BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.2-x}$Nd$_x$O$_{3-\delta}$ Proton Conducting Electrolyte for Intermediate Temperature Solid Oxides Fuel Cells

Jie-Yuan Lin$^{1,2}$, Xian-Zhu Fu$^3$, Gui-Hua Zhou$^2$, Jing-Li Luo$^{2,*}$, Karl T. Chuang$^2$, Alan R. Sanger$^2$, Ru-An Chi$^1$

$^1$School of Chemical Engineering & Pharmacy, Wuhan Institute of Technology, Wuhan, Hubei 430205, P.R. China
$^2$Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta T6G 2G6, Canada
E-mail: Jingli.Luo@ualberta.ca

Abstract: The sinterability, conductivity and chemical stability in CO$_2$ atmosphere are compared for a series of doped barium cerate perovskite oxides BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.2-x}$Nd$_x$O$_{3-\delta}$ ($0 \leq x \leq 0.2$) which synthesized using a solid state reaction method. Among the series of electrolytes doped with various amounts of Nd and Y, BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.15}$Nd$_{0.05}$O$_{3-\delta}$ has the optimal combination of sinterability and conductivity, and shows high CO$_2$ resistance. A solid oxide fuel cell using the BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.15}$Nd$_{0.05}$O$_{3-\delta}$ proton conducting electrolyte at 650-700 $^\circ$C efficiently co-produces electrical power and value-added ethylene from ethane.

Key words: Electricity, solid oxide fuel cell, proton conductor, conversion of ethane to ethylene, barium cerate

1. Introduction
Solid oxide fuel cells (SOFCs) have attracted much attention in recent years since they can produce electrical energy with high efficiency and they are more environmentally friendly when compared to conventional electricity generation from fossil fuels. Proton conducting electrolytes have higher ionic conductivity at lower temperatures compared to oxide ion conducting electrolytes, since protons have lower activity energy of transportation than oxide ions. To date, Y doped BaCeO$_{3-\delta}$ exhibits the highest proton conductivity among the reported perovskite oxides [1, 2]. However, Y doped BaCeO$_{3-\delta}$ is unstable in CO$_2$ containing atmospheres, thus limiting its application as electrolyte material for SOFCs [3-5]. Herein we report Zr, Y and Nd co-doped BaCeO$_{3-\delta}$ perovskite oxides as proton conducting electrolytes for IT-SOFC for conversion of ethane selectively to ethylene.

2. Experimental
2.1 Electrolytes preparation
Compounds having the generalized formula BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.2-x}$Nd$_x$O$_{3-\delta}$, where x ranges between 0 and 0.2, were prepared by solid state reactions. Starting materials BaCO$_3$, CeO$_2$, ZrO$_2$, Y$_2$O$_3$, and Nd$_2$O$_3$ were ball-milled in stoichiometric ratio for 24 h. The pressed mixtures then were calcined at temperatures in the range from 1100 $^\circ$C to 1400 $^\circ$C for 10 h to determine the optimum temperature. After a single perovskite phase was obtained, the resulted materials were ball-milled again for 24 h, pressed at 5 t in$^{-2}$ in a stainless steel mold to form discs, and sintered at 1500 $^\circ$C for 10 h with heating and cooling rates of 1 $^\circ$C.min$^{-1}$. Then gold paste was screen printed onto each side of polished pellets, calcined at 900 $^\circ$C for 30 min to obtain membrane electrode assemblies (MEA).

Instead of gold, platinum paste was used to prepare porous electrodes on proton conducting electrolytes of MEA for SOFC performance tests, as Pt is an active catalyst for conversion of ethane to ethylene and reduction of oxygen.

2.2 Characterization of electrolytes
The phase structure and the crystal lattice parameters for each electrolyte were determined at room temperature using a Rigaku Rotaflex powder X-ray diffractometer (XRD) with CuK$\alpha$ radiation. The morphology was investigated using a Hitachi S-2700 scanning electron microscopy (SEM).

The proton conductivity measurements were carried out using a Solartron 1287 electrochemical interface together with 1255B frequency response analysis instrumentation.

The chemical stability of sintered electrolytes in CO$_2$ atmosphere was determined using a TA SDT Q600 thermal gravity analysis (TGA) in a CO$_2$/He flow (CO$_2$ = 15 mL.min$^{-1}$; He = 100 mL.min$^{-1}$) from room temperature to 1200 $^\circ$C at a heating rate of 10 $^\circ$C.min$^{-1}$.

2.3 SOFC fabrication and test
The SOFC was fabricated by placing the Pt/electrolyte/Pt MEA between concentric pairs of alumina tubes in a vertical Thermolyne F79300 tubular furnace. After the SOFC reached the prescribed operating temperature, ethane and oxygen were supplied as anode and cathode feed gas, respectively. All the electrochemical tests were performed using a Solartron 1287 electrochemical interface together with 1255B frequency response analysis instrumentation. The outlet gas from...
the anode chamber was analyzed using a Hewlett-Packard model HP5890 GC having a thermal conductivity detector. The ethane conversion and ethylene selectivity were calculated according to the previously reported method [6].

3. Results and Discussion

3.1 Phase structure

Pressed stoichiometric mixtures of BaCO₃, CeO₂, ZrO₂, Y₂O₃, and Nd₂O₃ precursors for preparation of BaCe₀.7Zr₀.1Y₀.15Nd₀.05O₃₋δ electrolyte were heated at 1100 °C, 1200 °C, 1300 °C, and 1400 °C for 10 h in air (Fig. 1). Compared to the samples calcined at 1100 °C and 1200 °C, XRD of samples calcined at 1300 °C and 1400 °C showed only the perovskite phase.

3.2 Sinterability of the doped barium cerate

Figure 2 shows the surface SEM images of BaCe₀.7Zr₀.1YₓNdₓO₃₋δ (0 ≤ x ≤ 0.2) discs after sintering at 1500 °C for 10 h in air. When the Nd content was in the range of 5–15 mol % (mol % corresponds to the cation content in B position), very few pores were observed, and the grains size did not change significantly (12–15 μm). It's reasonable to say that Y and Nd co-doping appeared to improve the sinterability of the samples. SEM showed that the surfaces of Y and Nd co-doped samples sintered at 1500 °C were very dense compared to the samples containing no Y or Nd.

3.3 Conductivity of doped barium cerate

The conductivities of the doped barium cerate in humidified hydrogen atmosphere at temperature in the range 500-800 °C are compared in Fig. 3. Increasing the Nd content in the samples, the conductivity of BaCe₀.7Zr₀.1YₓNdₓO₃₋δ increases first then decreases. At 700 °C, the value of the BaCe₀.7Zr₀.1Y₀.15Nd₀.05O₃₋δ is 29 mS·cm⁻¹, which is the highest among the samples at the same test temperature.

3.4 Stability of the doped barium cerate

It is well known that doped-BaCeO₃₋δ perovskite oxide is unstable in CO₂ atmosphere at elevated temperature because the material reacts readily with CO₂ and so decomposes to ceria and BaCO₃ [9]. Fig. 4 shows the
TGA curves of $\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_{3-\delta}$ (BCY) and $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.15}\text{Nd}_{0.05}\text{O}_{3-\delta}$ (BCZYN) in CO$_2$ atmosphere. When the temperature was above 500 °C there was large weight uptake to a maximum of 10.1 % for BCY. In contrast, there was negligible weight uptake when BCZYN was heated in CO$_2$, showing that Zr doping improved the chemical stability of barium cerate in CO$_2$ atmosphere at high temperature [8].

3.5 Performance of the IT-SOFC

Since $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.15}\text{Nd}_{0.05}\text{O}_{3-\delta}$ demonstrated the best combination of conductivity and sinterability, as well as good chemical stability, it was used to fabricate SOFC with porous Pt anodes. Fig.5 shows the electro-chemical performance of the cell. The maximum power density of the cell was 54 mW.cm$^{-2}$ and the corresponding current density was 146 mA.cm$^{-2}$ at 650 °C. When the operating temperature was increased to 700 °C the maximum power density of the cell increased to 132 mW.cm$^{-2}$ at current density 302 mA.cm$^{-2}$.

Ethylene and electrical power were co-produced by conversion of ethane in the cell. Ethane conversion was 18.7 % at 650 °C, and ethylene selectivity was high to 90 %. The by-products in the anode chamber were mainly methane, with traces of H$_2$, CO and CO$_2$. At 700 °C ethane conversion increased to 38.1 %. However, ethylene selectivity decreased to 89 % and methane selectivity increased. Increased conversion of ethane to methane at higher operating temperatures showed that cracking of ethane increased, in competition with ethane dehydrogenation. Nevertheless, ethylene selectivity was much higher comparing to conventional oxidative dehydrogenation of ethane to ethylene [9].

4. Conclusions

Among Zr, Y and Nd co-doped barium cerate perovskite oxides synthesized using solid state reactions, $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.15}\text{Nd}_{0.05}\text{O}_{3-\delta}$ had the best combination of conductivity, sinterability, and good chemical stability in the presence of CO$_2$. An intermediate temperature SOFC with $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.15}\text{Nd}_{0.05}\text{O}_{3-\delta}$ as proton conducting electrolyte exhibited excellent performance for conversion of ethane selectively to ethylene with co-generation of electrical energy.

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References