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# Structure, sinterability, chemical stability and conductivity of proton-conducting $\text{BaZr}_{0.6}\text{M}_{0.2}\text{Y}_{0.2}\text{O}_{3-\delta}$ electrolyte membranes: The effect of the M dopant

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## ABSTRACT

$\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_3$  (BZY) may be one of the most promising proton conductors for hydrogen separation membranes and proton-conducting solid oxide fuel cells. Doping strategies have been widely applied to improve the sintering activity and conductivity of BZY ceramics. In this study, the phase structure, sinterability, chemical stability and conductivity of  $\text{BaZr}_{0.6}\text{M}_{0.2}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BZMY) compositions with various M cations of  $\text{Zr}^{4+}$ ,  $\text{Ce}^{4+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$  and  $\text{Gd}^{3+}$  with different ionic radii were comparatively studied. All the rare-earth dopants could improve the sinterability of BZY. As the ionic radii of the dopants decreased, the oxides are more and more stable in the  $\text{CO}_2$  atmosphere. EIS results indicated that a greater ionic conductivity was achieved for BZMY with a larger M dopant. Among the various composites, BZNY and BZCY showed favorable protonic conductivity at 600 °C in a wet 10%  $\text{H}_2$ -Ar atmosphere, with good sinterability and resistance to  $\text{CO}_2$  attack. A peak power density of 153  $\text{mW cm}^{-2}$  was achieved at 700 °C with a fuel cell that contained BZCY as an electrolyte and BSCF as a cathode.

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## 1. Introduction

Fuel cells, which are a type of membrane–electrode assembly that operates on hydrogen and other combustible fuels to generate electric power, could dramatically affect numerous areas related to our daily life, such as the environment, the economy, and energy security [1]. Electrolyte membranes are a key component of fuel cells; they are generally dense and sandwiched between two porous electrodes to function as barriers to prevent physical mixing of the fuel and oxidant and to act as permeable membranes that allow some specific conducting species ( $\text{H}^+$ ,  $\text{Li}^+$ ,  $\text{CO}_3^{2-}$  or  $\text{O}^{2-}$ ) to diffuse through, thus separating the electron flow through an external circuit [2–5]. Among the various types of fuel cells, solid oxide fuel cells (SOFCs), which use pure ionic-conducting oxides as electrolyte membranes and operate at elevated temperatures, are highly promising for power generation from fossil fuels and renewable biofuels with very high efficiency and low emissions. Recently, high-temperature protonic conductors (HTPCs) have also generated extensive attention. Proton-conducting electrolytes were

believed to provide improved power density at reduced temperature and to increase fuel efficiency for SOFCs because of the much greater mobility of protons compared to that of oxygen ions and because the diluting effect of oxidation products in the fuel gas in the anode chamber could be eliminated [6].

In 1981, Iwahara et al. first observed that some perovskite oxides, such as  $\text{SrCeO}_3$  and  $\text{BaCeO}_3$ , exhibited proton conductivity at high temperatures in the presence of water vapor [7]. The partial substitution of suitable rare-earth elements into  $\text{SrCeO}_3$ ,  $\text{BaCeO}_3$ ,  $\text{SrZrO}_3$ , and  $\text{BaZrO}_3$ , such as Ce, Y, Nd, Sm, Yb, In, Eu or Gd, was a general strategy to introduce proton conductivity into the oxides through the creation of oxygen-ion vacancies [8–13]. Some of these materials were later used as hydrogen separation membranes, hydrogen permeation membranes or electrolyte in SOFCs [14–16]. Both experimental and theoretical studies on the effects of B-site dopant cations and their concentration on the conductivity of  $\text{AB}_{1-x}\text{M}_x\text{O}_3$  oxides (A=Ba, Sr and B=Ce, Zr and M=La, Nd, Sm, Gd, Yb, Tb, Y, Tm, Lu, In and Sc) have been reported in the literature [17–21]. Among these proton conductors,  $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$  (BCY) exhibited the highest proton conductivities; unfortunately, BCY was unstable at high temperatures in the presence of  $\text{CO}_2$  and/or steam. Its practical use in hydrogen permeating membrane reactors and SOFCs is consequently limited because, in many cases, the operating atmospheres contain  $\text{CO}_2$  or

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H<sub>2</sub>O. In comparison, yttrium-doped barium zirconate (BZY) exhibited favorable chemical stability in CO<sub>2</sub> and good mechanical strength [22,23]. However, this refractory material requires a rather high sintering temperature (1700–2100 °C) as well as a long sintering time to achieve a dense microstructure. Such a high-temperature calcination could lead to the evaporation of barium, which, in turn, would decrease its conductivity and make the choice of suitable substrate material (anode or cathode) with sufficient porosity after the co-sintering difficult. To realize the practical use of BZY in SOFCs, improvement of the sintering behavior of BZY at reduced temperatures while maintaining its high conductivity and chemical stability is critical.

Solid-state reaction has often been used in the preparation of BaZrO<sub>3</sub>-based proton-conducting oxides. However, the material prepared by this approach requires high-temperature sintering to obtain both a single phase and a dense sample. The use of a conventional solid-state process for the synthesis of doped barium zirconate oxides to obtain products with sufficient phase purity requires that solid precursors be fired at elevated temperature for a prolonged time, such as 1400–1600 °C for more than 10 h, to ensure complete reaction between the solid reactants [24,25]. The sintering temperature can be reduced somewhat through the use of nanopowders obtained from advanced synthesis methods. However, nanosizing the starting powder alone is insufficient to improve the sinterability of BZY electrolyte. To further lower the sintering temperature of BZY, some researchers have recently successfully used sintering aids. However, many additives, including TiO<sub>2</sub>, MgO, MoO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub>, impaired the conductivity of BaZrO<sub>3</sub> [26–29]. In addition to affecting the conductivity, the dopant could also affect the sinterability of the oxides. However, simultaneously achieving high conductivity, high sinterability and excellent chemical stability through the use of a single dopant is difficult. Thus, the use of two or more dopants for the B-site was recently attempted and was found to be an effective strategy for improving the properties and performance of BaZrO<sub>3</sub>-based electrolytes [30–34]. However, a systematic investigation of the B-sites of BaZrO<sub>3</sub> with double cations has not been reported.

In this study, BaZrO<sub>3</sub> oxides with double-cation-doped B-sites and a nominal composition of BaZr<sub>0.6</sub>M<sub>0.2</sub>Y<sub>0.2</sub>O<sub>3-δ</sub> (BZMY) (M = Zr, Ce, Pr, Nd, Sm or Gd) were synthesized using an EDTA–CA complexing sol–gel process and systematically investigated according to their phase composition, sintering behavior, chemical stability and conductivity. The main purpose of this study was to elucidate the relationship between the properties of BZMY and the ionic radius of the dopant (M), thus providing useful guidance for the further development of proton-conducting oxides with improved properties and performance for functional applications, such as membrane reactors for hydrogen separation and SOFCs for electric power generation from fossil fuels.

## 2. Experimental section

### 2.1. Materials synthesis

Powders of the various BaZr<sub>0.6</sub>M<sub>0.2</sub>Y<sub>0.2</sub>O<sub>3-δ</sub> samples with different M dopants (BZMY, M = Zr, Ce, Pr, Nd, Sm and Gd) were synthesized via an EDTA–citrate complexing sol–gel process. Analytical-grade reagents of metal nitrates, including Ba(NO<sub>3</sub>)<sub>2</sub>, Zr(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O, Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, were used as the raw metal-containing materials. Both EDTA and citric acid were used as complexing agents. Taking the synthesis of BaZr<sub>0.6</sub>Ce<sub>0.2</sub>Y<sub>0.2</sub>O<sub>3-δ</sub> as an example, stoichiometric amounts of Ba(NO<sub>3</sub>)<sub>2</sub>, Zr(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O, Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O were first dissolved in deionized water to prepare a mixed solution.

EDTA and citric acid were then added to the solution at a ratio of 1:2:1 to the total metal cations. A proper amount of ammonia solution (41%) was also slowly dropped into the solution to adjust its pH value to approximately 8. With the presence of complexing agents, the solution status was maintained without the appearance of a precipitate during the evaporation of water until the formation of an amber-colored gel, which was pre-fired at 240 °C for 6 h to form a solid precursor and then calcined at 1000 °C for 10 h in air at a heating rate of 5 °C min<sup>-1</sup> to obtain the final product.

### 2.2. Basic characterization

Phase analysis of the various samples was performed by room-temperature X-ray powder diffraction (XRD) using an X-ray diffractometer (model D8 Advance, Bruker, Germany) equipped with a filtered Cu Kα radiation source (λ = 1.5418 Å). The diffractometer was operated at 40 kV and 35 mA within a 2θ scanning range of 10–90° at a step size of 0.02°. To determine the sinterability of BZMY, green pellets were prepared by first pressing the ceramic powders uniaxially at 50 MPa for 1 min; the sintering properties were evaluated by measuring of the relative densities of various pellets sintered at different temperatures for 10 h. The relative densities (compared to the theoretical density) were determined by the Archimedes method using water as the liquid medium. The microstructure of the sintered pellets was observed by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800). The average grain size of the sintered pellets was estimated from the FE-SEM micrographs.

Carbon dioxide temperature-programmed desorption (CO<sub>2</sub>-TPD) was performed to study the chemical stability of BZMY samples against CO<sub>2</sub>. An appropriate amounts of the BZMY electrolyte powders was introduced into a quartz tube and pre-treated in a CO<sub>2</sub> gas atmosphere with a flow rate of 40 ml min<sup>-1</sup> [STP] at 650 °C for 2 h in a home-constructed multipurpose temperature-programmed apparatus. After approximately 0.05 g of treated powder sample with a 40–60 mesh particle size was loaded into a U-type quartz tube with an inner diameter of ~3 mm, pure argon at a flow rate of 15 ml min<sup>-1</sup> [STP] was introduced to the reactor as the carrier gas and the reactor temperature was programmatically increased from room temperature to 930 °C at a rate of 10 °C min<sup>-1</sup>. The effluent gas was monitored by a mass spectrometer (model QIC-20, Hiden, UK). The amount of carbonate formed over the samples after they were treated in a CO<sub>2</sub> atmosphere was calculated on the basis of the CO<sub>2</sub> peak area using SrCO<sub>3</sub> as an external standard. Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption experiments were performed.

Anode-supported, thin-film electrolyte dual layer cells were fabricated via a dual dry pressing/co-sintering technique [35]. The anode consist of 60% NiO and 40% BZMY, Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> (BSCF) was applied as a cathode. The single-cell test was conducted over an in-lab constructed fuel cell test station 3% H<sub>2</sub>O humidified H<sub>2</sub> and ambient air were supplied as the fuel and the cathode atmosphere, respectively. I–V polarization curves were collected by a digital electrometer (Model 2420, Keithley, USA). The conductivity of BZMY and Electrochemical impedance spectra of single cells were measured by an AC method using an electrochemical workstation composed of a Solartron 1260A frequency response analyzer and a Solartron 1287 potentiostat. Two symmetrical porous Ag paste electrodes, which served as current collectors, were deposited onto both sides of polished dense BZMY pellets that had been sintered at 1600 °C for 10 h. Silver wires were attached as current leads. The measurements were conducted under 3% water-humidified 10% H<sub>2</sub>–Ar and dry 10% H<sub>2</sub>–Ar atmospheres from 700 °C to 500 °C at 50 °C intervals. The

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