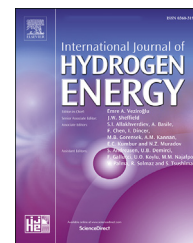


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# Effect of strontium and zirconium doped barium cerate on the performance of proton ceramic electrolyser cell for syngas production from carbon dioxide and steam

J. Sarabut<sup>a</sup>, S. Charojrochkul<sup>b</sup>, T. Sornchamni<sup>c</sup>, N. Laosiripojana<sup>d</sup>,  
S. Assabumrungrat<sup>e</sup>, U. Wetwattana-Hartely<sup>f</sup>, P. Kim-Lohsoontorn<sup>e,\*</sup>

<sup>a</sup> Department of Chemical Engineering, Mahidol University, Nakorn Pathom 73170, Thailand

<sup>b</sup> National Metal and Materials Technology Center (MTEC), Thailand Science Park (TSP), Phahonyothin Road, Khlong Nueng, Khlong Luang, Pathum Thani 12120, Thailand

<sup>c</sup> PTT Research & Technology Institute, PTT Public Company Limited, Thailand

<sup>d</sup> The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand

<sup>e</sup> Center of Excellence in Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

<sup>f</sup> The Sirindhorn International Thai-German Graduate School of Engineering, King Mongkut's University of Technology North Bangkok, Bangkok 10800, Thailand

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## ABSTRACT

Syngas has been produced from carbon dioxide (CO<sub>2</sub>) and steam using a proton ceramic electrolyser cell. Proton-conducting electrolytes which exhibit high conductivity can suffer from low chemical stability. In this study, to optimize both proton conductivity and chemical stability, barium cerate and doped barium cerate are synthesized using solid state reaction method: BaCeO<sub>3</sub> (BC), Ba<sub>0.6</sub>Sr<sub>0.4</sub>CeO<sub>3- $\alpha$</sub>  (BSC), Ba<sub>0.6</sub>Sr<sub>0.4</sub>Ce<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3- $\alpha$</sub>  (BSCY), and BaCe<sub>0.6</sub>Zr<sub>0.4</sub>O<sub>3- $\alpha$</sub>  (BCZ). The BC, BSC, and BSCY are calcined at 1100 °C for 2 h and BCZ is calcined at 1300 °C for 12 h, respectively. All samples exhibit 100% perovskite and crystallite sizes equal 37.05, 28.46, 23.65 and 17.46 nm for BC, BSC, BSCY and BCZ, respectively. Proton conductivity during steam electrolysis as well as catalytic activity toward the reverse water gas shift reaction (RWGS) is tested between 400 and 800 °C. The conductivity increases with temperature and the values of activation energy of conduction are 64.69, 100.80, 103.78 and 108.12 kJ mol<sup>-1</sup> for BSCY, BC, BSC, and BCZ, respectively. It is found that although BCZ exhibits relatively low conductivity, the material provides the highest CO yield at 550–800 °C, followed by BSCY, BSC, and BC, correlating to the crystallite size and BET surface area of the samples. Catalytic activity toward RWGS of composited Cu and electrolytes is also measured. Additional Cu (60 wt%) significantly increases catalytic activity. The CO yield increases from 3.01% (BCZ) to 43.60% (Cu/BCZ) at 600 °C and CO can be produced at temperature below 400 °C. There is no impurity phase detected in BCZ sample

\* Corresponding author.

E-mail address: [pattaraporn.k@chula.ac.th](mailto:pattaraporn.k@chula.ac.th) (P. Kim-Lohsoontorn).

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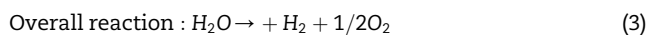
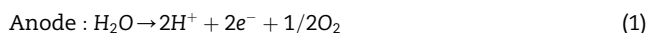
after exposure to CO<sub>2</sub>-containing gas mixture (600 °C for 5 h) while CeO<sub>2</sub> phase is detected in BSC and BSCY and both CeO<sub>2</sub> and BaO are observed in BC sample.

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## Introduction

Significant amount of carbon dioxide (CO<sub>2</sub>) has been released from processes involving energy conversion. The emission enhances the green-house effect and contributes to global climate change which could endanger environment and mankind. Consequently, CO<sub>2</sub> utilization as a carbon source for the production of fuels and chemicals has gained much interest. Proton ceramic electrolyser cells (PCECs) can convert CO<sub>2</sub> and steam into syngas (hydrogen (H<sub>2</sub>) and carbon monoxide (CO)) which is known as important precursor for industrial chemicals such as higher olefin and alcohols [1–5]. With CO<sub>2</sub> and H<sub>2</sub>O as a feed, H<sub>2</sub> is produced through steam electrolysis reaction (Eqs. (1)–(3)). Hydrogen then further reacts with CO<sub>2</sub> to form CO. The reverse water gas shift (RWGS) reaction provides syngas (H<sub>2</sub> and CO) as a product through Eq. (4).

Electrochemical reaction:



Thermochemical reaction:



The electrolyte of an electrolyser can be oxygen-ion (O<sup>2-</sup>) conductor or proton (H<sup>+</sup>) conductor. In theory, proton exhibits much smaller ionic radius comparing to oxygen-ion. Therefore, the mobility is relatively higher, leading to higher conductivity and the cell performance [6–9]. Proton-conducting electrolytes also permit a significant decrease in operating temperature (400–700 °C), resulting in increasing system robustness and reducing system cost [10,11].

However, the materials which exhibit high proton conductivity often suffer from poor chemical stability when being exposed to CO<sub>2</sub>-containing gas. Barium cerate (BaCeO<sub>3</sub>) is known to exhibit high proton conductivity but low chemical stability against CO<sub>2</sub> [9,12–19] while barium zirconate (BaZrO<sub>3</sub>) shows relatively higher chemical stability but lower proton conductivity [14,15,20–22]. Therefore, zirconium doped barium cerate (BCZ) has been used as an electrolyte and composites with metal as an electrode [23–26]. Doping trivalent such as Y<sup>3+</sup>, Yb<sup>3+</sup>, Nd<sup>3+</sup> and Gd<sup>3+</sup> into BCZ to achieve higher conductivity was also reported [8,11,13,14,16,17,20,21,25,29]. Strontium cerate (SrCeO<sub>3</sub>) exhibits conductivity and chemical stability against CO<sub>2</sub> and the performance lies between BaCeO<sub>3</sub> and BaZrO<sub>3</sub> [8,22,29]. Therefore, strontium doped barium cerate (BSC) and the BSC with trivalent doping have also been investigated [8,15,18,22,27–29].

The objective of this study is to optimize both proton conductivity and chemical stability by using a combination of the BaCeO<sub>3</sub> (exhibiting high proton conductivity), SrCeO<sub>3</sub>, and BaZrO<sub>3</sub> (exhibiting high chemical stability). The perovskite compositions of strontium doped barium cerate (Ba<sub>0.6</sub>Sr<sub>0.4</sub>CeO<sub>3- $\alpha$</sub> , BSC), and zirconium doped barium cerate (BaCe<sub>0.6</sub>Zr<sub>0.4</sub>O<sub>3- $\alpha$</sub> , BCZ) have been synthesized. To achieve higher conductivity, Y<sup>3+</sup> was also doped into SCB structure (Ba<sub>0.6</sub>Sr<sub>0.4</sub>Ce<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3- $\alpha$</sub> , BSCY). The electrochemical performance and catalytic activity of the samples were investigated. The catalytic activity of electrode and electrolyte materials toward RWGS reaction was discussed. The chemical stability of prepared samples when being exposed to CO<sub>2</sub> was also measured.

## Experimental

### Sample preparation

The BC, BSC, BSCY, and BCZ were prepared using solid state reaction method. Stoichiometric amounts of BaCO<sub>3</sub> (In house), CeO<sub>2</sub> (99.95%, Sigma Aldrich), SrCO<sub>3</sub> (99.9%, Sigma Aldrich), ZrO<sub>2</sub> (99.0%, Kanto Chemical Company), Y<sub>2</sub>O<sub>3</sub> (99.99%, Sigma Aldrich), were used as precursors. The precursors were mixed by ball milling for 24 h using zirconia balls having 5 mm and 10 mm diameter and ethanol (95%, Sigma Aldrich) as a medium, followed by drying in oven at 105 °C for 24 h and calcination at 1100 °C for 2 h (BC, BCS and BCSY) and 1300 °C for 12 h (BCZ).

To fabricate a button-type electrolyser, prepared powder of 3 g was pressed into a pellet at 1500 psi for 30 s and sintered at 1450 °C for 15 h. The sintering temperature and time could be reduced if sintering aid is added [30]. However, sintering aid was not applied in the sample, not to interfere the experimental results in this study. The relative density of fabricated cell was calculated and the method of calculation can be referred in our previous work [30]. The sintered cell was then coated by silver conductive paste (Sigma-Aldrich). The coated pellet was fired at 900 °C for 2 h, giving an electrode layer with an area of 0.785 cm<sup>2</sup> and a thickness of ~30 μm.

### Characterization

The X-ray diffraction (XRD) was used (BRUKER model D8 advance, using K $\alpha$  radiation of Cu) with scanned 2 $\theta$  between 10° – 80°. The phase was identified by comparing with JCPDS database. Crystalline size (d) was calculated using Scherrer equation:

$$d = \frac{0.9\lambda}{\beta_{\text{FWHM}} \cos(\theta)} \quad (5)$$

where  $\lambda$  is the wavelength (1.54 Å),  $\beta_{\text{FWHM}}$  is the full width for the half-maximum intensity of main peaks (FWHM), and  $\theta$  is diffraction angle.

%Perovskite was determined from Eq. (6) through a measuring of the intensity of XRD major peaks.

$$\%Perovskite = \frac{\sum_{i=1}^N I_{perovskite}}{I_T} \times 100 \quad (6)$$

where  $I_{perovskite}$  is the intensity of perovskite peaks,  $I_T$  is the total intensity of perovskite peaks and impurity peaks.

Surface area of the materials was measured through  $N_2$  adsorption and desorption (Autosorb 1-AG, Quantachrome).

### Electrochemical performance measurement

The electrochemical performance measurement was carried out between 400 and 800 °C with humidified  $H_2/N_2$  feed. Single cell polarisation curves were generated using linear sweep current techniques to obtain a V/I curve. A potentiostat (Metrohm Autolab, Netherlands) was used to control the voltage between open circuit voltage (OCV) and 1.5 V with a scan rate of 20 mV/s. Platinum wires were attached to the cell for an electrical connection. The cell was placed in a cell holder which was sealed using glass sealant (Ultra-Temp 516, Aramco, USA) to separate the gas environment of two electrode chambers. A vertical furnace (Chavachot, Thailand) was used to control the temperature of the test rig. The test system allowed variable gas compositions of steam, and  $H_2$  (20% $H_2O$ , 24% $H_2$  and 56% $N_2$ , 100 ml  $min^{-1}$  total flow rate) to be introduced to the electrode. After passing through flow controllers, the  $H_2$  line passes through the humidifier, which is a bubble column situated inside a thermocirculator bath, to saturate the gas with water.

The value of activation energy ( $E_a$ ) of conductivity can be related to proton conductivity. Activation energy of conduction decreases when proton conductivity increases. Proton conductivity was calculated using Eq. (7) and activation energy of conduction was calculated using Arrhenius, Eq. (8):

$$\sigma = \frac{LI}{VA} \quad (7)$$

$$\sigma = \frac{A}{T} e^{\frac{-E_a}{RT}} \quad (8)$$

When  $\sigma$  is proton conductivity ( $S\ cm^{-1}$ );  $L$  is the sample cell thickness (cm);  $I$  is a current (A);  $V$  is a controlled voltage (V);  $A$  is an electrode area ( $cm^2$ );  $T$  is temperature (K);  $E_a$  is an activation energy of conductivity ( $J\ mol^{-1}$ ); and  $R$  is gas constant ( $8.314\ J\ K^{-1}\ mol^{-1}$ ).

### Catalytic activity performance test

The activity toward reverse water gas shift reaction was tested between 400 and 800 °C with an interval of 50 °C, using a heating rate of 10 °C  $min^{-1}$ . The electrolyte powders were sieved to 70–100 nm. After that, 0.1 g of an electrolyte power was packed inside a 4 mm inner-diameter quartz tube reactor. A gas mixture of 10% $CO_2$ , 10% $H_2$  and 80% $Ar_2$  (100 ml  $min^{-1}$  total flow rate) was fed to the reactor. Out-gas products were detected by gas chromatography (GC-2014, Shimadzu CORP).

Composited Cu and electrolytes were also tested. The electrolyte power was mixed with CuO (98% CuO, Sigma

Aldrich) at a proper ratio to obtain a ratio of Cu to electrolyte at a 60:40 wt%. Mixed powder were sieved to 70–100 nm and 0.1 g of samples were used for catalytic activity test. The samples were reduced in-situ at 350 °C for 40 min in a flow of a 10%  $H_2/Ar$  mixture (20 ml  $min^{-1}$ ) prior to the reaction. The catalytic activity toward reverse water gas shift reaction was then performed.

### Chemical stability test

The chemical stability of the sintered pellets was carried out in  $CO_2$ -containing environment. The sintered pellet was placed in the cell holder and the cell ridge was sealed using glass sealant (Ultra-Temp 516, Aramco, USA). A vertical furnace (Chavachot, Thailand) was used to control the temperature of the rig. The cell was exposed to 10% $CO_2$ , 30% $H_2$  and 60% $N_2$  (300 ml  $min^{-1}$  total flow rate) at 600 °C for 5 h. The phases of the sintered pellets after  $CO_2$  exposure were analyzed using XRD.

The Goldschmidt tolerance factor ( $\tau$ ) was used to predict a distortion of a crystal structure and was related to chemical stability of a perovskite structure [23]. The factor can be calculated using Eq. (9), as result  $\tau = 1$  is for a perfect cubic perovskite.

$$\tau = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (9)$$

where  $r_A$  is the ionic radius of the A site which is  $Ba^{2+}$  (1.35 Å) or  $Sr^{2+}$  (1.18 Å);  $r_B$  is the ionic radius of the B site which are  $Ce^{4+}$  (0.87 Å),  $Zr^{4+}$  (0.72 Å), or  $Y^{3+}$  (0.9 Å); and  $r_O$  is the ionic radius of the oxygen  $O^{2-}$  (1.40 Å).

## Results and discussion

### Characterization

The XRD patterns of all prepared electrolyte powders were shown in Fig. 1. All samples exhibited perovskite structure (JCPDS 82-2425). There was no impurity phase detected and 100% perovskite was obtained in all prepared powder. The crystallite sizes calculated from XRD patterns are also

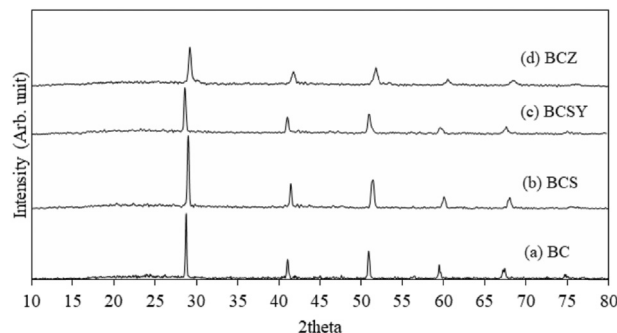


**Fig. 1 – The XRD patterns of synthesized electrolytes: (a) barium cerate (BC), (b) strontium doped barium cerate (BCS), (c) yttrium and strontium doped barium cerate (BCSY), and (d) zirconium doped barium cerate (BCZ).**

presented in Table 1. They were 37.05, 28.46, 23.65 and 17.46 nm for BC, BSC, BSCY, and BCZ, respectively. The crystallite sizes of the BCZ and the BSC are smaller than that of the BC due to a  $Zr^{4+}$  substitution at  $Ce^{4+}$  sites and a  $Sr^{2+}$  substitution at  $Ba^{2+}$  sites, resulting in a decreased unit cell volume. Relatively smaller size of  $Zr^{4+}$  ions (radius of 0.72 Å) substituted the larger  $Ce^{4+}$  ions (radius of 0.87 Å) and  $Sr^{2+}$  ions (radius of 1.18 Å) substituted  $Ba^{2+}$  ions (radius of 1.35 Å), respectively. When barium cerate was doped by  $Zr^{4+}$  ions and  $Sr^{2+}$  ions, the main peak shifted to a larger diffraction angle due to a decrease in lattice parameters as presented in Fig. 2. This result corresponded to other work [14] and confirmed the incorporation of  $Zr^{4+}$  ions in the BCZ as well as the  $Sr^{2+}$  in the BCS. For the BSCY sample, co-doping Sr and Y into barium cerate resulted in a shift of main peak to a lower diffraction angle due to an increase in unit cell volume.

#### Activation energy of conduction

The synthesized powder was prepared into a pellet and an V/I curve was generated between 400 and 800 °C. Fig. 3 presents the conductivity of electrolyte pellet and calculated activation energy of conduction. It was found that the conductivity increased with temperature and the BSCY pellet exhibited the highest conductivity, followed by BC, BSC and BCZ, respectively. The activation energy of conduction was 64.69, 100.80, 103.78 and 108.12 kJ mol<sup>-1</sup> for BSCY, BC, BSC, and BCZ, respectively. The H<sub>2</sub> production rate was also calculated from current at 1.1 V and 800 °C, and the rate was  $1.39 \times 10^{-8}$ ,  $3.38 \times 10^{-8}$ ,  $6.06 \times 10^{-9}$ , and  $1.24 \times 10^{-10}$  mol s<sup>-1</sup> for BC, BSC, BSCY, and BCZ, respectively.

The content of barium ion and zirconium ion can affect a proton conductor. It was reported that the conductivity increases with an increasing barium content [32] while the conductivity decreases with an increasing zirconium content [20]. A rare-earth ion dopant also affects BaCeO<sub>3</sub> proton conductor [18,31]. Fu and Weng [31] investigated the conductivity of various rare-earth ions doped BaCeO<sub>3</sub> (BaCe<sub>0.9</sub>M<sub>0.1</sub>O<sub>2.95</sub>, M is Gd, Nd, Sm and Y) and BaCe<sub>0.9</sub>Y<sub>0.1</sub>O<sub>2.95</sub> was reported to show relatively higher proton conductivity ( $9.20 \times 10^{-3}$  S cm<sup>-1</sup>) than BaCeO<sub>3</sub> ( $1.13 \times 10^{-4}$  S cm<sup>-1</sup>) at 800 °C in 5% H<sub>2</sub>–95% Ar while Wang et al. [18] reported that the conductivity of Ba<sub>0.6</sub>Sr<sub>0.4</sub>Ce<sub>0.8</sub>Y<sub>0.2</sub>O<sub>3-δ</sub> is between  $2.25 \times 10^{-2}$  and  $2.5 \times 10^{-2}$  S cm<sup>-1</sup>.

The % relative density was also calculated from the sintered electrolyte pellets and is presented in Table 1. It was

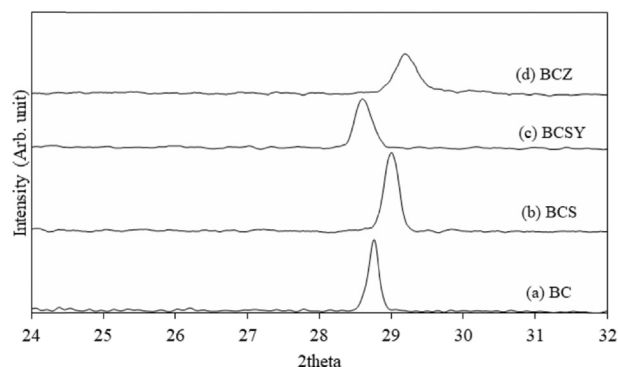


**Fig. 2 – Magnified scale of XRD patterns representing the shift in the main peak of (a) barium cerate (BC), (b) strontium doped barium cerate (BCS), (c) yttrium and strontium doped barium cerate (BSCY), and (d) zirconium doped barium cerate (BCZ).**

found that the BSCY exhibited the highest %relative density (87.22%), followed by BSC (85.99%), BC (70.15%), and BCZ (56.68%), respectively. The relative density could also affect the electrochemical performance of the electrolyte pellets. It should be noted that the relative density reported in this study was rather low. The relative density of the sample can be related to sinterability which mainly depends on mass transport diffusion mechanism and can be affected by factors such as starting power size, sintering temperature and time, and sintering additive. Although the relative density could be increased by adding a sintering additive [30], it was not applied in this study, not to interfere the experimental results.

Although doping barium cerate with  $Zr^{4+}$  and  $Sr^{2+}$  slightly increased activation energy of conduction (decreased conductivity), it was found that doping barium cerate with  $Zr^{4+}$  or  $Sr^{2+}$  significantly improved catalytic activity toward the RWGS reaction and  $Zr^{4+}$  dopant also helped improve chemical

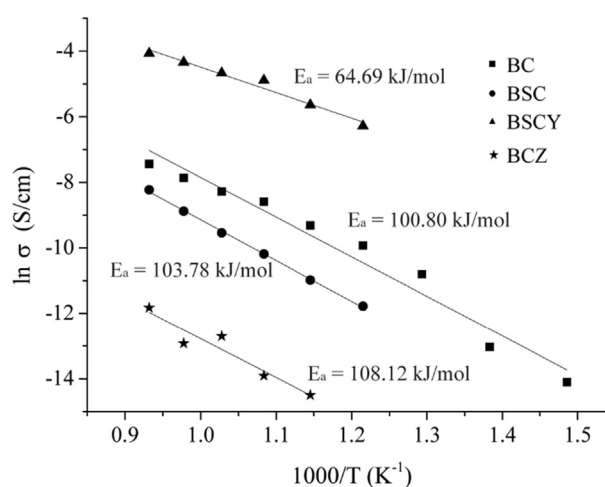


**Fig. 3 – Activation energy of conduction ( $E_a$ ) of fabricated electrolytes: barium cerate (BC), strontium doped barium cerate (BSC), yttrium and strontium doped barium cerate (BSCY), and zirconium doped barium cerate (BCZ).**

**Table 1 – %Perovskite, crystallite size, relative density, tolerance factor, and surface area of synthesized electrolyte powder and surface area of composited Cu/electrolytes.**

|                                                    | BC    | BSC    | BSCY    | BCZ    |
|----------------------------------------------------|-------|--------|---------|--------|
| % Perovskite                                       | 100   | 100    | 100     | 100    |
| Crystallite size (nm)                              | 37.05 | 28.46  | 23.65   | 17.46  |
| Relative density (%)                               | 70.15 | 85.99  | 87.22   | 56.68  |
| Tolerance factor ( $\tau$ )                        | 0.857 | 0.835  | 0.834   | 0.880  |
| BET surface area (m <sup>2</sup> g <sup>-1</sup> ) | 2.53  | 3.01   | 2.07    | 3.53   |
| BET surface area (m <sup>2</sup> g <sup>-1</sup> ) | Cu/BC | Cu/BSC | Cu/BSCY | Cu/BCZ |
|                                                    | 8.60  | 9.10   | 10.85   | 15.02  |

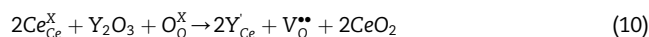
stability of the cell in CO<sub>2</sub>-containing environment (Sections [Catalytic activity toward RWGS reaction](#) and [Chemical stability](#)).

### Catalytic activity toward RWGS reaction

The catalytic activity was tested toward the RWGS reaction and the conversion of CO<sub>2</sub> and the yield of CO are presented in Fig. 4(a)–(d). It was found that the CO<sub>2</sub> conversion and the CO yield can be gained at a temperature between 550 and 800 °C for all electrolyte samples (Fig. 4(a) and (b)) and at a temperature between 400 and 800 °C for all composited Cu and electrolyte samples (Fig. 4(c) and (d)). The catalytic activity increased with increasing temperature. Adding Cu metal significantly increased catalytic activity of the samples and allowed the RWGS reaction to occur at the intermediate temperatures of an electrolyser. This could emphasize an advantage of a cermet type as an electrode for CO<sub>2</sub>/H<sub>2</sub>O-fed electrolyser. An increase in catalytic performance of Cu/BSCY toward the RWGS reaction is still unclear and requires further experimental investigation. However, the effect of catalyst support on Cu dispersion has been reported in other work [33]. This could be responsible for difference in catalytic performance of the electrolyte samples after adding Cu component.

An increase in catalytic activity of doped barium cerate when compared to bare barium cerate is not clearly known; however, it can be attributed to an increase in oxygen vacancy (V<sub>O</sub><sup>••</sup>), resulting from Zr<sup>4+</sup>/Sr<sup>2+</sup>/Yt<sup>3+</sup> substitution. Eq. (10)

represent the Yt<sup>3+</sup> substitution in Ce<sup>4+</sup> site, generating V<sub>O</sub><sup>••</sup>. Generated oxygen vacancy can help promote the conversion of CO<sub>2</sub> to CO and creates holes (h<sup>•</sup>), giving in Eq. (11) and Eq. (12).



Although BCZ presented low conductivity, the material showed relatively high catalytic activity toward the RWGS reaction. Catalytic surface acidity was also reported to increase with Zr content in other work [33]. The correlation between catalytic surface acidity and Zr content in the electrolyte sample has also become of interest.

### Chemical stability

Chemical stability of the electrolyte samples (BC, BSC, BSCY and BCZ) was investigated when exposing to a CO<sub>2</sub>-containing gas mixture (10%CO<sub>2</sub>, 30%H<sub>2</sub> and 60%N<sub>2</sub>, 300 ml min<sup>-1</sup> total flow rate) at 600 °C for 5 h. Fig. 5 presents the XRD patterns of all samples after the test. Impurity peaks (CeO<sub>2</sub>) was detected in the BSC and the BSCY samples while both CeO<sub>2</sub> and BaO were detected in the BC sample. The impurity phase was not observed in the BCZ sample. Although the products from

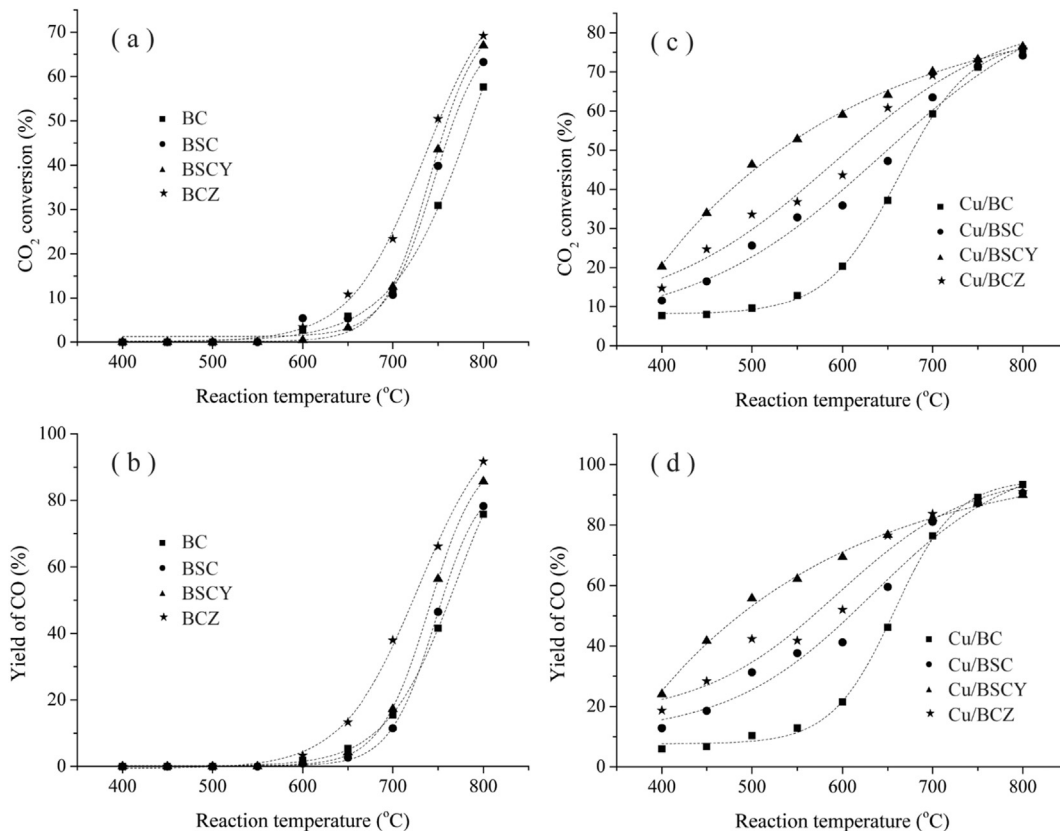


**Fig. 4 – Catalytic activity of electrolytes (BC, BSC, BSCY, and BCZ) and electrode materials (composited Cu/electrolytes) toward the reverse water gas shift (RWGS) reaction: (a) CO<sub>2</sub> conversion and (b) CO yield when using electrolyte powder as catalyst; (c) CO<sub>2</sub> conversion and (d) CO yield when using electrode powder as catalyst.**

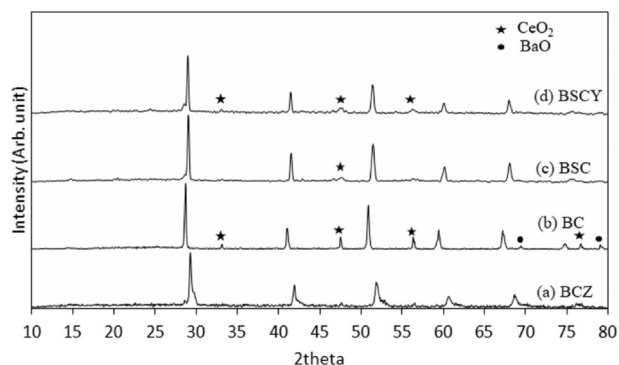


**Fig. 5 – The XRD patterns of the samples after being exposed to CO<sub>2</sub>-containing environment.**

BaCeO<sub>3</sub> perovskite reacting with CO<sub>2</sub> can be both BaCO<sub>3</sub> and CeO<sub>2</sub> [34], BaCO<sub>3</sub> was not detected in this study. Barium is easily removed from barium-based electrolyte when reacting with CO<sub>2</sub>; leading to BaO formation [35]. The BaO can further react with CO<sub>2</sub> to form BaCO<sub>3</sub> [35]. Goldschmidt's tolerance factor is generally used as a criterion for perovskite structure formation. Chemical stability of the barium zirconate-based materials was reported to increase with tolerance factor [13,17] and the factor was calculated and presented in Table 1. The BCZ exhibited the highest tolerance factor (0.880), followed by BC, BSC, and BSCY, respectively.

## Conclusion

The BC, BSC, BSCY, and BCZ were successfully synthesized using solid state reaction method with different calcination conditions. The effect of doping Zr<sup>4+</sup>, Sr<sup>3+</sup>, and Y<sup>3+</sup> in barium cerate structure was investigated in terms of electrochemical performance and catalytic activity. Activation energy of conduction of barium cerate decreased when doping with Zr<sup>4+</sup> and Y<sup>3+</sup>. The BSCY exhibited the lowest activation energy of conduction at 64.69 kJ mol<sup>-1</sup>. Although the BCZ sample presented relatively low conductivity with high activation energy of conduction (108.12 kJ mol<sup>-1</sup>), the sample offered high catalytic activity toward the RWGS reaction in terms of CO<sub>2</sub> conversion and CO yield. Moreover, the BCZ was rather stable after exposed to CO<sub>2</sub>-containing gas mixture at 600 °C for 5 h. There was no impurity phase detected in the BCZ sample, unlike the BC, BSC and BSCY samples which showed impurity phases after the exposure. Additional Cu in the form of Cu/electrolyte composite significantly improved catalytic activity toward the RWGS reaction. This implied that the use of cermet-type electrode could be preferable in an CO<sub>2</sub>/H<sub>2</sub>O-fed electrolyser.

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