Discovery and Understanding of the Ambient-Condition Degradation of Doped Barium Cerate Proton-Conducting Perovskite Oxide in Solid Oxide Fuel Cells

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DOI
10.1149/2.0371514jes

Publication date
2015

Document Version
Final published version

Published in
Journal of the Electrochemical Society

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Citation for published version (APA):

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Proton-conducting perovskite oxides such as doped barium cerate and barium zirconate are promising electrolytes for solid oxide fuel cells (SOFCs). Here we report that the typical high performance proton conductor, BaZr0.1Ce0.7Y0.2O3 (BZCY), is prone to physical, chemical and thereby electrochemical degradations as it ages under ambient conditions. This aging effect destroys the electrolyte disk and breaks down the perovskite lattice. Electrochemical measurements indicate degraded BZCY based SOFC suffers from significant performance losses, and various advanced materials characterization results confirm that this degradation of BZCY is exclusively caused by water and CO2 from the surrounding environment. The water molecules catalyze the degradation, initiating and promoting the carbonatation of BZCY. The subsequent reaction with CO2 creates two major phases: BaCO3 nano-rod single crystals and amorphous oxide mixtures. The entire process is visualized via TEM observations, based on which we propose that this occurs via the microcrystalline mechanism. As this mechanism does not incur significant segregations of decomposition products, the aged BZCY powder is easily regenerated by re-calcination. We then study the effects of doping on the stability of BZCY, showing that a higher Zr content obviously improves the aging resistance.

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Experimental

Materials and instrumentation.— X-ray diffraction (XRD) patterns were recorded using a Rigaku Geigerflex powder diffractometer equipped with a cobalt tube. X-ray photoelectron spectroscopy (XPS) was measured using a Kratos Analytical AXIS 165, in which a monochromated Al Ka (hv = 1486.6 eV) source was used under the pressure of 3 × 10–8 Pa. Fourier transform infrared (FTIR) spectra were measured on a Nicolet 8700 spectrometer. Thermogravimetric and differential scanning calorimetry analyses (TGA-DSC and TGA-MS) were run on a TA Instruments SDT Q600 coupled with a thermostat QMS 200 mass spectrometer. The temperature ramp rate was 10 °C min–1. Electrochemical measurements were done using a Solartron 1287 potentiostat with a 1255 frequency response analyzer.

The morphology of samples was characterized using a Keyence VHX-5000 digital optical microscope. Detailed microstructures were obtained using a JAMP-9500F field emission scanning electron microscope (FE-SEM). Transmission electron microscope (TEM) samples were prepared by spreading small amount of powders onto the copper grid, which were then studied under the electron beam using a Tecnai Osiris microscope operating at 200 kV equipped with a high angle annular dark field (HAADF) detector and an electron energy loss spectrometer (EELS). ChemiSTEM X-ray detection technology and Energy-dispersive x-ray spectroscopy (EDS) were used to study the chemistry of different phases, via quantitative analysis and elemental mapping.

Procedure for preparing BZCY nano-powders.— A version of this procedure was published in our earlier work. First, 0.06 mmol citric acid, a chelating agent, was diluted in 100 ml deionized water and the pH was adjusted to 3.6 using concentrated HCl. Then, 0.06 mmol Ba(NO3)2, 0.12 mmol ZrO(NO3)2, 0.072 mmol Ce(NO3)3 and 0.036 mmol Y(NO3)3 were added to the solution. The mixture was stirred for 24 h, and then filtered and dried at 100 °C overnight. The dried powders were refilled into Teflon autoclaves and placed in a muffle furnace at 600 °C for 8 h. After cooling to room temperature, the resulting powders were calcined at 900 °C for 24 h. The calcined samples were then ball milled and reground for 2 h. Finally, the obtained powders were sintered at 1500 °C for 5 h to obtain the final BZCY cathode powder.
water, and then stoichiometric amounts of metal nitrate precursors (0.02 mmol Ba(NO$_3$)$_2$, 0.014 mmol Ce(NO$_3$)$_3$·6H$_2$O, 0.004 mmol Y(NO$_3$)$_3$·6H$_2$O and 0.002 mmol ZrO(NO$_3$)$_2$·4H$_2$O) were added at a 3:2 molar ratio of citric acid: total metal ions. Finally, appropriate amount of NH$_4$NO$_3$ was added to the solution as the fuel and the pH was adjusted to ~8 using ammonium hydroxide. The solution was heated on the hot plate until self-combustion occurred, and the powder was then calcined at 1200 °C for 10 h to give the pure perovskite phase. BaCe$_{0.8}$Y$_{0.2}$O$_3$ (BCY) and BaZr$_{0.8}$Y$_{0.2}$O$_3$ (BZY) were synthesized similarly.

Procedure for electrochemical studies.— In the preparation of the BZCY electrolyte pellet, the calcined nano-powder was grinded in alcohol, dried and pressed into thick discs (~0.8 mm thick, 19.05 mm in diameter) which were densified via sintering in air at 1450 °C for 10 h. To avoid the evaporation of BaO, the disc was fully covered with fine BZCY powders during densification process, which had been proven as an effective way of minimizing the surface depletion of Ba. The membrane electrolyte assembly (MEA) was fabricated via applying Pt paste on both sides of BZCY disc. The natural degradation test, using both BZCY powder and discs, was carried out at room temperature (21 °C) in ambient air with atmospheric CO$_2$ (0.04 vol.%) and minor moisture (RH <35% which equals to ~0.11 vol.% H$_2$O vapor). In the accelerated degradation test, BZCY discs were placed in a sealed quartz tube with either dry or humidified (~0.3 vol.% H$_2$O) gases passing through at a flow rate of 50 ml min$^{-1}$ for 24 h.

Results and Discussion

Degradation of electrochemical performance.— In a typical electrochemical test, the BZCY electrolyte was incorporated into an electrolyte-supported SOFC button cell. The pristine Pt/BZCY/Pt button cells showed reasonable and highly repeatable electrochemical performances. However, this performance worsened for the cells after prolonged storage under ambient conditions. Figure 1 shows a typical example of this performance loss in which three distinct cells have been treated differently. In the polarization and power density plots in Figure 1a, the pristine Pt/BZCY/Pt cell showed a maximum power density of ~180 mW cm$^{-2}$. For another cell (cell I week A) which was stored in a beaker exposed to the ambient air with relative humidity, RH = (35 ± 7)% for a week at 21 °C, the power density dropped to ~160 mW cm$^{-2}$. To further evaluate the influence of humidity on the electrochemical performance, an additional control cell was kept in a desiccator for a week at 21 °C (cell I week B, instead of loading desiccant, we added saturated KI solution to keep the relative humidity at 68%). Here, more significant degradation was observed in comparison to cell I week A: the maximum power density decreased drastically to ~90 mW cm$^{-2}$.

Figure 1b shows the corresponding impedance spectra. Compared with the pristine cell, both the ohmic and charge transfer resistances of cell I week A increased slightly and this increase was substantially more noticeable for cell I week B. As the ohmic resistance is simply related with the electrical properties of the cell, we assumed that due to the moisture, new phases with higher resistance formed in both of the cells. Normally, the charge transfer resistance represents the catalytic properties of the triple-phase boundary (TPB). Its growth implied the deterioration of Pt-BZCY interfaces, correlating with the formation of higher resistance phases on the surface of BZCY.

Physical and chemical degradation of a BZCY electrolyte disc.— The electrochemical tests results in Figure 1 show that humidity played a vital role in the degradation of the Pt/BZCY/Pt cell in ambient air. To study the physico-chemical changes further, we ran an accelerated aging experiment on densified BZCY electrolyte discs, using a humidified air feed stream (RH = 100%) for 24 h at 21 °C. The degradation was examined using sequential optical microscopy and FE-SEM. Prior to the humidified air treatment, the disc surface was smooth, with relatively high mechanical strength and no Ba depletion (see Figures 2a and 2c). It was well-densified, with the grain boundaries clearly observed showing no micro-holes or -cracks. But after the exposure (Figure 2b), the disc became extremely fragile, losing its structural integrity completely (it fell to pieces under gentle finger pressure). The FE-SEM image in Figure 2d pertains to the fragments shown in Figure 2b. The microstructure of BZCY has changed dramatically: grain boundaries were blurred, and many rod-like nanostructures appeared, deposited on the surface of much larger particles (see the inset).

X-ray diffraction was used to identify the secondary phases in the degraded BZCY samples and to understand how these formed at
room temperature. The pristine BZCY sample was stable in both dry air and dry CO₂, showing no impurity peaks (see Figure 3). However, when moisture was added to the feed streams, the sample partially decomposed, giving BaCO₃ and CeO₂. As the doping ratios of zirconium and yttrium at the ‘B’ site of the perovskite were only 10% and 20%, respectively, their decomposition products could not be identified through XRD. Equation 1 shows one possible decomposition reaction:

\[
\text{BaZr}_{0.1} \text{Ce}_{0.7} \text{Y}_{0.2} \text{O}_{3-\delta} + \text{CO}_2 \\
\rightarrow \text{BaCO}_3 + 0.7 \text{CeO}_2 + 0.1 \text{ZrO}_2 + 0.1 \text{Y}_2 \text{O}_3
\]  

Since Y₂O₃ is hygroscopic, the final form of the yttrium compound in the degraded sample can vary considerably.²⁹ ³⁰ The yttrium might be present as a hydroxide, a carbonate, a hydroxycarbonate or an oxycarbonate (Equation 2–5). The actual composition of the yttrium compounds in the degraded BZCY sample was characterized using XPS and FTIR (see below). Nevertheless, it was clear that the combination of moisture and CO₂ caused this decomposition.

\[
\text{Y}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{Y(OH)}_3 \]  

\[
\text{Y}_2\text{O}_3 + 3\text{CO}_2 \rightarrow \text{Y}_2(\text{CO}_3)_3 \]  

\[
\text{Y}_2\text{O}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Y}_2(\text{OH})_3(\text{CO}_3)_y \]  

\[
\text{Y}_2\text{O}_3 + \text{CO}_2 \rightarrow \text{Y}_2\text{O}_3(\text{CO}_3)_y
\]

TEM measurements were then carried out to characterize the nanorods formed during the degradation. The rods’ thickness varied between 50–300 nm based on the bright-field image shown in Figure 4a. Moreover, the selected area electron diffraction (SAED) pattern in Figure 4b suggests that the nanorod is a BaCO₃ single crystal viewed from the [110] direction. This assignment was further supported by the dark-field micrograph shown in Figure 4c that was taken from the (002) reflection of BaCO₃ in the SAED pattern. The single-crystal formation was also confirmed by HRTEM (Figure 4d) which shows only one crystallographic orientation. We thus concluded that the degradation of BZCY led to the formation of BaCO₃ single-crystal nanorods.

Subsequently, we ran thermal analyses on both the pristine and the degraded samples (Figures 5a and 5b, respectively). The thermogravimetric analysis (TGA) show that the weight of the pristine BZCY sample was stable up to 1300 °C. The associated 3 wt% weight loss reflected the non-stoichiometric oxygen difference in the lattice at high temperatures.³¹ The smooth DSC curve also precluded major physical or chemical changes. Conversely, the degraded sample showed four stages of weight loss, corresponding to endothermic peaks in the DSC curve. The first, at ca. 100 °C, pertained to water evaporation. The other three stages showed also strong CO₂ signals in the TGA-MS of the effluent (Figures 5b and 5c, the signal was delayed to 400–1220 °C due to retention time). Thus, those weight changes probably arose from the decomposition of carbonates. A control experiment using pure BaCO₃ confirmed that its decomposition temperature was higher than 900 °C, in agreement with published data.³² According to the decomposition temperature reported elsewhere,³³,³⁴ the second and third stages of weight loss are likely due to the two-step decomposition of (hydrated) hydroxycarbonate, Equation 6,

\[
\text{Y}_2(\text{OH})_3(\text{CO}_3)_y \rightarrow \text{Y}_2\text{O}_3 + \text{H}_2\text{O} + 2\text{CO}_2
\]

The presence of yttrium hydroxycarbonate was further confirmed by XPS and by FTIR spectroscopy. Figure 6a shows the yttrium 3d core level high resolution X-ray photoelectron spectra of the degraded BZCY sample, with an overlap of the 3d⁵/₂ and the 3d³/₂ core electrons. The peaks with binding energies of 155.8 eV and 157.7 eV for the Y 3d⁵/₂–3/₂ doublet were assignable to the doped Y in BZCY.³⁵ The other peak pair had a positive chemical shift, implying that the Y atoms have bonded to more electronegative groups. This agreed with the formation of yttrium hydroxycarbonate which was known to have positive chemical shifts compared with yttrium oxide.³⁶ Similarly, in the C 1s spectrum (Figure 6b), besides the adventitious carbon that pertained to water in the effluent (Figures 5b and 5c, the signal was delayed to 400–1220 °C due to retention time), the peaks with binding energies of 285.8 eV and 287.7 eV for the C−O−C and C−O−H at 286.5 eV, C=O, O−C=O and CO₃²⁻ between 288–290 eV,³⁷ all supporting the formation of hydroxycarbonate in degraded BZCY sample.

The FTIR spectra shown in Figure 7 also confirm the presence of carbonate species. In the spectrum of pristine BZCY, the broad band between 3000–3600 cm⁻¹ represented the stretching vibration mode of the water O−H bond. The other notable peak located at ~1400 cm⁻¹ pertained to minor carbonate species, originating from the degradation of pristine BZCY sample during its transfer to XPS chamber. In the spectrum of degraded BZCY, another band attributable to the
Figure 5. TGA-DSC curves of (a) pristine BZCY and (b) degraded BZCY; and TGA-MS curves of (c) degraded BZCY, the CO\textsubscript{2} in the effluent was analyzed by mass spectrometry.

Figure 6. The core-level high resolution XPS spectra showing the yttrium 3d and carbon 1s in the degraded BZCY sample.

Figure 7. FT-IR spectra of (a) the pristine and (b) the degraded BZCY sample.

Figure 8. TEM image of two BaCO\textsubscript{3} nano-rods growing from BZCY matrix. This was confirmed by the elemental mapping data shown in Figures 8b–8e. Interestingly, the analysis showed an yttrium-rich stripe within the nano-rod. This enriched phase was also noticeable in Figure 8a (indicated by the arrow). As neither Ce nor Zr was detected within this square area, this heterogeneity implied an uphill diffusion and segregation of the Y species from the originally uniform oxide. The driving force for this was the chemical potential change during the crystallization of the new compound, yttrium hydroxy carbonate.

Effects of doping elements and degradation reversibility.— To examine the effect of dopants over the stability of BZCY against aging degradation, BZY and BCY samples were also exposed to humidified air stream (RH = 100\%) for 24 h at room temperature. The diffraction patterns shown in Figure 9a reveal that both samples contained BaCO\textsubscript{3} impurities after the treatment. However, the degradation of BCY was much more pronounced. We therefore concluded that (i) yttrium-doped barium cerate, and likely barium zirconate too, was vulnerable to the degradation in humid air at room temperature. This was also supported by the thermodynamic calculations. In fact, zirconate was
widely documented as steam and atmospheric CO₂ resistant at typical SOFC working temperatures,23,24 more work needs to be done to fully understand the origin of the tiny amount of impurities in the treated BZY sample; and (ii) a higher Zr doping ratio slowed down the aging degradation of BZCY.

The diffraction patterns in Figure 9b show that the degradation process is reversible. After 24 h in humidified air, the partially decomposed BZCY powder was not re-mixed or re-homogenized, but directly re-calcined at 1200 °C for 10 h, which surprisingly returned a pure BZCY pervoskite. This full regeneration had important practical implications for SOFC manufacturing, as the high-temperature sintering step during the fabrication can remedy any earlier decomposition of the electrolyte.39

The degradation mechanism.— To understand the BZCY degradation process and mechanism, we must look at how the BaCO₃ nano-rod single crystal formed. Visualization of the compositional as well as the morphological changes of BZCY during the aging provides a powerful way to explore it from nanoscale.40,41 Interestingly, all of the nanorods observed in TEM images (see Figures 4a, 4d and 10a)
had sharply faceted ends and uniform cross-sections. They were extruded from the underlying BZCY matrix, causing the collapse of the perovskite crystals and the formation of a crucible-like structure at the bottom of the nanorod (see Figure 10a). The SAED pattern (Figure 10a, inset) indicates that this crucible was amorphous, and the EDX mappings show that all Y, Zr, and Ce species were constrained within this region. This indicated that, in addition to the formation of BaCO3 single crystals, the decomposition of BZCY also led to the formations of amorphous ZrO2 and CeO2 (cf. the broad and weak peak of CeO2 in the diffraction pattern in Figure 3).

Based on these observations, we suggested that the aging decomposition of BZCY followed a microcrucible mechanism.42,43 In this process, a liquid and a solid phase coexisted: the liquid phase dissolved Ba ions out of the solid matrix, forming a crucible-shaped structure underneath. The new BaCO3 phase then grew as a nanorod with essentially an identical diameter as the liquid spot as shown in Equation 7.

\[
\text{Ba(OH)}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + \text{H}_2\text{O} \quad \text{(7)}
\]

In consideration of the presence of protonic defects in BZCY, the hydroxide might form initially at the oxygen vacancy sites,44 the reaction is shown in Equation 8 following the Kröger-Vink notation:

\[
\text{H}_2\text{O} + \text{VO}^\bullet + \text{O}_\infty \rightarrow 2\text{OH}^\bullet + \text{O}_\infty \quad \text{(8)}
\]

Meanwhile, the extrusion of Ba compound and the formation of extra water (Equation 7) readily caused the dilution of Ba ions in the liquid solution, driving more barium ions underneath to dissolve. The Ba-depleted zone in the underlying BZCY substrate would gradually form a crucible-like structure (see Figure 11b). With the continuous leaching of Ba ions from the BCZY lattice, the perovskite complex oxide would be finally destructed to form a crucible filled of simple oxides mixture. Due to the low temperature, the oxides did not crystallize (cf. the amorphous phase shown in Figure 10a). Accordingly, the microcrucible provided an effective diffusion pathway of Ba ions to the liquid phase, enabling the epitaxial growth of the BaCO3 single-crystal and eventually the nano-rod formation.

Figure 11 shows a cartoon of the degradation mechanism. It is initiated by sorption of water and the subsequent formation of hydroxide liquid solution on the surface (Figure 11a).20 In the presence of CO2, the hydroxide was reacted to give BaCO3, which grew as a nanorod with essentially an identical diameter as the liquid spot as shown in Equation 7.

\[
\text{Ba(OH)}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + \text{H}_2\text{O} \quad \text{(7)}
\]
During the degradation, the liquid phase, interface and underlying solid micro crucible formed simultaneously. This complex dynamic process enabled the morphological alternations of BaCO₃ nanorod. Our TEM results showed two distinct morphologies. The first is shown in Figure 11c representing two joined nanorods, formed either by merging two adjacent microcrucibles or via the formation of a new BaCO₃ nucleation site within the same microcrucible. An example of this morphology with a ‘stepped end’ is shown in Figure 10a. The second is a single long and “fat” nanorod (Figure 11d) suggesting the nanorod can grow in both width and length directions. This can explain the varied diameters of the nanorods in Figure 4a.

In general, the degradation process of BZCY in ambient air at room temperature involved a synergistic effect of CO₂ and H₂O. The key reactions here were determined as the formation of carbonates (see Equation 1), though the subsequent formation of Y₂(OH)₂(CO₃)₂ might coexist (see Equation 4). The doping elements, such as Zr, have been proven to be able to increase the stability of cerate against decomposition. Their segregations near the grain boundary regions and the resulting space charge effect rendered these regions less-vulnerable to the degradation. Accordingly, rather than proceeding from the grain boundary defects, the decomposition started from the bulk cerate grain, where the minor depletion of dopant might occur. This caused intragranular fractures and ultimately the loss of mechanical integrity (cf. the degraded BZCY sample in Figure 2d).

Conclusions

Although the proton-conducting BZCY electrolyte is stable and robust at the high temperatures of SOFC operation, it degraded in ambient air at room temperature. This abnormal process was actually a reaction with CO₂ from the air, and was catalyzed by water. The degradation destroyed the electrolyte disc, which then lost its electrochemical performance. Our results showed that both moisture and CO₂ were needed to start the degradation process. The absorbed water molecules facilitated the formation of Ba ions traps and the growth of BaCO₃ nano-rod single crystals directly from the BZCY surface. This occurred via the so-called ‘micro crucible mechanism’. The decomposition of BZCY also produced amorphous ZrO₂, CeO₂, and Y₂O₃, and presumably Y₂(OH)₂(CO₃)₂ as well. Each degradation cycle released one water molecule, so water was a true catalyst in this remarkable reaction. Interestingly, the decomposition was fully reversible upon calcination at 1200°C. Nevertheless, to avoid electro-chemical performance loss and unexpected additional complexities to the fuel cell system, we highly recommend that fabricated SOFCs containing doped barium cerate and/or zirconate components should be stored in a dry or CO₂-free environment.

Acknowledgments

N.Y., W.W., T.G., J.L.L acknowledge the Strategic Project Grant of Natural Sciences and Engineering Research Council (NSERC) of Canada. Part of this research was supported by the Research Priority Area Sustainable Chemistry of the University of Amsterdam, http://suschem.uva.nl. All authors gratefully acknowledge RIEM project from NSERC-MRS.

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