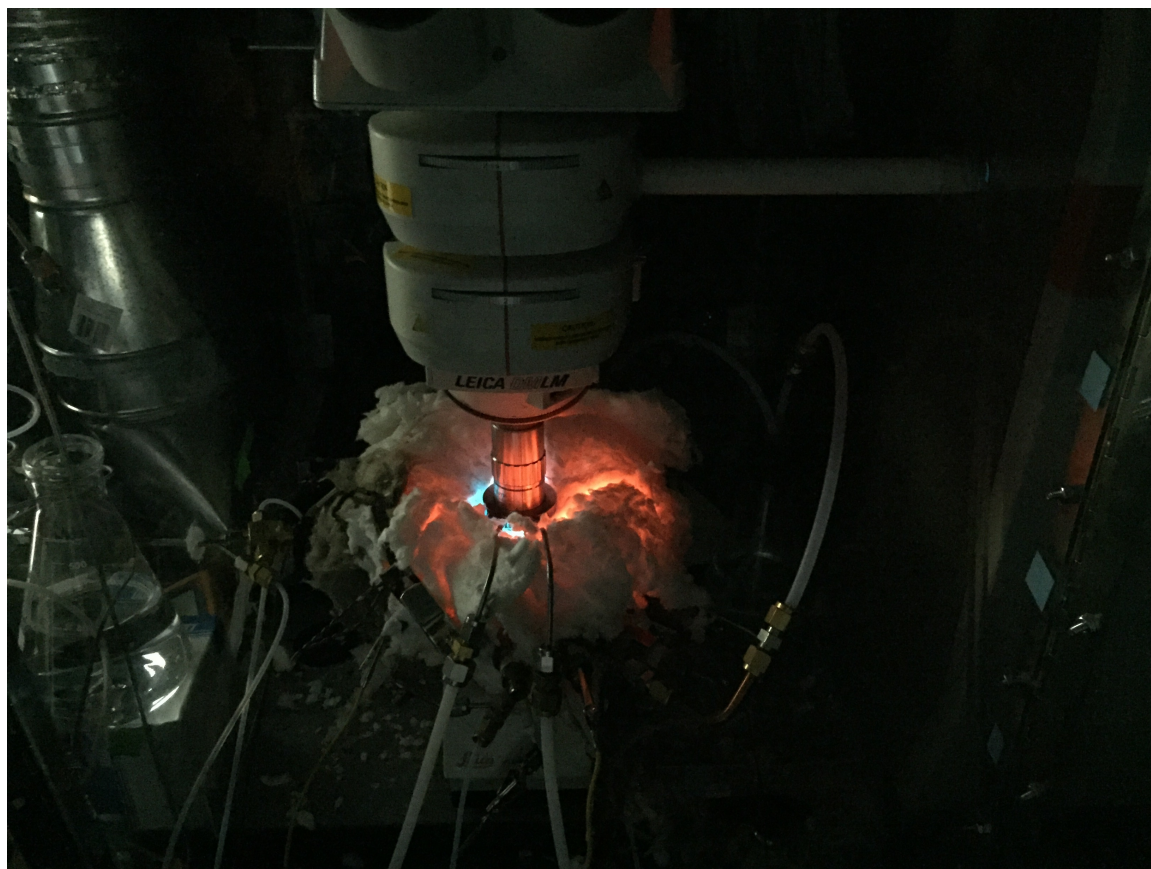


Figure B.10: SAwCER operating on the stage of the Renishaw In Via microscope.

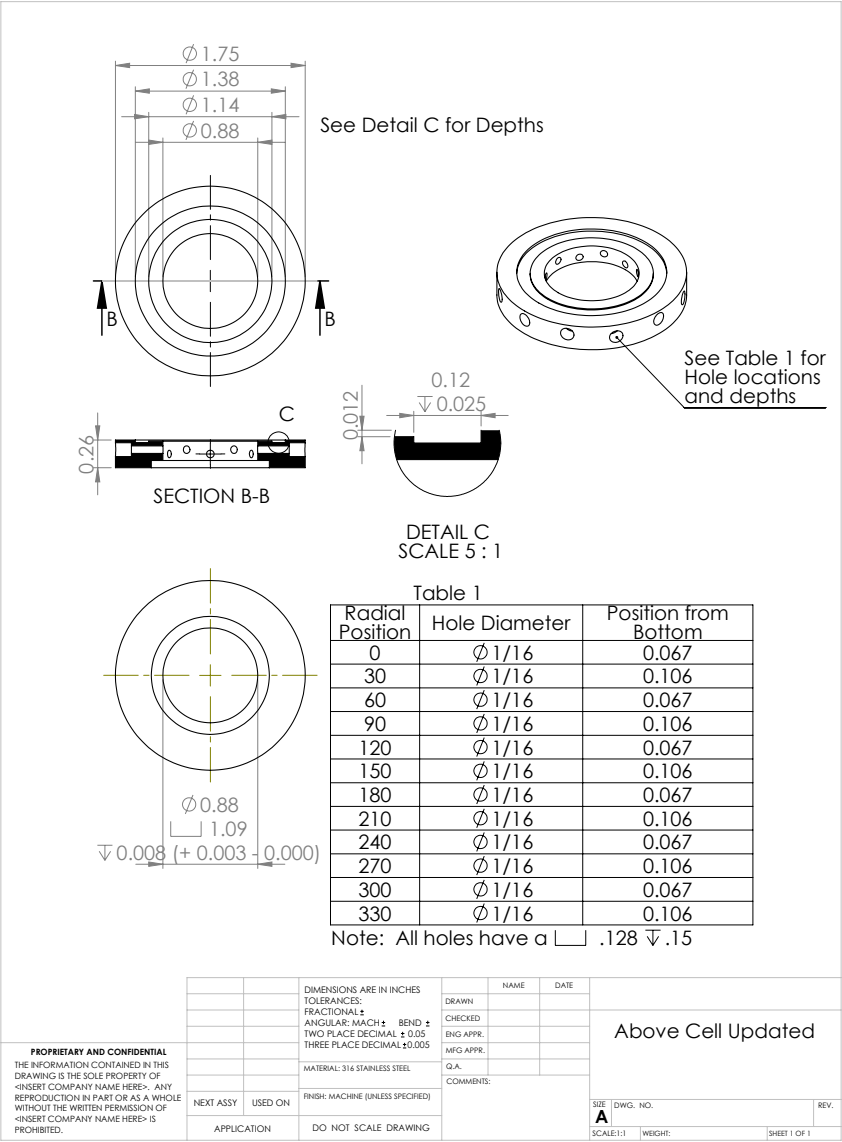


Figure B.11: Technical Drawing for the gas manifold above the cell

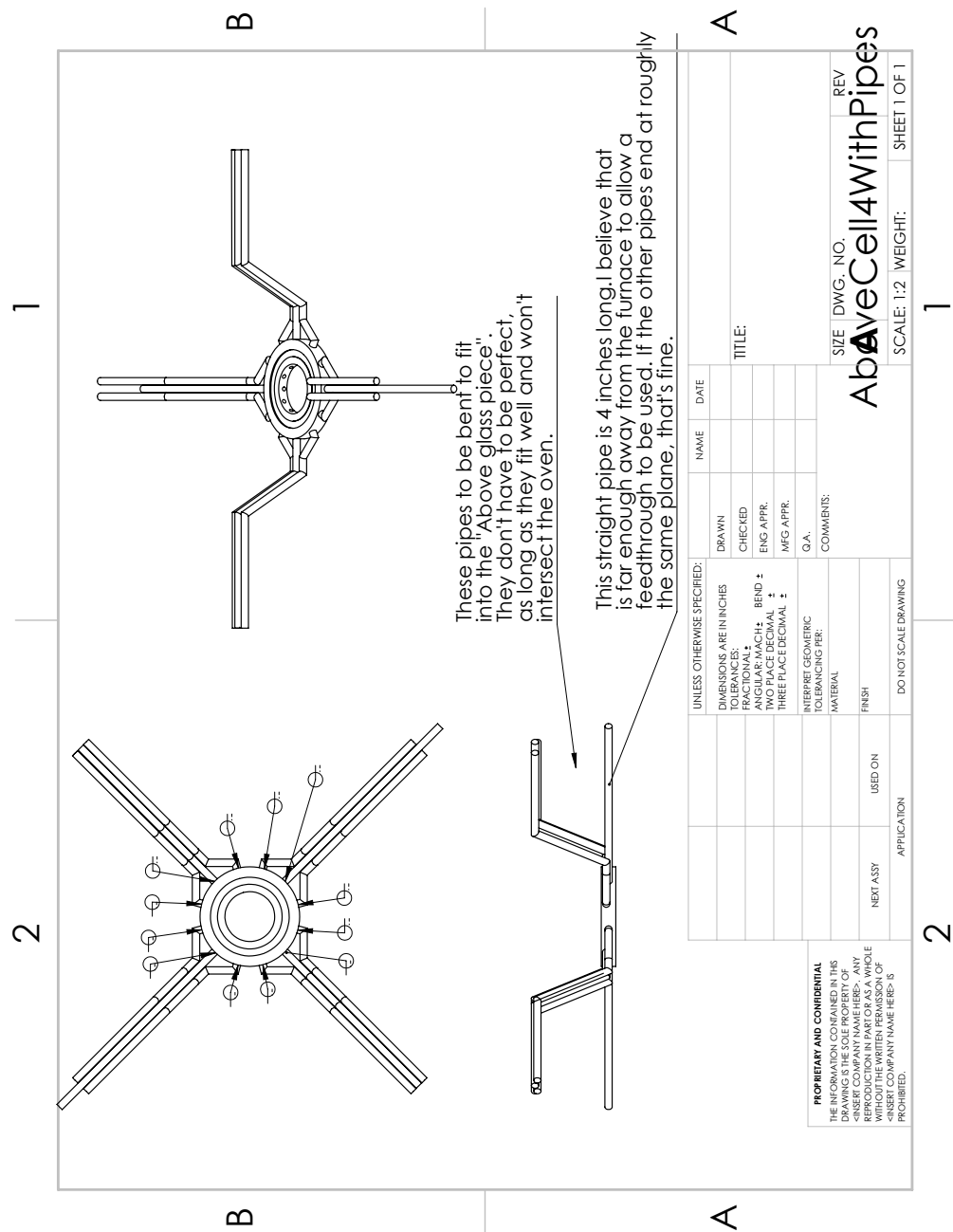


Figure B.12: Technical Drawing for the gas manifold above the cell with pipes and weld marking.

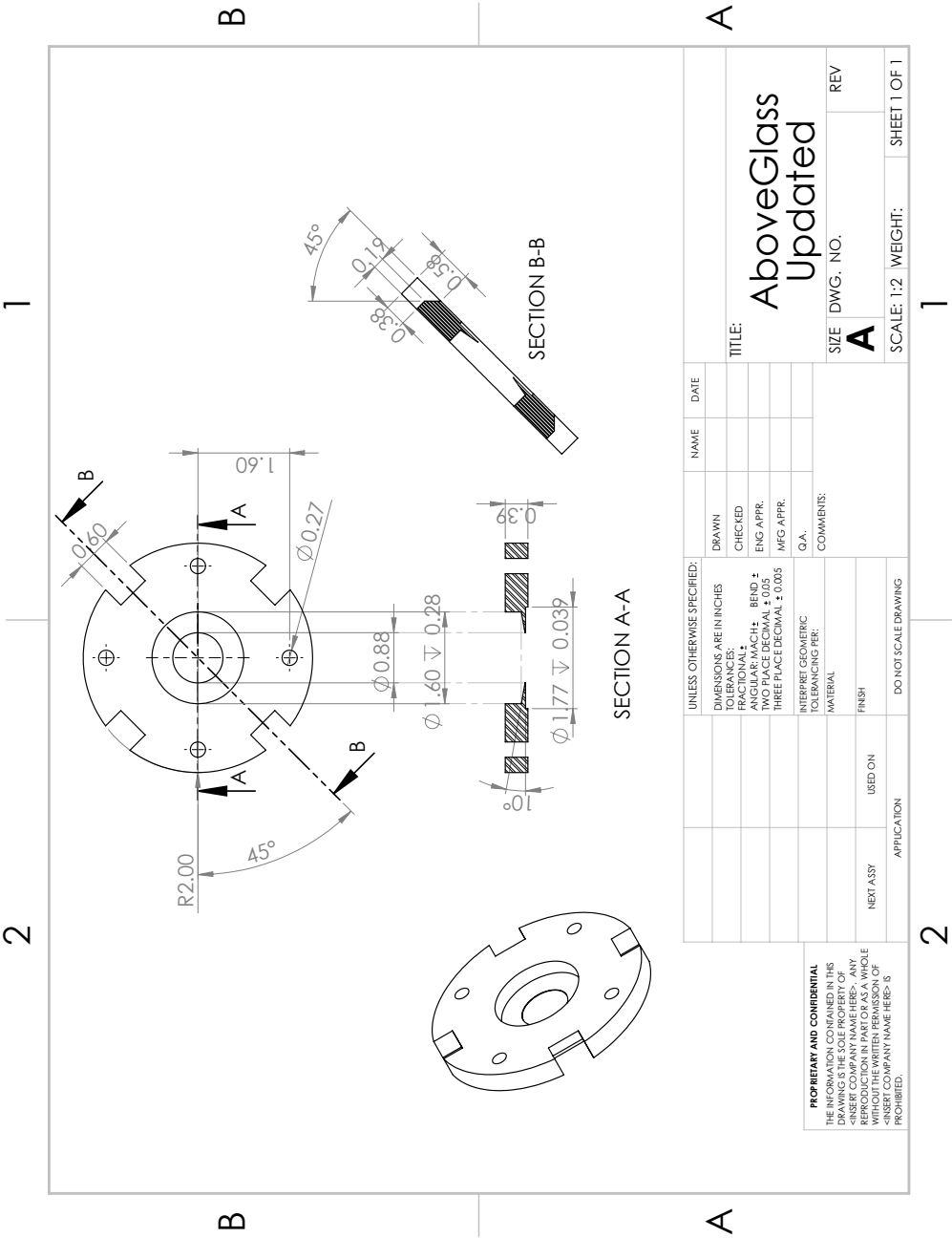


Figure B.13: SawCER upper piece technical drawing.

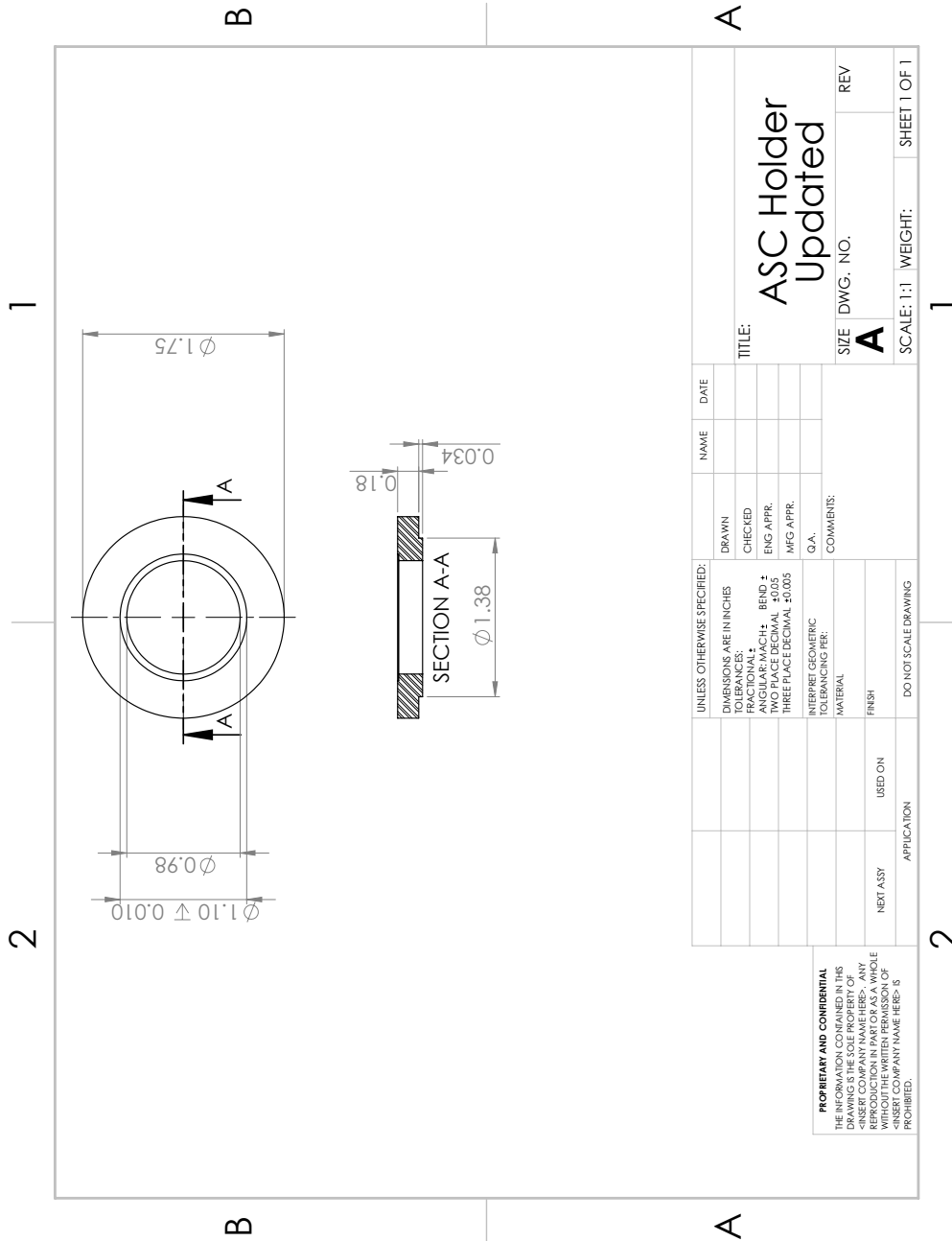


Figure B.14: Cell holder piece technical drawing.

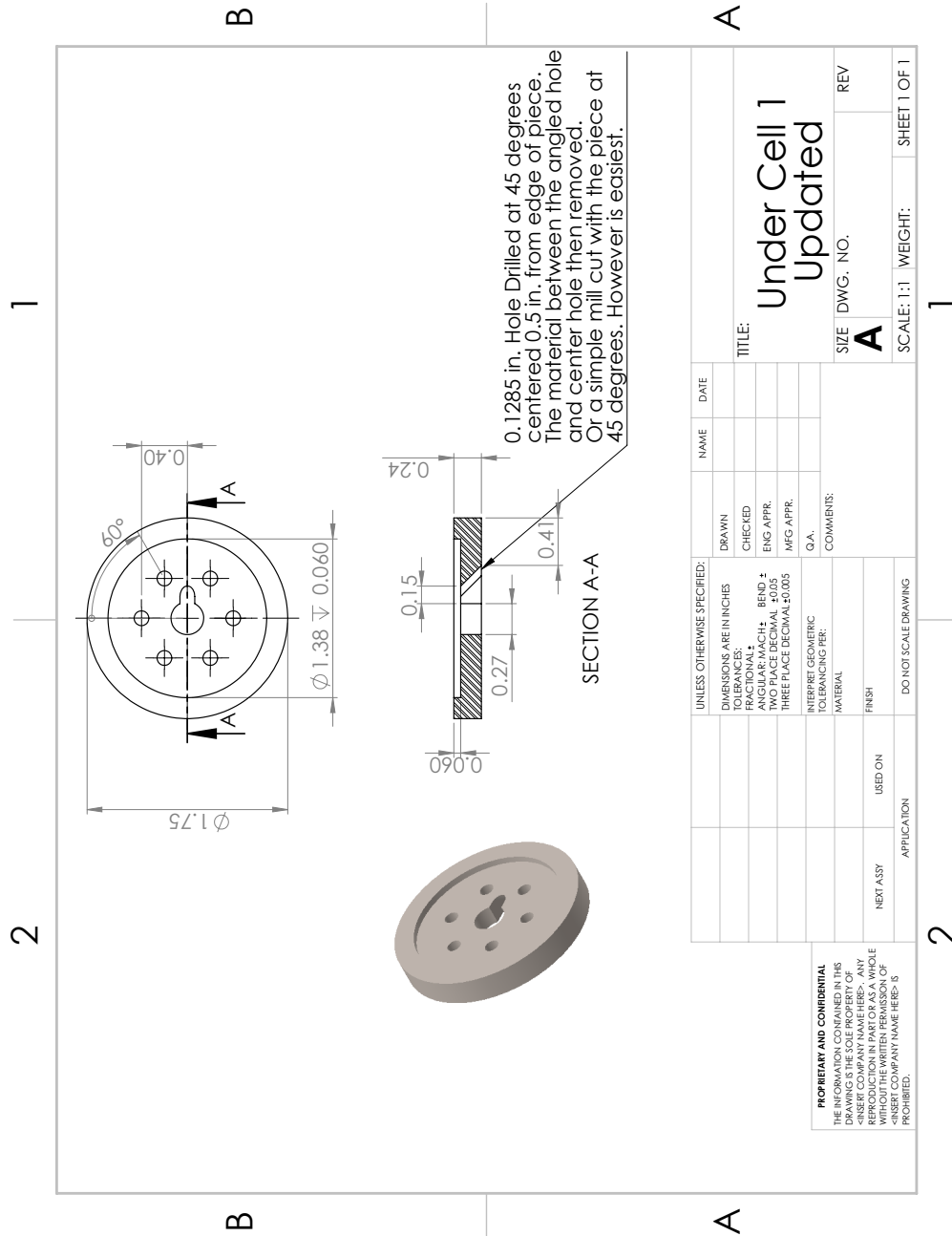


Figure B.15: Lower gas manifold technical drawing.

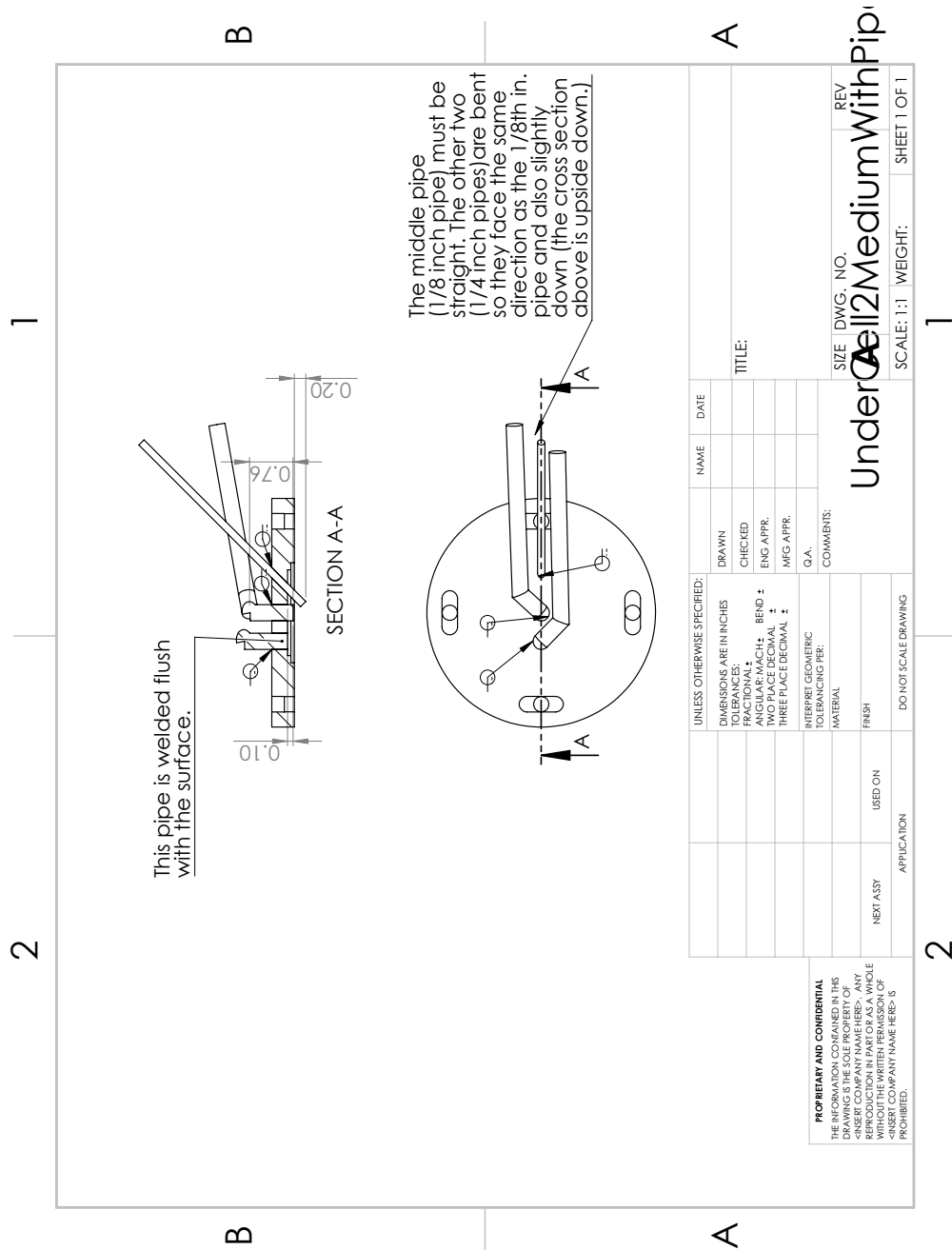


Figure B.16: SAWCER lower piece technical drawing.