Properties of Pr and In-doped BaZrCeY-based electrolyte for Proton Conducting Fuel Cell systems

Nur Lina Rashidah Rashid1, Mahendra Rao Somalu1,*, Andanastuti Muchtar1,2, Wan Nor Roslam Wan Isahak3

1Fuel Cell Institute, Universiti Kebangsaan Malaysia, UKM Bangi, 43600 Selangor, Malaysia
2Centre for Materials Engineering and Smart Manufacturing (MERCU), Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, UKM Bangi, 43600 Selangor, Malaysia
3Research Centre for Sustainable Process Technology (CESPRO), Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, UKM Bangi, 43600 Selangor, Malaysia

*Corresponding author e-mail: mahen@ukm.edu.my

Abstract. Proton conducting oxides are potential electrolyte candidates for intermediate-temperature solid oxide fuel cell (SOFC) because of their attractive advantages such as excellent ionic conductivity and moderate activation energy for proton transfer. At present, many investigated protons conducting oxides are BaCeO$_3$ and BaZrO$_3$-based materials. In this study, BaCeZrY-based electrolyte doped with Pr and In was synthesised by microwave-assisted glycine nitrate process. The synthesised powders showed a single cubic perovskite phase without any additional phases and thus have potential application in Proton Conducting Fuel Cell systems.

1. Introduction
Solid oxide fuel cells (SOFCs) are contemplate as optimistic substitute sources of energy production because of their favorable proficiency, hostile pollution emission, and fuel pliable [1]. At present, the major challenge in Solid Oxide Fuel Cell technology is reducing their operating temperature from 1000 °C to 800 °C to reduce fabrication cost and improve lifespan durability. Supersede electrolyte materials from regular oxygen ion conductors with protonic conductors is the other auspicious approach to fulfill the requirements. Compared with oxygen-ion conductors, protonic conductors are better potential electrolyte materials of SOFCs at intermediate temperate of approximately 400–700 °C because of their attractive advantages, such as high ionic conductivity and low activation energy for proton transfer [2, 3]. Thus, proton-conducting electrolytes possess good ionic conductivity and conjectural electrical efficiency than oxygen-ion conductors within a targeted temperature span.

Perovskite-type oxides likes BaZrO$_3$, SrZrO$_3$, BaCeO$_3$, and SrCeO$_3$ doped with rare-earth elements are protonic conductors [4]. BaCeO$_3$ electrolyte exhibits inadequate chemical and thermal stabilities but showed very lofty proton conductivity in the middle of redox cycles, whereas BaZrO$_3$ electrolyte exhibits the opposite. For BaCeO$_3$ high temperature proton conductors, the doped trivalent elements are sharply linked with proton procreation and transference, which are recommended by trial and simulation outcomes. Amsif et al. [5] contemplated BaCeO$_3$ doped with a series of rare-earth elements
exhibited total conductivities on the ionic radius of the dopants and a subordination of grain boundary, grain size, or bulk. BaCeO$_3$ doped with Y, Sm, and Gb present reasonably large electric conductivity. Gu et al [6] explore ability of dopants on conductivity along with sinterability of BaCe$_{0.85}$Ln$_{0.15}$O$_3$ \_δ (LZ= Y, Yb, Gb) ceramics. Y-doped BaCeO$_3$ display the highest conductivity, whereas the sinterability was correlated to the dopant ionic radius and thermodynamic. The benefits from both BaCeO$_3$ and BaZrO$_3$ materials considered quite high conductivity and stable electrolyte which been generally debate for proton conducting fuel cell application [7, 8]. But the challenges of BaZrCeO$_3$ materials, have highly sintering temperature for long period to get materials with an acceptable relative density [9, 10]. There were several reported which by added metal oxide to BZCY-based may increase the sinterability [11-13]. Numerous synthesis techniques have been utilised to create BaCeO$_3$-based powders, as well as sol-gel method, combustion, hydrothermal reaction and solid-state reaction have been reported in legion literatures. The sol-gel method has drawn superb curiosity because it can produce powders with splendid structural similarity, moderate residue CO$_2$ level and nanoscale particle sizes. However, one of the large disputed for practical deployment is the choice of a relevant electrolyte material with a processability and chemical stability for continual operation in working conditions. A new-fangled electrolyte for intermediate-temperature proton conducting fuel cell (PCFC) appliance must be developed.

In this study, synthesis of BaZrCe-based electrolyte with Y, Pr and In dopant was conducted by microwave assisted glycine nitrate process and their powder characteristics, such as TGA, XRD and SEM analysis, were determined. Comparison will be also made between pure BZCY and the doped-BZCY for further study.

2. Experimental Procedure
2.1 Preparation of Electrolyte
BaCe$_{0.4}$Zr$_{0.3}$Y$_{0.1}$O$_{3.5}$ \_δ (M= Pr, In) powders were synthesised by microwave-assisted glycine-nitrate combustion method. BaZr$_{0.4}$Ce$_{0.4}$Y$_{0.2}$O$_{3.5}$ was used as precursor compounds and denoted as S1, whereas the prepared BaCe$_{0.4}$Zr$_{0.4}$Y$_{0.1}$M$_{0.1}$O$_{3.5}$ powders doped with Pr and In were denoted as S2 and S3, respectively. Raw materials for Ba(NO$_3$)$_2$, ZrO(NO$_3$)$_2$·xH$_2$O, Y(NO$_3$)$_2$·6H$_2$O, Ce(NO$_3$)$_3$·6H$_2$O, In(NO$_3$)$_3$·xH$_2$O and Pr(NO$_3$)$_3$·6H$_2$O were used as starting materials, whereas glycine was chosen as a fuel agent. Metal nitrate was added one by one into a beaker and dissolved in deionised water. The metal nitrate salt solution was stirred on a hot plate without heating for 20 h to form metal complexes. Metal ions with a fuel molar ratio of 1:4 were used for combustion. The glycine was added in the solution and heated in a microwave oven (SHARP, 2450 MHz, 900W) until the solution was burnt and formed a dry yellow gel. The dry gel was cooled down on a crucible plate for a few minutes and crushed to obtain a powder. The powder was then calcined between 1100–1300 °C with the heating rate of 10 °C min$^{-1}$ for 10 hours in a furnace to form pure powders.

2.2 Characterization of powders
To dried powders from room temperature to 1300 °C, thermogravimetric analysis (TGA) was performed at heating rate of 10 °C/min. The morphology, crystal structure, and phase of the electrolyte were dispose using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques.

3. Results and discussions
3.1 Properties of the prepared powders
In the TGA analysis (Figure 1), all the nitrates underwent thermal decomposition to give the metal oxide, nitrogen dioxide and oxygen. For example, the following equation showed the decomposition of barium nitrate.

$$2\text{Ba(NO}_3)_2 + \text{heat} \rightarrow 2\text{BaO} + 4\text{NO}_2 + \text{O}_2$$

The thermal decomposition for metal nitrates becomes increasingly thermally stable, as shown in the decreasing group in the periodic table. Thus, metals adjacent the lowest of the reactivity series usually
decompose easily at high temperature. This phenomenon is due to the increased bond strength among atoms as they approach the top of the reactivity series, thereby causing difficulty in breaking the strong bonds. The increased thermostability of the electrolytes can be summarised as follows:

BZCY > BZCYIn > BZCYP

To study the reaction during the perovskite phase structure formation, we analysed simultaneous TG-DTA curves of the samples from room temperature to 1400 °C (Figure 2). In terms of thermal stability, nitrate was more uncertain than carbonate and hence easily decompose. Figure 2 shows that three regions were obtained in TG-DTA of the powders. For BZCY powder, the gradual weight loss was 0.98% up to 200 °C and was due to absorption of water molecules. The added weight loss along with exothermal peaks in DTA revealed that the decomposition of sample takes place in two steps. The weight loss from 500 °C to 600 °C was due to the combustion of the metal nitrates and co-oxidation. A small weight loss was discovered at temperature higher than 1000 °C, which was because barium carbonate thermal decomposition. TG curve displayed an exorbitant weight loss starting at around 700–800 °C with a match exothermal effect, which was related to the decomposition of BaCO$_3$ and the formation of powder with the release of CO$_2$ [14, 15].

![Figure 1. Thermogravimetric analysis of hydrated BaZrCeYMO$_{3.6}$ (M= Pr, and In) materials](image1)

![Figure 2. DTA analysis of BZCY, BZCYP, and BZCYIn powders](image2)
XRD spectra of the mixed raw materials calcined at different temperature are displayed in Figure 3.

![XRD patterns for BCZY, BCZYIn and BCZYPr calcined at 1100, 1200 and 1300°C.](image)

**Figure 3.** XRD patterns for BCZY, BCZYIn and BCZYPr calcined at 1100, 1200 and 1300°C.

At 1100 °C, BaCO$_3$ was detected as well with the unreacted oxides Y$_2$O$_3$, ZrO$_2$ and CeO$_2$. At 1200 °C, small peaks remained because of BaZrO$_3$ however the perovskite phase of the BCY–BZY solid solution was closely formed. By increased temperature to 1300 °C, indicated that the reaction was nearly complete which the peaks vanish, and those of the single perovskite remained. Many researchers have obtained BaCeO$_3$-BaZrO$_3$ solid solutions by calcined the powder materials at 1000–1400 °C, which is lean on type of dopants and concentration of dopants [16-19]. Y-doped barium cerate zirconate (BCZY), unreacted alkaline earth compound, whether BaO, Ba(OH)$_2$, and BaCO$_3$ was firing multiple calcination step to obtain these processes which depending on temperature and atmosphere. By XRD, in an amorphous phase which hardly be detected even though small amounts of the impurities.

![SEM images of BaZr$_{0.4}$Ce$_{0.4}$Y$_{0.1}$M$_{0.1}$O$_{3-δ}$ (M = Pr and In) powder calcine at 1300 °C for 10 h](image)

**Figure 4.** SEM images of BaZr$_{0.4}$Ce$_{0.4}$Y$_{0.1}$M$_{0.1}$O$_{3-δ}$ (M = Pr and In) powder calcine at 1300 °C for 10 h
Figure 4 shows the surface morphology of BaZr$_{0.4}$Ce$_{0.4}$Y$_{0.1}$M$_{0.1}$O$_{3-\delta}$ (M = Pr and In) samples. After calcined at 1300 °C, all the elements were well distributed in the compound. The grain size and porosity were considered for conductivity analysis in future studies.

4. Conclusion
The strategy of adding Pr and In into BCZY enhances the electrolyte performance compared with the conventional BCZY electrolyte in terms sinterability. In this study, TGA showed that 1300 °C was the best calcinating temperature at which to obtain a single cubic perovskite phase sample and results well agreed with the XRD pattern. SEM images indicated that the synthesised powders were well distributed and can be used as electrolytes in proton conducting fuel cell (PCFCs). However, further investigation on the electrical characterisation and stability of the electrolytes in CO$_2$ environment is necessary to confirm their performance. Next progress will be continuing in future publication.

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