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# High-performance $Y_{0.9}In_{0.1}BaCo_3(Zn,Fe)O_{7+\delta}$ swedenborgite-type oxide cathodes for reduced temperature solid oxide fuel cells

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## ABSTRACT

With the goal of improving the electrochemical performance while maintaining good phase stability, the Fe-substituted swedenborgite-type  $Y_{0.9}In_{0.1}BaCo_3Zn_{1-x}Fe_xO_{7+\delta}$  series of oxides have been investigated as cathode materials for solid oxide fuel cells (SOFCs). All the samples with  $0 \leq x \leq 0.8$  were obtained as single-phase oxides with the P31c space group. Both the  $x = 0$  and 0.2 samples were stable after 120 h exposure to 600, 700, and 800 °C, while the  $x = 0.6$  and 0.8 samples showed instability at 700 and 800 °C. The  $x = 0.4$  sample was stable at 600 and 800 °C, but generated a  $BaCo_3$  impurity phase at 700 °C. The reversible oxygen absorption tendency of these materials was found to increase with increasing Fe content. Increasing the Fe content in the range of  $0 \leq x \leq 0.4$  was found to reduce the polarization resistance in the  $Y_{0.9}In_{0.1}BaCo_3Zn_{1-x}Fe_xO_{7+\delta} + Gd_{0.2}Ce_{0.8}O_{1.9}$  composite cathodes, and the  $x = 0.4$  sample was found to have performance superior to that of the well-studied  $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$  (BSCF) cathode in the range of 400–700 °C, making it an attractive cathode candidate for intermediate temperature SOFCs.

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## Introduction

Solid oxide fuel cells (SOFCs) are power generation devices that offer high energy conversion efficiency and fuel flexibility without the need for precious metal catalysts, unlike the low-temperature fuel cells [1–3]. However, SOFCs traditionally operate at temperatures in the range of 800–1000 °C, which presents unique materials challenges and hamper the commercialization efforts. The high operating temperatures require the use of expensive, specialized materials that can withstand the high-temperature environment, which dramatically increases the cost of stack assembly. These

difficulties have generated immense interest in reducing the SOFC operating temperatures, but the traditional SOFC cathode materials offer poor performance at temperatures below 800 °C. Therefore, one of the main areas of SOFC investigation is to develop cathode materials that can operate in the intermediate-temperature (IT) region (600–800 °C) or in the low-temperature region ( $T < 600$  °C) [1–14].

Recently, swedenborgite-type  $RBa(Co,M)_4O_{7+\delta}$  ( $R = Y, In,$  and  $Ca$ ;  $M = Co, Zn, Fe, Ga,$  and  $Al$ ) oxides have been shown to have favorable thermal expansion and electrochemical performance properties in these reduced temperature ranges [8–16]. However, these materials have traditionally been observed to decompose after long-term (e.g., 120 h) exposure

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to SOFC operating temperatures in the range of 600–800 °C, but recent work by our group has shown that these materials can be stabilized through selective substitutions in both the R and M sites [8–16]. One of the most frequently used substitutions is the replacement of Co by Zn as the high concentration of  $\text{Co}^{2+/3+}$  in the tetrahedral sites is thought to be the main source of instability in these materials [8]. However,  $\text{Zn}^{2+}$  with a stable  $3d^{10}$  configuration diminishes the electronic conductivity and the catalytic activity for the oxygen reduction reaction (ORR), degrading the overall electrochemical performance [8].

Previous work with the swedenborgite-type system for SOFC cathodes has shown that a composition of  $\text{YBaCo}_3\text{ZnO}_{7+\delta}$  has good electrochemical performance but tends to decompose at lower temperatures, while  $\text{InBaCo}_3\text{ZnO}_{7+\delta}$  has lower performance but superior low-temperature stability [8,10,12,13]. Recently, our group has shown that a composition of  $\text{Y}_{0.9}\text{In}_{0.1}\text{BaCo}_3\text{ZnO}_{7+\delta}$  is stable at all temperatures, but with an electrochemical performance similar to that of the unsubstituted  $\text{YBaCo}_3\text{ZnO}_{7+\delta}$  cathode [13]. Another frequently used R-site cation is  $\text{Ca}^{2+}$ , which enhances the electrochemical performance, but severely destabilizes the phase and tends to require an increased Zn content to compensate and stabilize the phase [8,11]. Further investigation of the stabilization effect with In substitution has shown that it can successfully stabilize a composition of  $\text{Y}_{0.5}\text{In}_{0.1}\text{Ca}_{0.4}\text{BaCo}_3\text{ZnO}_{7+\delta}$  without requiring an increased Zn substitution [14]. These results suggest that it may be possible to utilize the stability promoting effect of In to reduce the required concentration of Zn, thereby improving the electrochemical performance.

As the octahedral-site stabilization energy (OSSE) of  $\text{Co}^{2+/3+}$  shows a preference for octahedral coordination, it is likely that replacing Zn with an increasing concentration of Co will rapidly destabilize the phase, leading to decomposition at the operating temperatures [5,8]. However, with an OSSE of zero,  $\text{Fe}^{3+}$  is far more stable in the tetrahedral sites, while not drastically diminishing the electronic conductivity and ORR activity unlike Zn substitution. Accordingly, we present here an investigation of the  $\text{Y}_{0.9}\text{In}_{0.1}\text{BaCo}_3(\text{Zn,Fe})\text{O}_{7+\delta}$  series of cathodes with lower Zn contents with the goal of discovering a stable cathode with enhanced electrochemical performance for reduced-temperature SOFCs.

## Experimental methods

### Materials synthesis

The  $\text{Y}_{0.9}\text{In}_{0.1}\text{BaCo}_3(\text{Zn,Fe})\text{O}_{7+\delta}$  samples were synthesized by conventional solid state reaction (SSR) methods. Stoichiometric amounts of  $\text{Y}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{BaCO}_3$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{ZnO}$ , and  $\text{Fe}_3\text{O}_4$  required to produce 10 g of product were mixed with ethanol in an agate mortar and pestle for 1 h, dried, pressed into pellets, and calcined in air at 1000 °C for 12 h [8–14]. The resultant pellets were then ground into powder, pressed again, and sintered in air at 1200 °C for 24 h [8–14]. After sintering, the pellets were annealed in air at 900 °C for 6 h and slowly cooled to room temperature at a rate of  $1\text{ °C min}^{-1}$  [13,14].

The  $\text{Y}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$  (YDC) electrolyte powder was synthesized by the glycine nitrate process (GNP) [17,18]. Stoichiometric

amounts of  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$  required to produce 3 g of product were dissolved in deionized (DI) water with glycine ( $\text{NH}_2\text{CH}_2\text{COOH}$ ) in a cations: glycine molar ratio of 1:1 and heated on a stir plate until a gel was formed. The gel was then heated until combustion and the resultant powder was calcined in air at 600 °C to ensure removal of any remaining organic species [13,14].

The  $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$  (GDC) powders were synthesized by SSR and GNP methods. For SSR, stoichiometric amounts of  $\text{CeO}_2$  and  $\text{Gd}_2\text{O}_3$  required to produce 20 g of product were ball-milled in ethanol for 36–48 h with 1 mol% (metals basis)  $\text{Ni}(\text{NO}_3)_2$  as a sintering aid [19,20]. The mixture was then dried, pressed into pellets, and sintered in air at 1550 °C for 24 h. The GNP process was identical to the synthesis of YDC, but with  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  instead of  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ .

### Materials characterization

After synthesis and annealing, the  $\text{Y}_{0.9}\text{In}_{0.1}\text{BaCo}_3(\text{Zn,Fe})\text{O}_{7+\delta}$  powders were characterized by x-ray diffraction (XRD) with  $\text{Cu K}_\alpha$  radiation. The XRD patterns were analyzed with the MDI Jade program ([www.materialsdata.com](http://www.materialsdata.com)) and refined to calculate lattice parameters.

The long-term phase stabilities of the  $\text{Y}_{0.9}\text{In}_{0.1}\text{BaCo}_3(\text{Zn,Fe})\text{O}_{7+\delta}$  samples were determined by long-term exposure to intermediate-temperature solid oxide fuel cell (IT-SOFC) operating temperatures. The samples were heated at a rate of  $2\text{ °C min}^{-1}$  in alumina crucibles in a box furnace and allowed to dwell at temperatures of interest for 120 h before cooling to room temperature at the same rate. Powders were placed on top of small pelletized platforms made of the same material to avoid reaction with the alumina plates. Three separate tests were conducted at 600, 700, and 800 °C, and the resultant powders were characterized by XRD to determine phase stability [8–14].

The oxygen content and oxidation state of (Co,Fe) at room temperature were determined by iodometric titration [21]. Thermogravimetric analysis (TGA) (Netzsch STA 449 F3) was utilized to determine the change in oxygen content during thermal cycling. TGA data were collected during two consecutive heating/cooling cycles at a rate of  $3\text{ °C min}^{-1}$  from 80 to 900 following a 15 h dwell at 900 °C during the first heating cycle to allow for oxygen contents to normalize [13,14].

### Electrochemical characterization

Composite cathodes were manufactured by ball-milling equal parts by mass of  $\text{Y}_{0.9}\text{In}_{0.1}\text{BaCo}_3(\text{Zn,Fe})\text{O}_{7+\delta}$  and GDC powders in ethanol for 36–48 h [9,13,14]. The composite cathodes were then dried and mixed with an organic binder (Heraeus V006) in a 60: 40 cathode: binder weight ratio to create an ink [13,14]. YDC inks were prepared by mixing the YDC powder with the binder in a 50: 50 ratio without prior ball milling [13,14].

The polarization resistances ( $R_p$ ) of the composite cathodes were measured on 8 mol % yttria stabilized zirconia (8YSZ) electrolyte supported symmetric cells in the range of 400–800 °C by AC impedance spectroscopy using a Solartron 1260 FRA impedance analyzer. The thickness of the electrolyte supports was between 150 and 200  $\mu\text{m}$  (FuelCellMaterials.com). YDC interlayers between the cathode and electrolyte

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