In Operando Vibrational Raman Studies of Chlorine Contamination in Solid Oxide Fuel Cells
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Vibrational Raman spectroscopy coupled with voltammetry and impedance measurements was used to explore the effects of chlorine on solid oxide fuel cell (SOFC) performance and durability. SOFC anodes were exposed to 110 ppm dry CH3Cl at 650 °C for up to four hours while intermittently exposing the cell to methane for ten minute intervals. In these experiments Raman spectroscopy was used to monitor carbon accumulation kinetics. Electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV) measurements performed under CH4 following 1 hour of exposure to CH3Cl showed marked degradation. This degradation was less apparent when the SOFC was operated with H2 in the presence of CH3Cl. With methane and CH3Cl, peak power diminished at a rate of 14% per hour. Observable carbon accumulation during CH3Cl exposure became less pronounced over time. Eventually, carbon formation was suppressed completely suggesting that the primary effect of the Cl contaminant was deactivation of the Ni catalyst with respect to CH bond dissociation. SOFC performance with H2 in the presence of CH3Cl remained largely unchanged. Interestingly, these effects of Cl on SOFC performance with methane proved partially reversible as electrochemical performance and carbon accumulation behavior were recovered upon removal of the CH3Cl from the fuel feed.

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Manuscript submitted June 19, 2015; revised manuscript received August 14, 2015. Published August 28, 2015.

Solid oxide fuel cells are electricity-generating devices capable of fuel-to-electricity conversion efficiencies of more than 80% when combined with heating applications.1–3 These efficiencies far outpace even the most modern fossil fuel fired power plants.4 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.5–8 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 deposits, sulfur, chlorine, silicon, phosphorus, and mercury. Each can cause premature degradation of SOFC materials.9–15 Many, if not all, of these impurities have been studied extensively using electrochemical methods. Techniques such as electrochemical impedance spectroscopy (EIS) 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.16–18

Optical spectroscopy has been used extensively to study degradation in SOFCs caused by carbon accumulation.13,15–19 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 CH4 and CO2) at relatively low temperatures (700 °C).20 However, the effects of contaminants on carbon accumulation with cells operating on even the simplest carbon-containing fuels are un-known. 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.21 Many other contaminant combinations exist 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 these resources contain many different contaminants.12,23

Syngas, a popular fuel for electricity production, is produced primarily 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.24 Water scrubbing can only partially mitigate chlorine contamination with up to one third of the original Cl concentration remaining in the fuel stream.20 Even at concentrations as low as 20 ppm, chlorine is responsible for significant degradation of SOFC anodes.25 However, completely removing chlorine contaminants from the fuel stream of an SOFC is both costly and complicated.25,26 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 (CH3Cl), 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 electrolyte.
interlayer and a 50 μm LSM with an LSM-GDC interlayer on opposite sides of the MEA. Small 3 × 3 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 3.0 °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 in addition to the argon 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. EIS spectra were acquired at OCV over a frequency range of 100,000 to 0.1 Hz with an AC amplitude of 10 mV. LSV data were acquired with a sweep rate of 0.1 V/sec. Once cell performance was quantified, methane exposures commenced. Specifically, 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 (under CH4). 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. 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 platform for the experimental studies. While the GDC interlayer of the FCM assemblies can complicate correlation between the electrochemical and spectroscopic data, this architecture (with the GDC functional layer) is representative of SOFC devices produced commercially. Typical EIS and LSV data of an MEA operating on hydrogen at 650 °C are shown in Fig. 1. The sloped LSV (Fig. 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.28 The EIS data (Fig. 1b) show a low bulk resistance (Rbulk) of 2.75 Ω. This resistance is slightly higher than typical experiments that are run at temperatures between 675 °C and 800 °C. 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. Both LSV and EIS show regular, minor performance degradation as evidenced by lower current densities and higher polarization resistances, respectively, when exposed to carbon without CH3Cl present.21 We chose to model the EIS spectra using the 4-element RC circuit shown in Fig. 2.29-32 The first element, Rbulk, corresponds to ohmic resistance of the electrolyte, contact resistances of the setup, the GDC interlayer, and other parts of the anode and cathode not active in the overall reactions. The remaining elements are RC circuits, all of which contribute to the overall polarization resistance Rpol. 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.33,34 Often the electrode activation process elements overlap and are difficult to differentiate, which is why only two arcs are visible in the EIS spectrum (Fig. 1b). Only part of the mass transfer arc is visible, starting at ~1 Hz.

Chlorine has no thermodynamically stable, spectroscopically visible products that form at 650 °C, but chlorine’s effects on Ni-based anodes operating with CH4 are readily apparent in the carbon accumulation data. Fig. 3a shows a Raman spectrum of typical carbon accumulation on the anode of an SOFC. Three peaks are discernable: 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.35,36 Carbon formation kinetics were measured by plotting the “G” peak intensity versus time (Fig. 3b). These traces were acquired at a polarization of 50% Imax as chlorine poisons the cell. Given its low concentration, we assume that carbon accumulation from the CH3Cl is negligible. Before CH3Cl is added to the fuel stream, Ni anodes exposed to CH4 show rapid carbon accumulation (red circles). With the introduction of CH3Cl to the fuel stream, accumulated carbon becomes much less stable. At only 29 minutes of exposure to CH3Cl,
Figure 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 CH₃Cl for different amounts of time. The red circle and square traces were acquired before and after CH₃Cl exposure, respectively.

Figure 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.)

the maximum carbon signal intensity from CH₄ drops to less than half of its early-time, maximum signal. (blue triangles) The carbon signal intensity continues to drop as the chlorine exposure is prolonged, and eventually (after ~174 minutes of CH₃Cl 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 (Fig. 4a). Halting the CH₃Cl exposure and allowing the cell to stabilize under hydrogen or argon led to partial recovery of performance. The first exposure to CH₄ after the CH₃Cl had been removed resulted in observable carbon accumulation with absolute intensity at approximately half of that observed prior to CH₃Cl exposure (Fig. 3a). The effects of CH₃Cl exposure on cell performance were more pronounced than the typical degradation generally observed from simple carbon accumulation from CH₄.13

Signs of cell degradation are observed in both LSV (Fig. 4a) and EIS (Fig. 4b). LSV traces from MEAs operating with CH₄ in the presence of CH₃Cl 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 or argon. However, the shape of the recovered LSV differed from the LSV trace acquired prior to CH₃Cl 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 CH₃Cl (Fig. 4b). When the CH₃Cl was removed, R_{bulk} returned to its pre-exposure limit (2.75 Ω) 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 CH₄, benchmark LSV and EIS results run under hydrogen showed very little degradation during the entire duration of exposure to CH₃Cl (Fig. 5). Figure 6 shows the potential vs. time traces of the cell under galvanostatic polarization. Prior to CH₃Cl exposure, cell potential remained constant when polarized. However, polarized cells exposed to CH₃Cl showed steadily diminishing performance. During the early stages of CH₃Cl exposure while operating under galvanostatic conditions, the cell potential decreased in magnitude. This behavior became more pronounced with increasing number of exposures. Eventually, the cell potential passed through 0.0 V indicating that electrochemical oxidation of CH₄ was no longer thermodynamically favorable.32 Similar behavior has been observed for polarized cells in the absence of any fuel13 and assigned to either electrochemical oxidation of the Ni anode or to O²⁻ recombination at the anode (and a corresponding cell potential of ~0 V). However, we believe that neither of these reactions occurs here given the absence of any apparent NiO feature in the Raman spectra. Like the electrochemical behavior and carbon accumulation kinetics, this behavior proved partially reversible following removal of the CH₃Cl and reconditioning the anode with H₂. Nevertheless, a small degree
of irreversible anode degradation was evident in cells that had been polarized in the presence of CH\textsubscript{3}Cl. This degradation was observed as in the form of smaller current densities at similar overpotentials when the post-exposure cell was operated with a clean CH\textsubscript{4} feed.

**Discussion**

Published reports describing chlorine contamination of SOFC anodes have proposed that, like sulfur, 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. However, since nickel chloride species are volatile at operational temperatures, any species that do form will likely sublimate, 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.

The experiments described above suggest much more aggressive degradation (extrapolated to ~15% per hour) when Cl is present with SOFCs operating with CH\textsubscript{4}. Even allowing for differences in exposure conditions, such extreme degradation in so short a time raises the prospect that these effects arise from a cooperative degradation mechanism involving both carbon and chlorine simultaneously. This hypothesis is supported by both the potential vs. time plots (Fig. 6a) and the LSV plots (Fig. 4a). Both experiments show a rapid decrease in performance when the cell is exposed to carbon (in the form of CH\textsubscript{4}) and CH\textsubscript{3}Cl simultaneously, but not when exposed to hydrogen and CH\textsubscript{3}Cl simultaneously (Figs. 4 and 5). Despite the fact that the hydrogen exposures were completed after the methane performance had dropped to very low levels, the cell appeared to be operating normally under hydrogen with little to no performance loss (Fig. 6b). The LSV traces showed similar results, with only small amounts of degradation associated with normal operation being apparent (Fig. 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. Given that metal dusting with carbon occurs on the order single hours and metal dusting with chlorine (and H\textsubscript{2}) occurs on the timescale of days, we presume that the observed accelerated degradation mechanisms when both CH\textsubscript{4} and CH\textsubscript{3}Cl 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. Fig. 4b shows that the both $R_{\text{bulk}}$ and $R_{\text{pol}}$ increased over time. However, upon CH\textsubscript{3}Cl removal and subsequent recovery using hydrogen or argon, $R_{\text{bulk}}$ returns to its pre-poisoned state, $R_{\text{pol}}$, on the other hand, increased by 37% during CH\textsubscript{3}Cl exposure but only recovered 20% of that increase. Typical degradation with clean methane shows an increase in $R_{\text{pol}}$ but not $R_{\text{pol}}$, implying that carbon accumulation via direct CH\textsubscript{4} decomposition affected connectivity between the electrolyte and the anode.
Consequently, the increase in polarization resistance appears to result from chlorine exposure, and this increase in $R_{\text{pol}}$ 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$_3$Cl 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.\textsuperscript{45}

The EIS Nyquist plots presented in Figure 4b show an overall increase in both $R_{\text{C1}}$ and $R_{\text{C2}}$, even after the CH$_3$Cl is removed from the fuel stream. $R_{\text{bulk}}$ showed a marked increase during exposure to CH$_3$Cl. As indicated earlier, $R_{\text{bulk}}$ 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 4b is found by viewing the same imaginary impedance data as a function of frequency in a Bode plot. Figure 7 shows the frequency dependent impedance for a cermet anode.\textsuperscript{24,31} 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$_3$Cl 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.\textsuperscript{45}

Figure 7. Imaginary impedance data plotted against frequency with virgin cell data subtracted from subsequent data to highlight differences in spectra during exposure to CH$_3$Cl early (blue circles), during exposure late (blue upright triangles), and after recovery (red inverted triangles).

Conclusions

Raman spectroscopy coupled with electrochemical methods have been used to study the effects of CH$_3$Cl 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$_3$Cl. 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$_3$Cl had a negative effect on the electrolyte, EIS data show that the irreversible poisoning occurred strictly on the anode of the fuel cell, with $R_{\text{bulk}}$ 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.

Acknowledgments

The authors gratefully acknowledge support for this work from the Office of Naval Research (N000141410326).

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