Yttria-stabilized Barium Zirconate (BZY) Surface Reactivity at Elevated Temperatures

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Abstract.

Material changes in yttrium-doped barium zirconate, $BaZr_{0.8}Y_{0.2}O_{3-x}$ (BZY), were studied using *in-situ* Raman spectroscopy and *ex-situ* XPS analysis. During *in-situ* Raman analysis samples were heated to temperatures of 300-600 °C and exposed to both dry and humidified H_2 atmospheres. At the lower temperatures (300 – 450 °C), a new vibrational peak appears in the Raman spectra during exposure to humidified H_2. The appearance of this feature is reversible, dependent on previous sample history, and is likely the result of the formation of new, secondary phase formation.

Keywords: Raman spectroscopy, ceramic, energy generation, oxidation, perovskites

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Introduction.

As energy conversion strategies evolve to meet an increasing demand for clean, sustainable power production, solid-oxide electrochemical cells have drawn attention for their ability to efficiently convert fuel into electricity (as a fuel cell) or species such as CO_2 and H_2O into high value products including CO and H_2 through electrolysis. While solid oxide fuel cells (SOFCs) have matured to the point where they are now produced commercially, high temperature proton ceramic fuel cells (PCFCs) are a newer technology that has begun attracting interest.[1–4] PCFCs are attractive relative to SOFCs because of the low activation energy associated with proton transport and correspondingly lower device operating temperatures. SOFCs require that oxide anions diffuse from the cathode to the anode through a solid oxide electrolyte - typically yttria stabilized zirconia (YSZ) – and the ~100 kJ/mole activation energy for oxide diffusion requires that SOFCs operate at temperatures of 650˚C and higher.[2] In contrast, the activation energy for proton conduction through PCFC electrolytes is only ~50 kJ/mole[5] and PCFCs can operate at temperatures as low as 300˚C. Additionally, PCFCs have higher conversion efficiencies with hydrocarbon fuels because water is produced at the cathode and does not dilute the anode fuel stream. An added PCFC asset is higher resistance to carbon accumulation due to reverse Boudouard reactions.[2,6–8] Despite these appealing properties, however, PCFC development is limited by uncertainties surrounding the materials used as PCFC electrolytes and electrodes. Specifically, questions about material compatibility and stability under conditions relevant for PCFC operation limit understanding about chemical mechanisms responsible for electrochemical oxidation/reduction as well as charge transport through the electrolyte. These questions must be resolved so that materials can be optimized for PCFC performance and durability and so that discoveries made in the laboratory can be scaled-up to enable commercial production.[2]

The most common electrolytes used on PCFCs are barium based perovskite materials, including yttrium-doped barium zirconate $BaZr_{0.8}Y_{0.2}O_{3-x}$ (BZY) and yttrium-doped barium cerate $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-x}$ (BZCY). These materials exhibit good protonic conductivity under hydrogen atmospheres at intermediate temperatures between 300 and 600˚C.[9–12] Barium cerates exhibit higher proton conductivities but are chemically unstable in the presence of acidic gases (such as CO or water vapor), while the barium zirconates offer greater chemical stability but lower proton conductivities.[11]

Both materials have additional challenges associated with their use as electrolytes including zirconia densification and Ba volatilization. As a result, considerable effort has focused on materials processing in order to minimize sintering temperatures and sintering times.[3,6,13–15] What is less well known is how a material like BZY behaves under conditions commonly encountered in functioning PCFCs. Specifically, at PCFC operating temperatures under strongly reducing or humidified conditions, BZY's composition and structure remains largely uncharacterized. These properties are particularly relevant given that surface segregation and local oxidation states play critical roles in a material's electrocatalytic and charge transport capabilities.[13,16,17] Furthermore, experiments performed on SOFC materials have demonstrated clearly that *in situ* conditions can change material phases and charge/vacancy distributions.[18,19]

In this communication we examine the surface properties of BZY using Raman spectroscopy and *in-situ* operating conditions to provide insight and analysis of this PCFC electrolyte's properties and material changes that occur under reducing and humidified atmospheres. While BZY Raman spectra have been recorded previously, results have been inconsistent,[13,20–22] and a more thorough understanding of how vibrational signals change as temperature and fuel compositions are varied is required to fully relate charge transport properties and reactivity to electrolyte composition. Results presented below show that BZY's surface structure is sensitive to local ambient conditions and to processing history. Specifically, *in situ* Raman data show the appearance of a new vibrational band when BZY is exposed to humidified H_2 at temperatures between 300 and 450˚C. Raman spectra acquired from BZY under dry H_2 and humidified Ar show no evidence of this change. Complementary *ex situ* XPS experiments correlate this new vibrational feature with an increase in Ba oxidation in the material's surface structure that will result either from material segregation or from distortions of BZY's cubic perovskite structure. Together, these complementary findings raise questions about the mechanisms responsible for BZY's ion transport properties in functioning PCFCs.

Experimental.

Commercially purchased BZY ($BaZr_{0.8}Y_{0.2}O_{3-x}$) powder (Fuel Cell Materials) was mixed with 1 wt.% NiO as an added sintering aid. The powder was ball milled and freeze-dried prior to heat treatment at 1200 °C for 8 hours. The prepared powder was then pressed into 1" pellets and heat treated at 1400 °C for 10 hours with a ramp rate of 2 °C/min. Raman spectra were acquired with the final pellets to check for homogeneity. A representative image of the final prepared BZY pellets and corresponding XRD data with assigned Miller indices are shown in Figure 1.

For *in-situ* experiments, 120 mg chips from prepared BZY pellets were heated in a CCR1000 Linkam stage with gas flows of 50 sccm. Raman spectra of the samples were collected using a Renishaw InVia spectrometer coupled to a 488nm Ar-ion laser with 30 second exposure times. Backscattered light was directed though an edge filter with a 150 cm^{-1} low frequency cut off. Initial experiments to test the material's thermal stability involved collection of Raman spectra at every 50 °C from room temperature to 650 °C under an Ar-only environment. For material stability under different gas-phase environments, chips were heated to 300 °C, 400 °C, and 500 °C and exposed to atmospheres consisting of either dry or humidified (3% H_2O) Ar and H_2 for periods of 30 – 120 minutes. In cases where material changes occurred (e.g. 400 °C, humidified H_2) reversibility was determined by repeatedly changing between humidified and dry fuel conditions. During cool-down, Raman spectra were collected every 50 °C under either dry or humidified Ar.

XPS data were collected for chip samples showing a 548 cm^{-1} vibrational feature in the Raman spectrum, and chip samples without. All XPS data were collected using a Physical Electronics 5600 system with SmartSoft XPS software. Survey scans were collected in the range of 0 to 1400 eV. Additional multiplex scans of the Ba 3d, O 1s, Zr 3d and Y 3d peaks were also collected.

Results.

As a candidate PCFC electrolyte material, BZY should be thermally and chemically stable under conditions commonly encountered during operation. This criterion means that BZY should retain its composition and structure at temperatures up to 600˚C and under a host of gas phase compositions including oxidizing and reducing environments with and without steam. Considerable effort has focused on optimizing conditions for sintering BZY electrolytes to prevent barium

volatilization and precipitation of secondary phases above 1600 ˚C, but fewer studies have examined material stability in conditions relevant to PCFC operation. While BZY is known to be more chemically stable than the comparable BZCY electrolyte material, operating temperatures and gas conditions make *in-situ,* composition-specific analysis of PCFC materials difficult.

In situ Raman spectra shown below provide clear evidence that a new material forms on the BZY surface under conditions relevant to PCFC operation. Specifically, when exposed to humidified H_2 between 300˚C and 450˚C, a new feature appears at 548 cm^{-1} on a timescale of ~20 minutes in BZY's Raman spectrum implying some degree of material segregation and/or oxide depletion (SI Figure 1). In this communication, data are shown for samples kept at 400˚C. These changes - detailed below - do not occur at temperatures below 300˚C nor are they observed above 450˚C. Furthermore, these changes also depend on the sample's history. If BZY is exposed first to dry hydrogen (between 300˚ and 450˚C) for more than 30 minutes before the ambient atmosphere is changed to humidified H_2, the reported 548 cm^{-1} Raman feature *does not* appear, nor are changes evident when BZY is exposed to a humidified, inert atmosphere (Ar with 3% steam). When this new material forms, it can be preserved by cooling the sample to room temperature under humidified H_2. Exposure to dry H_2 at temperature causes the Raman feature to disappear on a timescale of ~30 minutes. Complementary *ex situ* XPS spectra suggest that this new feature in the Raman spectrum corresponds to a preferential accumulation of oxidized Ba at the BZY surface.

Figure 2a shows Raman spectra for room temperature BZY and BZY at 400˚C when exposed first to H_2 and subsequently to humidified H_2. All three spectra are dominated by a large, broad feature centered approximately at 720 cm^{-1}. While undoped barium zirconate is known to adopt a cubic Pm3m unit cell, the addition of yttrium forces the material to adopt a tetragonal unit cell with no symmetry-allowed Raman bands expected. Nevertheless, the broad feature observed at ~ 720 cm^{-1} (Figure 2 and SI Figure 2) has been widely observed and has been assigned to defects induced by yttrium addition into the lattice.[20,21] For the BZY samples prepared, this broad feature was observed at all temperatures sampled. The only noticeable difference between spectra is a small but reproducible 5 cm^{-1} shift to higher energies of the 720 cm^{-1} band when the dry H_2 atmosphere changes to humidified

H_2. While one expects to observe a shift to lower frequency as a material heats (due to lattice expansion)[23] the observed blue shift when changing the ambient environment from dry H_2 to humidified H_2 is likely a result material hydration. Similar observations relating blueshifts of Raman frequencies to material hydration have previously been reported in the literature for Ba containing oxides.[24,25]

If BZY is heated to temperature and *first* exposed to humidified H_2, a new vibrational feature appears in the Raman spectrum at 548 cm^{-1} (Figure 2b). This new feature becomes stronger with longer exposure to humidified H_2 and coincides with a stronger red shift and a narrowing of the main BZY peak at ~700 cm^{-1}. When samples were returned to room temperature under humidified H_2, the 548 cm^{-1} feature remains sharp while the ~700 cm^{-1} feature broadens again to its original linewidth. (SI Figure 3). As the sample cooled, the ratio of the 548 cm^{-1} to the main peak at ~ 700 cm^{-1} increased and the fluorescence observed near 1500 cm^{-1} at elevated temperatures disappeared. Taken together, these observations point to measurable changes in BZY structure/composition that depend on exposure history.

The appearance of the 548 cm^{-1} feature required both humidified H_2 and a specific temperature window (300-450˚C). Under both humidified and dry Ar the vibrational feature at 548 cm^{-1} did not appear (SI Figure 4). Exposure to humidified Ar following the appearance of the 548 cm^{-1} feature resulted in a slight intensity drop after 60 minutes (SI Figure 5) further emphasizing that a reducing, humidified environment (rather than an inert humidified environment) is necessary to drive material changes in BZY. The effects of initial humidity were further analyzed by exploring how this reactivity depended on pre-exposure to dry H_2. BZY samples were subjected to long term reduction (> 30 minutes) with dry H_2 at 400˚C and this treatment suppressed appearance of the 548 cm^{-1} band after steam was added to the H_2. This result suggests that dry H_2 passivates the BZY surface. (Here, we acknowledge that the our definition of 'surface' is deliberately ambiguous. Using the 488 nm laser wavelength described above coupled with the given system optics, Raman experiments are expected to have a sampling depth of ~4-6 μm.) If initial exposure to dry H_2 was kept to 30 minutes or less, the 548 cm^{-1} band would eventually appear once the incident atmosphere was changed to humidified H_2

Under these conditions – limited exposure to dry H_2 – the 548 cm^{-1} band's growth and disappearance was reversible (SI Figure 6).

While definitively assigning the 548 cm^{-1} Raman peak remains a challenge, Raman spectra of related perovskites containing Ba suggest that the peak at 548 cm^{-1} is the result of either M-O bending or stretching modes.[26–28] An alternative explanation is that humidified H_2 forces a reconstruction of the BZY surface structure and volatile Ba forms a new surface phase that gives rise to the 548 cm^{-1} band.

Growth of the 548 cm^{-1} band is relatively slow as shown by the kinetics data in Figure 3. The kinetic trace measures the 548 cm^{-1} signal intensity at 30 second intervals. The data show that exposure to humidified H_2 for close to 1200 seconds was required in order to observe measurable signal (> 20-30 counts). After 1200 seconds, the intensity at 548 cm^{-1} continued to increase steadily, leveling off at around 3000 seconds. As mentioned above, in cases where initial reduction with dry H_2 was kept to under 1800 seconds, appearance of the 548 cm^{-1} band was reversible. The kinetics of the 548 cm^{-1} removal is shown in SI Figure 7. Similar to the kinetics of the peak appearance, the kinetics of the peak disappearance shows a steady drop in signal intensity after 900 - 1200 seconds of exposure to dry H_2. Representative data illustrate that at least 30 minutes of exposure to dry H_2 were required before the 548 cm^{-1} peak disappeared completely.

In order to characterize the material changes responsible for the appearance of the 548 cm^{-1} Raman feature, X-ray photoelectron spectroscopy (XPS) experiments were performed using BZY samples that had been cooled under humidified H_2 (and showed the 548 cm^{-1} band at room temperature) and samples where the 548 cm^{-1} band was absent. Figure 4a shows a survey scan representative of both materials, indicating that no unexpected materials or contaminants were present in the either sample. Instead, samples contained features assigned to Ba, Zr, Y, and O. Higher resolution or "multiplex peaks" were acquired for the main Ba, Zr, Y, and O, (Figure 4 and SI Figure 8). The most revealing data from XPS studies were related to the differences observed in the oxygen 1s multiplex scans. Figure 4b shows that the traditional O 1s singlet was split into a doublet for both types of samples, implying two distinguishable oxide species. The ratios of the two peaks differed by 10% between the two samples; other elements that showed ratio differences between peaks of ~1-2 %.

In samples where the 548 cm^{-1} feature was present the ratio of the higher to lower binding energy peaks was 0.88, while in the sample where the 548 cm^{-1} feature was not present, the peak ratio was 0.78. Analysis using standard reference material databases assigned the oxygen species present at the lower binding energy (~ 529 eV) to ZrO_2 while the peak present at the higher binding energy (~ 531 eV) corresponds to BaO.[29] (We assume that Y-bound oxygen was below detection limits.)

Given the lack of significant changes in the XPS data from the Ba, Y, and Zr 3d multiplex scans of the two samples (SI, Figure 8), we conclude that the oxidation states of these elements are not changing. Rather, we propose that these changes observed in the XPS O 1s data are due either to BaO segregation on the surface and in the near-surface region *or* incorporation of more defects into the BZY perovskite lattice that further lifts the symmetry constraints on allowed vibrational Raman transitions. The higher volatility and a lower melting point of BaO compared to cubic ZrO_2 or YSZ supports a hypothesis that Ba is more mobile and likely to separate into a Ba-rich phase.[30] If and how this process would be enabled by humidified H_2 (but not with dry H_2 or humidified Ar) remains an open question and in need of further study. In samples subject to longer exposures of dry H_2, the XPS data support a picture where the near-surface structure is stable with regards to composition. (After 60 min exposure to dry H_2, BZY appears to be insensitive to the addition of steam. See Figure 2.a) The XPS multiplex scans of the Ba, Zr, and Y 3d electrons shown in SI Figure 8 show slight shifts to higher binding energies for samples exposed to humidified fuels (i.e. sample with the 548 cm^{-1} Raman feature) as expected with more surface oxygen present. While the Ba and Zr spectra show the expected 3d doublet resulting from spin-orbit splitting, the multiplex spectra for Y are not as simple. Multiplex scans spectra of the Y show a band at lower binding energies associated with a reduced surface oxidation state.[18] This surface reduced state of Y remains regardless of sample type.

The findings presented above are suggestive, and represent, to our knowledge, some of the first direct *in-situ* materials specific measurements carried out with PCFC materials. While strong reducing conditions with dry fuel (for > 30 minutes) render the BZY material chemically stable, exposure to humidified fuel changes BZY's near-surface composition or structure. Raman data

coupled with XPS data can be explained either by the formation of a new secondary phase that is likely due to Ba segregation *or* by an increasing number of defects in the BZY perovskite lattice that enables vibrational transitions to become Raman active. How the material changes of BZY under various conditions correspond to material changes in other PCFC electrolytes, such as the BZCY material remains unknown. One expects that the oxidative storage capacity of Ce in BZCY will lead to different surface chemistry compared to BZY. Future work will compare the two types of electrolyte materials and determining whether or not the changes observed in the Ba activity or binding lead to mechanical or catalytic changes when used as a full PCFC electrolyte. Results derived from understanding the connection between intrinsic material properties, structure, and stress tolerance of BZY materials will enhance the understanding of proton conducting ceramics as promising candidates for SOFC type applications.

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Supplementary Material Available: Supplementary Figures 1 – 7 include Raman spectra of BZY at room temperature and temperatures not included in the manuscript. Also included in Supplementary Figures are results from additional experiments detailing spectral changes and kinetics associated with BZY changes resulting from exposure to humidified Ar, humidified H_2, and dry H_2 exposure. Supplementary Figure 8 shows XPS multiplex scans of Ba, Zr, and Y 3d electrons for BZY that has been processed.

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Figure Captions.

Figure 1. Representative image of prepared BZY pellet and corresponding XRD spectrum.

Figure 2. Representative Raman spectra of BZY chip sample exposed to dry H_2 followed by humidified H_2 (a) and chip sample directly exposed to humidified H_2 upon heat up (b). Spectra in (b) show the appearance of a new Raman feature at 548 cm^{-1} related to oxidation of Ba in the lattice.

Figure 3. Kinetics of the 548 cm^{-1} peak appearance illustrating that exposure to humidified H_2 for greater than 1200 seconds is necessary for changes to occur. The gas phase environment above the BZY changed from Ar to humidified H_2 at $t = 0$. Gas residence time in the chamber was < 10 sec.

Figure 4. XPS survey scan (a) and XPS multiplex scan of the oxygen 1s peak (b). Multiplex data shows a difference in the peak ratios of the peaks centered at ~532 eV and ~529 eV for samples with the 548 cm^{-1} Raman feature and samples without.